2D-IR Spectroscopy

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Mixed IR/Vis Two-Dimensional Spectroscopy: Chemical Exchange beyond the Vibrational Lifetime and Sub-ensemble Selective Photochemistry**

*Luuk J. G. W. van Wilderen, Andreas T. Messmer, and Jens Bredenbeck**

Abstract: *Two-dimensional exchange spectroscopy (2D EXSY) is a powerful method to study the interconversion (chemical exchange) of molecular species in equilibrium. This method has recently been realized in femtosecond 2D-IR spectroscopy, dramatically increasing the time resolution. However, current implementations allow the EXSY signal (and therefore the chemical process of interest) only to be tracked during the lifetime (T_1) of the observed spectroscopic transition. This is a severe limitation, as typical vibrational T_1 are only a few ps. An IR/Vis pulse sequence is presented that overcomes this limit and makes the EXSY signal independent of T_1. The same pulse sequence allows to collect time-resolved IR spectra after electronic excitation of a particular chemical species in a mixture of species with strongly overlapping UV/Vis spectra. Different photoreaction pathways and dynamics of coexisting isomers or of species involved in different intermolecular interactions can thus be revealed, even if the species cannot be isolated because they are in rapid equilibrium.*

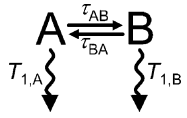
Two-dimensional EXSY was introduced by Ernst and Jeener in NMR spectroscopy,[1] where it became a standard method for investigating millisecond to second kinetics.[2] Recently, the concept of 2D EXSY has been transferred to femtosecond IR spectroscopy,[3] opening a unique access to ultrafast equilibrium processes that have been difficult or impossible to study before. 2D-IR EXSY has been applied in the study of rapidly interconverting conformers, the making and breaking of intra- and intermolecular interactions, dynamics of proteins, and ligand migration inside a protein.[3,4]

2D-IR EXSY functions by tracking the time evolution of a molecular species (such as a conformer) by a label that consists of an IR excitation of a specific vibration. Structural changes of the labeled molecular species caused by chemical exchange are revealed by frequency changes of the labeled vibration. A major problem is that the label quickly wears off owing to vibrational relaxation (VR); T_1 is typically a few ps or less.[5] The same problem occurs in NMR spectroscopy because of spin relaxation, albeit on a different timescale. This has led to the common belief that the time window during which exchange kinetics can be followed is fundamentally limited by relaxation of the monitored spectroscopic transition. Herein, we show how to overcome this limitation by introducing the VIPER (vibrationally promoted electronic resonance) 2D-IR experiment, which solves the problem by storing the information that the molecule has been vibrationally excited (in other words: labeled) in an electronically excited state. In this way, the lifetime of the vibrational information is extended to the lifetime of the electronically excited state, potentially extending the probing window for exchange by several orders of magnitude.

The very same pulse sequence furthermore opens exciting possibilities in photochemistry, because sub-ensembles within a mixture (certain conformers, isomers, or species with different intermolecular interactions) can be selected by the narrow-band IR pulse for subsequent electronic excitation. Therefore, different reaction pathways and dynamics of sub-ensembles can be discovered even if they are in fast dynamic equilibrium and exhibit identical UV/Vis spectra (sub-ensemble selective photochemistry).

We first recapitulate briefly the conventional 2D-IR EXSY experiment. We then explain the concept of VIPER 2D-IR, and demonstrate it on coumarin 6 (C6). We subsequently show that it allows the measurement of chemical exchange by tracking the H-bond formation and dissociation between C6 and the H-bond donor methanol up to waiting times that are more than 100 times longer than the vibrational T_1, both in the S_0 and S_1 states. Finally, we discuss the application of VIPER 2D-IR for sub-ensemble-selective studies in photochemistry.

A conventional 2D-IR EXSY experiment depends on the timescales of exchange kinetics (τ) and VR (T_1), as illustrated in Scheme 1 for the case of two interconverting species A and B. Dependence on orientational relaxation can be eliminated using magic angle polarization. Figure 1 shows the corresponding 2D-IR spectra for such a system, assuming that A and B have a vibrational mode with a lifetime $T_1 = T_{1,A} = T_{1,B} = 11$ ps, which changes its wavenumber upon interconversion ($\tau_{EXSY} = (1/\tau_{AB} + 1/\tau_{BA})^{-1} = 3.5$ ps, $\tau_{AB} = \tau_{BA}$). The two species in exchange may for example be the H-bonded and non-H-bonded form of a molecule. In a conventional 2D-IR experiment, the IR_{pump} pulse arrives at t_0 and excites a vibration. The vibrational ground state is depopulated and the $\nu = 1$ state populated, creating negative difference signals



Scheme 1. Chemical exchange and its relevant time constants.

[*] Dr. L. J. G. W. van Wilderen, Dr. A. T. Messmer, Prof. Dr. J. Bredenbeck
Institut für Biophysik, Johann-Wolfgang-Goethe-Universität
Max-von-Laue-Strasse 1, 60438 Frankfurt (Germany)
E-mail: bredenbeck@biophysik.uni-frankfurt.de

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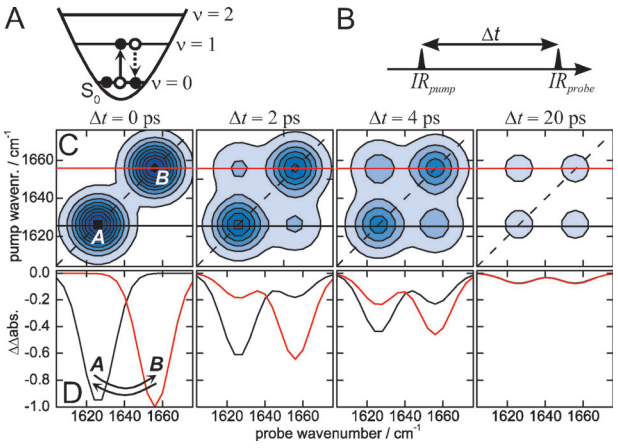

Figure 1. Principle of the conventional 2D-IR EXSY experiment. A) In a 2D-IR experiment, molecules (black circles) are vibrationally excited by the IR_{pump} (black arrow). VR (dashed arrow) leads to ground-state recovery and decay of the 2D-IR signal. B) Pulse sequence used in conventional 2D-IR EXSY in the pump probe implementation. C) 2D-IR spectra at different waiting times Δt for two exchanging species A and B (see Scheme 1). See Ref. [7] for a theoretical treatment of 2D EXSY. D) Cross-sections along the horizontal lines in the 2D-IR spectra of (C).

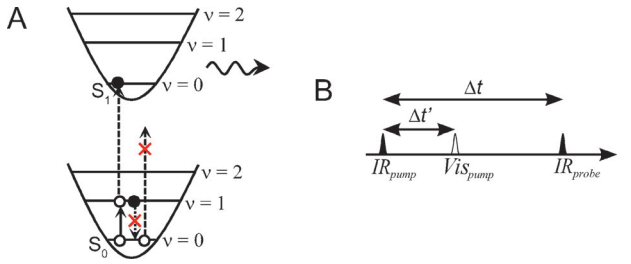

Figure 2. Principle of VIPER 2D-IR. A) In VIPER 2D-IR, the off-resonant Vis_{pump} (long-dashed arrow) is applied after the IR_{pump} (black arrow) and removes population from $\nu = 1$ (not from $\nu = 0$, long-dashed arrow with red cross), thereby preventing ground-state recovery (short-dashed arrow 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). B) VIPER 2D-IR pulse sequence.

(blue in Figure 1) on the diagonal.[6] The positive excited state absorption is omitted for simplicity in Figure 1. With increasing waiting time Δt between the IR_{pump} and IR_{probe} the $\nu = 1$ population relaxes and $\nu = 0$ recovers (Figure 1 C and D). Therefore, in the absence of exchange the diagonal peak intensities decay with $T_1 = 11$ ps. If chemical exchange occurs (for example, H-bonds are broken or formed during Δt), cross-peaks grow in at the expense of the diagonal peaks with $\tau_{EXSY} = 3.5$ ps (Figure 1 C and D). However, these cross-peaks also decay, which is due to VR with T_1. It is therefore obvious that signals containing information on exchange are only detectable while the vibration remains excited; that is, while the species stays labeled. If exchange is slow compared to VR, the signal decays to the noise level before noticeable exchange occurs and thus no information on exchange kinetics can be obtained by conventional 2D-IR spectroscopy. It might be argued that improving the signal-to-noise ratio (S/N) of the experiment will extend the observation window for exchange kinetics. However, a higher S/N will not help much because VR follows exponential kinetics; for example, if $T_1 =$ 2.0 ps, even increasing the S/N by an order of magnitude (in most cases not an easy undertaking for the experimentalist) will extend the observation window only by about 4.6 ps. However, exchange processes might occur on the hundreds of picoseconds or nanosecond timescale. Thus a different approach is required.

To overcome the problem that VR deletes the signal that reports exchange kinetics, we introduce the VIPER 2D-IR pulse sequence (Figure 2). As described above, in a 2D-IR experiment molecules are vibrationally excited by the IR_{pump}. VR leads to ground state recovery (GSR) and thus decay of the 2D-IR signal. In VIPER 2D-IR (Figure 2 A), a visible pulse (Vis_{pump}) removes population from $\nu = 1$ (not from $\nu =$ 0) and transfers it to an electronically excited state (double resonance excitation[8]), thereby preventing GSR and generating a persistent 2D-IR signal that contains information on exchange kinetics. Importantly, the Vis_{pump} is kept off-resonance with the electronic transition. The IR_{pump} can shift the molecule into resonance with the Vis_{pump} either through direct excitation of a Franck–Condon (FC) active mode or through intramolecular vibrational energy redistribution (IVR) from the initially excited mode into FC active modes.[9] Subsequently, the population relaxes with the electronic lifetime T_{el}. Ultimately, this again leads to GSR and concomitant decay of the VIPER 2D-IR signal. However, while typical T_1 values of polyatomic molecules in solution are in the range of hundreds of fs to a few ps, T_{el} can be much longer, extending to the ns or even μs timescale. A considerable extension of the observation window for exchange processes over many orders of magnitude can thus be achieved. In extreme cases, the excited-state population can undergo further photochemistry and not return to the initial ground state at all. In this case, an eternal VIPER 2D-IR signal is generated that can be used for EXSY measurements.

The VIPER 2D-IR experiment differs from previous mixed Vis/IR 2D experiments in that a combination of an off-resonant Vis_{pump} and a resonant IR pre-excitation is required for electronic excitation. Triggered exchange spectroscopy,[4f] which is used for correlating vibrations of reactant and product of a light-triggered process, and transient 2D-IR spectroscopy,[10] which collects 2D-IR spectra after electronic excitation, both use a resonant Vis_{pump} and the signals of these methods just decay with the vibrational T_1.

When the interconverting species have UV/Vis spectra that are sufficiently distinct from each other, 2D UV/Vis exchange spectroscopy could be envisioned as an alternative approach. However, IR spectra usually are very sensitive to changes in conformation, H-bonding or similar, frequently leading to novel, separate bands, that can be selectively addressed by IR excitation, while such species typically differ little or not in their UV/Vis spectrum. Furthermore, UV/Vis absorption bands of the excited state frequently overlap with those of the ground state.

So far, our focus has been on the signals resulting from the interconverting species A and B in the electronic ground state, and we explained the use of these signals to probe

ground-state chemical exchange. Corresponding signals of the electronically excited states A* and B* can exist as well, and will be discussed for our test case C6 (Figure 4 and Figure 6). This type of signal can be used to measure exchange in the excited state or to selectively study the photochemistry of a sub-ensemble that has been picked by the narrow band IR_{pump} and promoted to the electronically excited state, for example, a certain conformer.

To demonstrate the VIPER 2D-IR experiment, we chose C6 as a model system. C6 (Figure 3A) has three well-separated bands in the 1550–1800 cm^{-1} region (Figure 3B), which are caused by two ring modes at 1588 cm^{-1} and

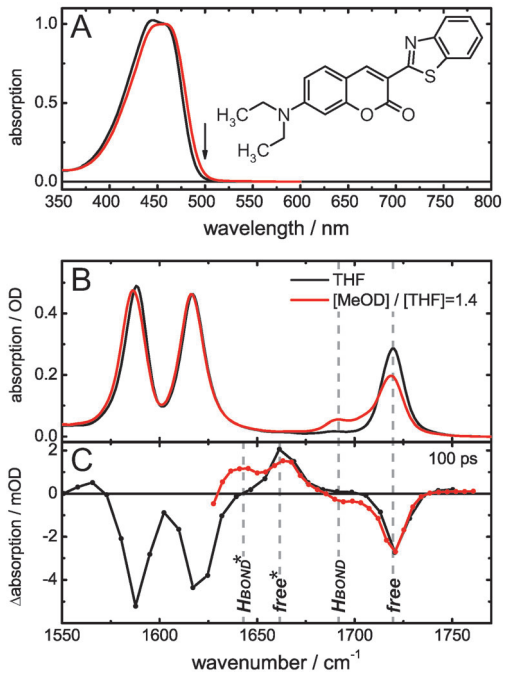

Figure 3. Spectroscopic properties of C6 in THF without (black) and with MeOD (red). A) Vis absorption spectrum (concentration 0.85 mM) and structure of C6. The arrow denotes the excitation wavelength used for the VIPER 2D-IR experiments. B) Absorption in the IR (concentration of 85 mM; the spectrum of the MeOD sample is scaled; optical pathlength 250 μm). C) TRIR spectra at 100 ps after visible excitation.

1616 cm^{-1} and one C=O stretching mode at 1719 cm^{-1} (see the Supporting Information, Figure S2 for DFT computations). After addition of deuterated methanol (MeOD), a new band appears at 1691 cm^{-1} that corresponds to the H-bonded carbonyl moiety (C=O). Even at high excess of MeOD ([MeOD]/[C6] = 800), two populations of free and H-bonded C6 are observed. The influence of MeOD on the UV/Vis spectrum (Figure 3A) is small. Figure 3C shows the transient IR (TRIR) spectrum 100 ps after resonant visible excitation in the presence and absence of MeOD. T_{el} of C6 in n-decane and methanol is about 2 ns.[11] In the absence of MeOD, three negative (bleach) signals are observed in the TRIR spectrum corresponding to the absorption bands of the ground state. The positive signal at 1661 cm^{-1} is the C=O absorption in the S_1 state.[12] Upon addition of MeOD, an additional C=O bleach at 1694 cm^{-1} is observed, as expected from the steady-state spectrum. Also in the S_1 state, H-bonding to the C=O leads to an additional band that appears at 1641 cm^{-1}. Monitoring exchange between the H-bonded and the free C6 thus should be possible both in the S_0 and S_1 state.

To confirm that the VIPER 2D-IR approach works, we collect 2D-IR spectra of C6 on a timescale far beyond the vibrational T_1 time (Figure 4). The signal is plotted as the

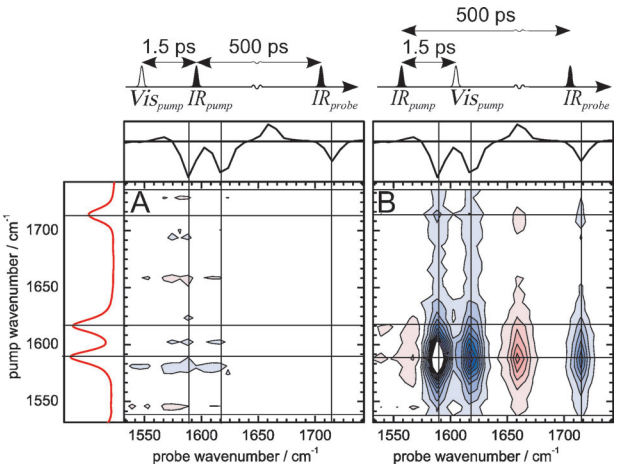

Figure 4. VIPER 2D-IR spectra of C6 in THF at more than 100 x T_1. A,B) show the VIPER 2D-IR spectra for different pulse order. The FTIR (red) and the TRIR spectrum 500 ps after visible excitation at 500 nm (black) are also shown. Both 2D spectra share the same color scheme (blue is negative, red positive). One contour is 21 μOD (the 1588 cm^{-1} diagonal peak is cut-off at −0.2 mOD).

difference of the 2D-IR spectrum with Vis_{pump} on and the 2D-IR spectrum with Vis_{pump} off (see the Supporting Information). To this end, we have chosen the delay Δt between IR_{pump} and IR_{probe} to be $\Delta t = 500$ ps, which is several hundred times longer than T_1 (about 1 ps, see Figure 5 and the Supporting Information, Figure S3 for VR), so that the conventional 2D-IR signal will long have decayed. If now an off-resonant Vis_{pump} is applied, the VIPER 2D-IR spectrum is "switched on" if the Vis_{pump} comes 1.5 ps after the IR_{pump} (Figure 4B), and it is "switched off" if it comes 1.5 ps before the IR_{pump} (Figure 4A). Only in the first case, the IR_{pump} has the effect of shifting the molecule into electronic resonance with the Vis_{pump}, and only then a long-lived VIPER 2D-IR signal is

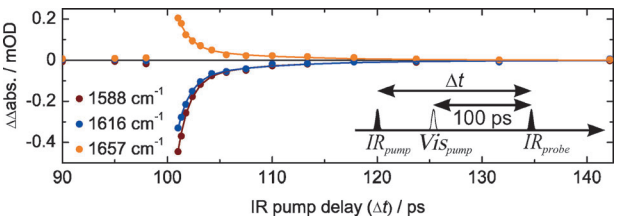

Figure 5. Evolution of the VIPER 2D-IR signal resolves VR and cooling to the solvent. The Vis_{pump} has a fixed delay with respect to the IR_{probe} (wavenumber in legend) while the IR_{pump} (1588 cm^{-1}) is scanned in time. The continuous lines represent a simultaneous fit of two exponentials having lifetimes (errors) of 1.2 (0.1) and 9 (2) ps.[14]

generated. We found VIPER to work at wavelengths tested from 490 nm to 520 nm. The Vis_{pump} may excite a small part of the S_0 population directly because it overlaps with the tail of the absorption spectrum (Figure 3A). This background signal is subtracted. The obtained VIPER 2D-IR spectrum in Figure 4 differs from a conventional 2D-IR spectrum in that it has no contribution from $\nu = 1$ states (because they have long decayed after 500 ps). Instead, horizontal cuts through the VIPER 2D-IR spectrum resemble the TRIR spectrum shown in the top panels of Figure 4A,B, scaled by the efficiency of the IR_{pump} to promote the system to S_1. The efficiency is higher, the more the IR-induced shift of the visible absorption spectrum brings it in overlap with the Vis_{pump}. This coupling between the excited vibration and the electronic transition corresponds to the FC factor of each respective mode. The fact that the VIPER 2D-IR signal vanishes for an off-resonant IR_{pump} confirms that resonant IR excitation is a prerequisite for signal generation and two-photon absorption of an IR photon and a Vis photon via a virtual level plays no or a negligible role. It appears that the ring mode at 1588 cm^{-1} has the highest FC factor of the three modes, meaning that it is most strongly coupled to the electronic transition, whereas the ring mode at 1616 cm^{-1} and the C=O mode (1719 cm^{-1}) appear less-coupled.[13] Previous work has estimated the FC ratios of the same modes with similar results.[8b]

In the following, we investigate how the VIPER 2D-IR signal evolves as a function of delay time between the IR_{pump} and Vis_{pump}, that is, how it depends on the relaxation of the initial vibrational excitation. In the VIPER 2D-IR measurement in Figure 5, the Vis_{pump} is set to arrive 100 ps before the IR_{probe}, that is, the vibrational excitation will have long decayed. The IR_{pump} is tuned to be resonant with the ring mode at 1588 cm^{-1} and scanned in time over the Vis_{pump}. The amplitude of the VIPER 2D-IR signal is plotted. As expected, the signal is absent when the IR_{pump} arrives after the Vis_{pump}. As soon as the IR_{pump} precedes the Vis_{pump}, the VIPER 2D-IR signal appears. With increasing delay between the two pump pulses, the signal decays again. All of the traces can be fitted with two exponentials having lifetimes (errors) of 1.2 (0.1) ps and 9 (2) ps. 2D-IR measurements (Supporting Information, Figure S3) reveal the same time constants as VIPER 2D-IR. These lifetimes correspond well with previous work, where a less than 2 ps component has been interpreted as VR of the excited mode with accompanying IVR and a solvent-dependent 7 to 14 ps component has been assigned to cooling of the molecule (energy transfer to the solvent).[15] The VIPER 2D-IR signal thus persists even for delays between IR_{pump} and Vis_{pump} that are much longer then the T_1 of 1.2 ps of the initially excited mode. Importantly, this result shows that for a successful VIPER 2D-IR experiment it is beneficial but not necessary to have direct strong coupling between the initially excited mode used to select a sub-ensemble and the electronic transition. It is sufficient for reaching the electronically excited state in VIPER 2D-IR that the cross-section of the molecule for the Vis_{pump} is changed by IVR to FC-active modes. This effect is well-known from the investigation of IVR using IR-pump–UV-probe spectroscopy[9] as well as for double-resonance IR/UV gas phase experiments.[16] For observing the EXSY signal, the frequency of the initially excited vibration has to shift after electronic excitation, which can be caused by various effects. For investigating sub-ensemble specific photochemistry by VIPER 2D-IR, such a shift is not required. The selectivity and therefore the ability to measure exchange is not compromised by IVR, as it occurs within the species that has been initially excited by the IR_{pump}. This is not to be confused with the long-lived heat signal that can be generated in 2D-IR spectra after VR and thermalization of the excitation.[17] Such heat signals are useless, as the selectivity of the initial excitation is lost and therefore information about exchange kinetics cannot be retrieved. The effect of IVR to shift the Vis spectrum considerably extends the range of problems that can be studied by VIPER 2D-IR.

The experiments described above show that it is possible to store information on vibrational excitation in a long-lived electronic degree of freedom and to read it out again in the IR. In the following we demonstrate that this opens up the possibility to monitor chemical exchange that is much slower than T_1. To this end we prepared a mixture of C6 with MeOD in THF that contains a fraction of molecules with an H-bond to the C=O moiety of the dye and a fraction without H-bond. Figure 6A shows the TRIR spectrum of C6 in the presence

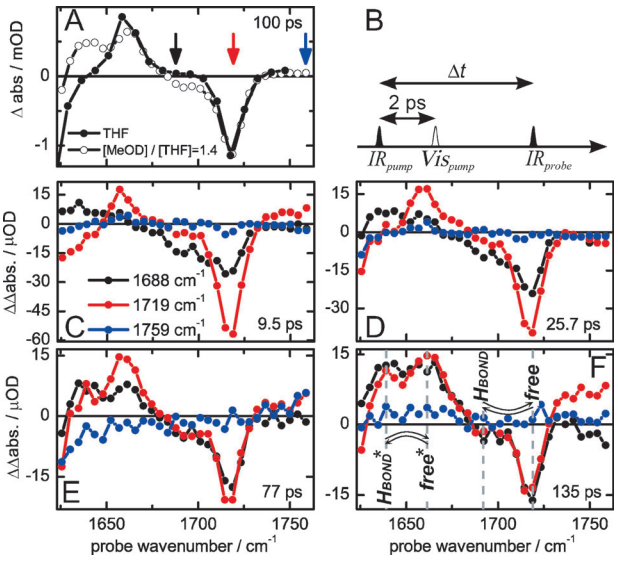

Figure 6. VIPER 2D-IR EXSY beyond T_1. A) TRIR spectra for C6 with and without MeOD in the C=O region. C–F) Cross-sections of the VIPER 2D-IR spectra of the sample with MeOD, pumped at the wavenumbers corresponding to the colored arrows in panel A. Note that signals at wavenumbers other than the IR_{pump} correspond to cross-peaks. The delay time Δt (B) is depicted in (C)–(F), which share the same tick increment of 15 µOD.

and absence of MeOD at 100 ps to show the influence of H-bond formation on the spectrum. As discussed before in the context of Figure 3C, both in S_1 (positive bands) and in S_0 (negative bands) there exist H-bonded and free species of C6. We therefore expect to see exchange between the free and H-bonded S_0 species but also between free and H-bonded S_1 species as indicated by the exchange arrows in Figure 6F.

Exchange rates in S_0 and in S_1 can of course be different. Generally, for applying the VIPER experiment, it is not necessary that the exchange process observed in the ground state bleach has a counter part in the electronically excited state. VIPER 2D-IR spectra are now recorded in the presence of MeOD. Figure 6C–F show the time evolution of selected cuts through the VIPER 2D-IR spectra in analogy to the cuts shown in Figure 1D. The cuts are chosen such that the IR_{pump} is either resonant with the H-bonded C=O (black curve, $\nu_{pump} = 1688\ cm^{-1}$), the free C=O (red curve, $\nu_{pump} = 1719\ cm^{-1}$) or off-resonant (blue curve, $\nu_{pump} = 1759\ cm^{-1}$) as a control experiment. In contrast to the signals obtained with a resonant IR_{pump}, the control experiment is featureless as expected, demonstrating again that the IR_{pump} has to be resonant to create a VIPER 2D-IR signal.

As a consequence of chemical exchange, we expect to observe the appearance of cross-peaks between the free and the H-bonded C=O with increasing delay, both for S_0 and for S_1. This effect is illustrated best using the cuts at $\nu_{pump} = 1719\ cm^{-1}$ (red curve), with the IR_{pump} resonant with the free C=O (red arrow in Figure 6A). At early delay ($\Delta t = 9.5$ ps, Figure 6C), we observe a signal that corresponds to the free C=O, both for the S_0 (labeled "free" in Figure 6F at $1719\ cm^{-1}$) and the S_1 state (the position labeled "free*" at $1657\ cm^{-1}$). As the delay is increased, cross-peaks to the H-bonded C=O become more and more pronounced owing to chemical exchange. They can be observed both in S_0 (the position labeled "H_{BOND}" at $1697\ cm^{-1}$) and even clearer in the S_1 (the position labeled "H_{BOND}*" at $1639\ cm^{-1}$). The bands correspond to the C=Os in their vibrational ground state, as vibrational excitation has already decayed. In the cuts at $\nu_{pump} = 1688\ cm^{-1}$, with the IR_{pump} resonant with the H-bonded C=O, the exchange process is observed as well. However, we already start with a considerable fraction of directly excited free C=O (Figure 6C) owing to the $14\ cm^{-1}$ width of the IR_{pump} and the large population of free C=O. At long delays ($\Delta t = 135$ ps, Figure 6F), the two cuts resemble each other, as chemical exchange has led to complete equilibration between H-bonded and free C=O, both for S_0 as well as the S_1 state (compare Figure 1D, last panel).

An exact exchange time constant is difficult to estimate owing to the small number of available time points and noise, but the process is clearly not completed after 77 ps (Figure 6E), long after VR of the C=O marker mode used here (Supporting Information, Figure S3C). The current experiment only used about 100 nJ of IR excitation power, the signal size could thus be considerably increased using higher excitation power. Narrow band pulses with up to 400 times more pulse energy have been used in 2D-IR experiments.[18] Alternatively, VIPER could be implemented with Fourier-transform (FT) 2D-IR spectroscopy using a pair of broad band pulses for IR excitation, either in a pump-probe[19] or box-CARS geometry.[20] In FT 2D-IR spectral resolution does not have to be traded for time resolution as is the case for narrow band excitation and a higher S/N ratio can be achieved. An advantage of narrow band excitation is the ability to measure selected cuts through 2D-IR spectra, while in FT 2D-IR always a whole 2D spectrum has to be obtained. Measuring cuts is of importance when for example, the excited state dynamics of a certain sub-ensemble is under investigation as explained below.

The above VIPER experiment furthermore confirms the ability to carry out sub-ensemble selective time-resolved IR spectroscopy in a mixture of species (sub-ensemble selective photochemistry). Note that the VIPER 2D-IR cut at $\nu_{pump} = 1719\ cm^{-1}$ at early delay ($\Delta t = 9.5$ ps, Figure 6C) resembles the TRIR spectrum of the MeOD-free sample (Figure 6A, closed circles), even though the spectra are obtained for a sample that contains an excess of MeOD. This illustrates that it is possible to select a certain molecular species out of a mixture by the narrow band IR_{pump} (for example, a conformer or H-bonded state) and study its time evolution during a photochemical process. Applications in synthesis are also conceivable.

In summary, we have demonstrated that VR can be overcome in 2D-IR exchange spectroscopy and chemical exchange can be measured long after VR is over. This is achieved by the addition of an off-resonant Vis or UV laser pulse shortly after a resonant IR pump pulse. The experiment makes explicit use of the coupling between vibrational and electronic degrees of freedom. In this way, information on the IR excitation can be stored in an electronic degree of freedom. The 2D-IR exchange signal then persists with the electronic lifetime that can be considerably longer than typical vibrational lifetimes. In certain cases, where electronic excitation leads to structure changes (for example, isomerization or dissociation), extremely long-lived or even "eternal" 2D-IR exchange signals can be generated. A prerequisite for application of our approach is that the IR_{pump} modulates the Vis or UV cross-section of the molecule. Importantly, direct vibronic coupling between the marker mode and the electronic transition is not necessarily required, and IVR into FC active modes of the molecule after IR excitation is sufficient for reaching the electronically excited state.

An intriguing application of the VIPER 2D-IR pulse sequence demonstrated herein is to record time resolved IR spectra of photochemical processes of distinct species in a mixture that have been selected by the IR excitation pulse. This sub-ensemble selective photochemistry is a particularly powerful approach if the species of interest cannot be isolated and studied separately, for example, because of rapid dynamic equilibrium between conformers. Even selective investigation of the photochemistry of identical molecules in different local environments can be achieved if the change in environment affects a vibrational frequency of the molecule, as is the case for the H-bonding equilibrium investigated here.

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