

VIBRATIONAL EXCITATION AFTER ULTRAFAST INTRAMOLECULAR PROTON TRANSFER: A STUDY UNDER CONDITIONS OF TIME-DEPENDENT RESONANCE RAMAN CROSS SECTIONS

W. Werncke, V. Kozich, and J. Dreyer

Max-Born-Institut, Max-Born-Strasse 2A, D-12489 Berlin, Germany
werncke@mbi-berlin.de

Keywords: *molecules, proton transfer, time-resolved, resonance Raman scattering*

Abstract: Vibrational excitation and energy redistribution after the ultrafast intramolecular proton transfer cycle of TINUVIN is investigated by a combined picosecond Stokes and anti-Stokes resonance Raman study. We show that a low-frequency proton transfer promoting mode serves as the major accepting mode.

Introduction:

2-(2'-hydroxy-5'-methyl-phenyl)benzotriazole (TINUVIN) is a photostabilizer under-going a reaction cycle of intramolecular photo-induced proton transfer within about 1 ps [1].

It is still unknown which mode(s) accept(s) the huge excess energy of this process [2]. A prominent role of a low-frequency mode at 469 cm^{-1} is indicated by coherent oscillations during and after the reaction cycle as well as by resonance Raman data. This mode which contains a coordinate changing the O...N separation in the intramolecular hydrogen bond has been identified as a proton transfer promoting mode [3, 4].

To identify the accepting modes we studied vibrational excitation and energy redistribution of TINUVIN after the proton transfer cycle. We applied two-color picosecond resonance Raman spectroscopy [5]. Assignment of the vibrations is based on DFT calculations.

Measurements of vibrational kinetics after the proton transfer cycle:

TINUVIN dissolved in cyclohexane ($5 \cdot 10^{-3}\text{ mol/l}$) was electronically excited around 350 nm, and Stokes- and anti-Stokes resonance Raman spectra were probed at 310 and 325 nm, respectively. The kinetics of Stokes resonance Raman intensities of three prominent Raman lines (469 , 685 and the spectrally unresolved doublet ($1422/1449\text{ cm}^{-1}$) at 1435 cm^{-1}) show a sub-picosecond decrease followed by a recovery within about 30 ps (Fig. 1A). Time-resolved anti-Stokes resonance Raman intensities of the three modes are depicted in Fig. 1B. The $1422/1449\text{ cm}^{-1}$ doublet shows a fast rise of intensity close to our temporal resolution being in contrast to the much slower rises of the 469 and 685 cm^{-1} modes approaching their maxima at about 7 and 10 ps delay times, respectively.

Determination of vibrational excess populations, discussions:

As the proton transfer cycle is ultrafast it can not be the reason for the slow recovery of Stokes resonance Raman intensities which is shown in Fig. 1A. As it is demonstrated in [6] it is mainly due to the time-dependent resonance Raman scattering cross sections depending on vibrational excitation. Therefore, to exclude this influence [7] instead of relating vibrational excess populations directly to anti-Stokes Raman intensities, we determined ratios of time-dependent anti-Stokes Raman to the corresponding time-dependent Stokes resonance Raman intensities which are plotted in Fig. 1C. Excitation of the modes is characterized by introducing "mode temperatures" which follow from these intensity ratios for each individual mode. They are compared with the maximum temperature of the molecule of about 1200 K which could be achieved by heating with the excess energy of the reaction [2]. At earlier times "mode temperatures" indicate pronounced non-thermal vibrational population distributions. For instance, 5 ps after excitation the ratio for the 469 cm^{-1} mode (corresponding to a temperature of 2300 K) is significantly higher than any possible temperature demonstrating that this mode acts as an accepting mode. For time delays longer than 15 ps the molecule is thermalized and the modes cool down with the same temperature.

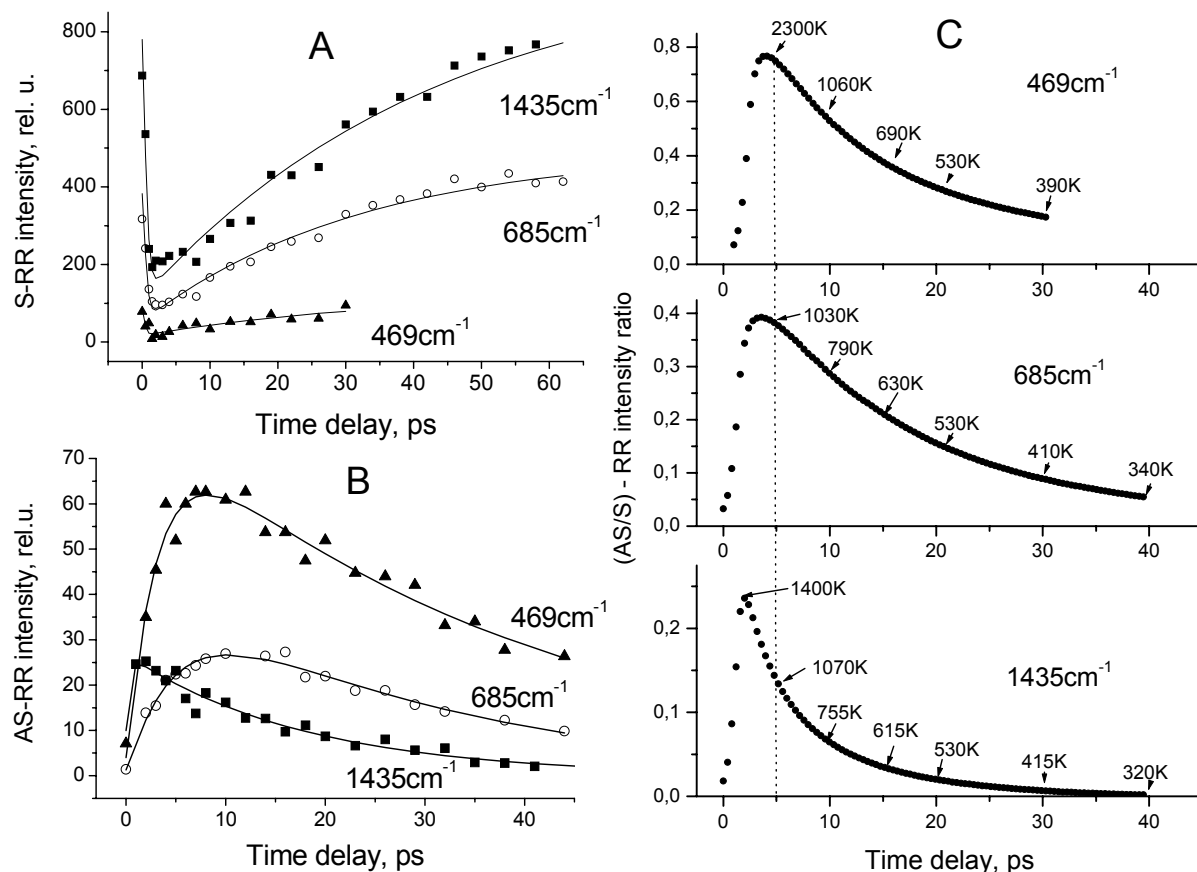


Fig. 1 A: Time dependence of Stokes resonance Raman (S-RR) intensities
 B: Time dependence of anti-Stokes resonance Raman (AS-RR) intensities
 C: Time dependence of (AS/S)-RR intensity ratios

In conclusion, we have demonstrated, that with time-dependent resonance Raman cross sections direct information on vibrational temperatures or more in general, vibrational excess populations can be derived from combined anti-Stokes and Stokes resonance Raman intensity measurements.

For the first time we show that a low-frequency proton transfer promoting mode which is known to be coherently excited on a femtosecond time scale, later on also contains a considerable excess of vibrational energy. Strong excess population of this mode emphasizes its particular role in proton transfer and in internal vibrational energy redistribution.

Acknowledgements:

Financial support from the German Science Foundation is highly acknowledged.

References:

1. M. Wiechmann, H. Port, F. Laermer, W. Frey, and T. Elsaesser, Chem. Phys. Lett. **165**, 28 (1990).
2. K. Lenz, M. Pfeiffer, A. Lau and T. Elsaesser, Chem. Phys. Lett. **229**, 340 (1994).
3. C. Chudoba, E. Riedle, M. Pfeiffer and T. Elsaesser, Chem. Phys. Lett. **263**, 622 (1996).
4. M. Pfeiffer, K. Lenz, A. Lau and T. Elsaesser, Chem. Phys. Lett. **268**, 258 (1997).
5. V. Kozich, W. Werncke, A.I. Vodchits and J. Dreyer; J. Chem. Phys. **118**, 1808 (2003).
6. V. Kozich and W. Werncke, submitted to ICORS 2004
7. K.T. Schomacker and P.M. Champion, J. Chem. Phys. **90**, 5982 (1989).