

Femtosecond infrared pump – stimulated Raman probe spectroscopy: the method and its first application to study vibrational relaxation pathway in liquid water

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Abstract. We apply femtosecond-infrared pump- stimulated Raman probe spectroscopy (fs-IR-SRS) which provides sub-100 fs time resolution, spectral resolution better than 10 cm^{-1} and the 100 cm^{-1} to 4000 cm^{-1} probe bandwidth to study vibrational relaxation pathway after vibrational excitation of OH stretching mode in HDO in the system composed of 30 % of HDO in D_2O .

1 Introduction

The major goal of the contemporary ultrafast vibrational spectroscopy is to provide material scientists, biologists and physical chemists with a detail dynamical image of inter- and intramolecular interactions, of molecular dynamics and to some degree of supramolecular structuring of matter. On the top of the inherent features of vibrational spectroscopy, the perfect vibrational time-resolved method should provide time resolution better than 50 fs, spectral resolution better than 10 cm^{-1} and the possibility of simultaneous observation of dynamical changes in the whole range of molecular vibrations after some perturbation of a system. For some scientist an access to low frequency intermolecular vibrational modes below 500 cm^{-1} would be a huge additional advantage of a method. Such method is difficult to achieve mainly due to Fourier-transform limitation of an optical pulses which can provides spectral bandwidth in the range: 100 cm^{-1} - 500 cm^{-1} .

Yet, in recent years, a big step toward the desired method was made thanks to progress in generation of broadband infrared (IR) continuum through laser beam filamentation in air [1]. As result broadband IR probe pulses (from around 400 cm^{-1} to around 3300 cm^{-1}) were successfully applied in femtosecond IR and 2-dimensional IR spectroscopy (2DIR) [2] Earlier, this sort of method was attempted to achieve by Kaiser and Laubereau [3] followed by Dlott and co-worker [4] who all applied IR pump – Raman probe scheme of experiments. Thanks to inherent features of Raman scattering these methods provided multiplex detection but their time-resolutions were picosecond either due to the existing technology of IR pulses generation at that time (Kaiser & Laubereau) or because of picosecond Raman probe pulse being a trade-off between time and spectral resolution of the method (Dlott).

2 Concept of experiment

In this work we present a new method: femtosecond infrared pump – stimulated Raman probe spectroscopy (fs-IR-SRS). In the femtosecond stimulated Raman spectroscopy (FSRS) the Raman transition is induced with two pulses: narrow-bandwidth picosecond pulse to initialize the Raman transition and a broadband ultrashort probe pulse to stimulate the Raman transition. [5] All information about the system available in this process is contained in the ultrashort probe pulse. The time resolution of FSRS is limited only by the cross-correlation of the first excitation pulse and the probe pulse, which can be easily below 50 fs. It was demonstrated in [6], the spectral resolution is limited mainly by the Raman pump spectrum and is independent of other pulses used in FSRS. This way one can circumvent a traditional frequency – time transform relation which limits typical pump-probe experiments. In our modification of the initial concept of FSRS we replace visible actinic pulse with a femtosecond infrared pulse which promote vibrational transition in a system.

3 Experimental

The optical setup is powered with commercial femtosecond Yb:KGW amplifier (Pharos, Light Conversion) which produces 200 fs pulses centred at 1030 nm. The tuneable (in the range: $1.2\ \mu\text{m}$ – $6\ \mu\text{m}$) infrared pulses are generated in a two-stages Optical Parametric Amplifier (OPA) of own design with a potassium titanyl arsenate – (KTA)

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crystal used in a second stage of amplification. The scheme of generation of infrared pulses was detailedly presented in here: [7]. The Raman probe beam (white light) is generated by focusing small portion of energy in a Sapphire plate. Our method of the generation of narrow-bandwidth tuneable Raman pump pulse was described elsewhere: [8]. The isotopic solution of 30 wt. % of HDO in D₂O was prepared by mixing D₂O (Cambridge Isotope Laboratories Inc., 99.9 % of D atoms) with an appropriate amount of H₂O (ultrapure water, Millipore Direct Q3 UV). All experiments we perform on a thin (around 50 μm) film of water flowing between two metal wires.

4 Results

The “proof-of-concept” experiment of fs-IR-SRS we performed with IR pump pulse centred at 3300 cm^{-1} (4 μJ) which matches an energy of OH stretch 0 \rightarrow 1 vibrational transition. The cross-correlation of the IR pump pulse and white light probe was around 95 fs. In the Raman spectral range: 3100 cm^{-1} -3800 cm^{-1} we observe a fast decaying transient SRS signal of the OH stretch vibrations (see Fig. 1a). The transient signal is composed of the bleaching at 3460 cm^{-1} related to depopulation of the ground state of OH stretching and the increased intensity at 3290 cm^{-1} which we assign to anharmonically shifted 1 \rightarrow 2 transition of OH stretch vibrations. The bleaching signal decays with relaxation time $t_1^{\text{OH}} = 290 \pm 30$ fs (see: time traces in Fig. 1b) which agrees well with relaxation time of OH stretch in pure H₂O [9]. It is known from fs-IR studies that such short vibrational lifetime is a result of ultrafast Förster resonance energy transfer (FRET) between neighbouring OH groups. [10] At high isotopic dilution (<8 % of HDO in D₂O) the FRET contribution is negligible and observed vibrational lifetime of OH stretch is much longer (around 700 fs) [11]. In a system studied by us (30 % HDO in D₂O) the significant FRET contribution results in the vibrational lifetime similar to that of pure H₂O.

Another transient signal is present in the spectral range characteristic for OD stretching vibration (2300 cm^{-1} -2900 cm^{-1} , Fig. 1a) After the decay of the pronounced cross-phase modulation artefact we observe a decaying transient SRS signal composed of bleaching at around 2605 cm^{-1} and increased intensity at around 2400 cm^{-1} . The bleaching signal at 2605 cm^{-1} decays with relaxation time of $t_1^{\text{OD}} = 400 \pm 100$ fs which corresponds well with vibrational relaxation time of OD stretch in pure D₂O. [12] We suspect that this transient signal may originate from anharmonic coupling between OH stretch and OD stretch vibrations in HDO molecules. At the current state of experimental work and analysis we cannot exclude however, that the transient signal in the OD stretch range results from thermalization of the sample.

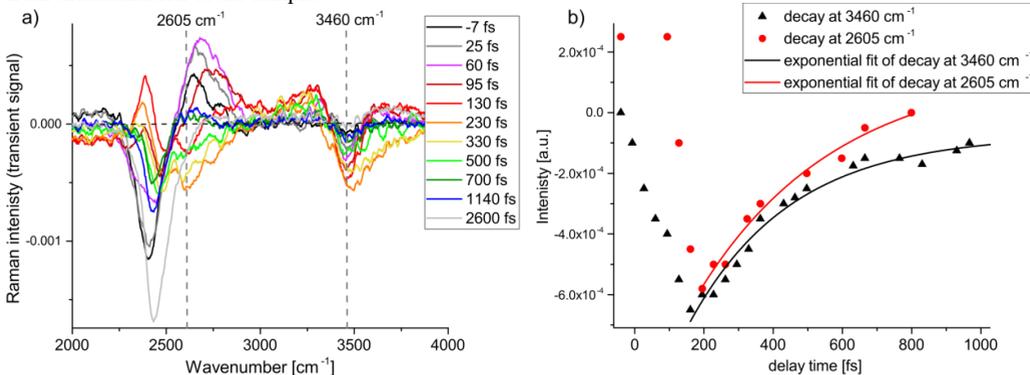


Fig. 1 - Transient SRS spectra of water at several delay times after infrared excitation at 3300 cm^{-1} of OH stretching mode of HDO (a), time traces of the transient SRS signal at 2605 cm^{-1} (circles) and 3460 cm^{-1} (triangles) together with monoexponential fits to the data.

5 Conclusions

We have constructed a unique setup for femtosecond infrared pump -stimulated Raman probe spectroscopy which provides sub-100 fs time resolution, spectral resolution better than 10 cm^{-1} and the 100 cm^{-1} to 4000 cm^{-1} probe bandwidth thanks to a multiplex ability of stimulated Raman process. We applied this technique to study vibrational relaxations pathway in the system composed of 30% HDO in D₂O and we determined vibrational relaxation times of OD stretch (400 \pm 100 fs) and OH stretch (290 \pm 30 fs) vibrations which are in good agreement with vibrational lifetimes determined earlier with femtosecond IR spectroscopy.

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References

1. P.B. Petersen, A. Tokmakoff, *Opt. Lett.*, **35** 12, p. 1962-1964 (2010)
2. K. Ramasesha, L. De Marco, A. Mandal, A. Tokmakoff, *Nature Chem.*, **5** p. 935 (2013)
3. A.Laubereau, S.F. Fischer, K. Spanner, W. Kaiser, *Chem. Phys.*, **31** 3, p. 335-344.(1978)
4. J.C.Deák, L.K. Iwaki, D.D. Dlott, *J Phys. Chem. A*, **102** 42, p. 8193-8201 (1998)
5. P. Kukura, D.W. McCamant, S. Yoon, D.B. Wandschneider, R.A. Mathies, *Science*, **310** 5750, p. 1006-1009 (2005)
6. Z. Sun, J. Lu, D.H. Zhang, and S.-Y. Lee, *J Chem. Phys.*, **128** 14, p. 144114 (2008)
7. M. Nejbauer, M. Pastorcak, T. Kardaś, Y. Stepanenko, C. Radzewicz. (*Conference Presentation*). in *SPIE LASE*. **10516** SPIE. (2018)
8. M. Nejbauer, C. Radzewicz, *Opt. Express*, **20** 3, p. 2136-2142 (2012)
9. S.T. v. d. Post, C.-S. Hsieh, M. Okuno, Y. Nagata, H.J. Bakker, M. Bonn, J. Hunger, *Nature Comm.*, **6**: p. 8384 (2015)
10. S. Woutersen, , H.J. Bakker, *Nature*, **402** 6761 p. 507-509 (1999)
11. S Woutersen, E. Uli, H.-K. Nienhuys, H. J., Bakker, *Phys. Rev. Lett.*, **81**(5): p. 1106--1109.1998
12. L. Piatkowski, K.B. Eisenthal, H.J. Bakker, *Phys. Chem. Chem. Phys.*, **11** 40 p. 9033-9038 (2009)