

Intra- and Intermolecular Vibrational Coupling in a Polymerization Reaction

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Vibrational coupling of N=C=O stretching vibration at 2270 cm⁻¹ with lower frequency modes in two reactants of a polymerization reaction are studied with 2D IR spectroscopy. The observed coupling with 1530 cm⁻¹ modes indicates that this vibration could contribute to the chemical reaction coordinate.

In our recent study of polymerization, we have revealed statistically an increase of up to about 20% in the chemical reaction rate by excitation of definite vibrational modes of the reactants, which belong to, or are coupled to the reaction coordinate. The subject of our study was a step-growth reaction of the polyurethane formation resulting from the chemical reaction between toluene-2,4-diisocyanate (TDI) and 2,2,2-trichloro-1,1-diol (chloral hydrate or TCD) [1].

The strongest, well separated IR band, which is convenient for the reaction rate control, and contributes to the reaction coordinate, is the 2270 cm⁻¹ N=C=O band of the TDI [1]. We performed 2D IR spectroscopy to study the coupling of the mentioned vibrational mode with other vibrational modes in the mixture of equimolar solutions of the reactants TDI and TCD in dimethyl sulfoxide (DMSO).

Our 2D IR set-up has two independent tunable fs optical parametric oscillators (OPA) working at a repetition rate of 2-4 kHz [2]. To measure 2D spectra, we used a pump-probe geometry, a data accumulation, and a data processing system similar to the one described in [3]. The probe signal is detected by a double array HgCdTe detector with 16 pixels. The scan of the pump wavelength is done with a help of a Mach-Zehnder interferometer.

Upon excitation of the N=C=O stretching vibration in a TDI/TCD mixture we observe vibrational dynamics around 1530 cm⁻¹, in a well separated spectral range. This indicates strong intramolecular coupling of these vibrational modes.

Furthermore, investigations of the reactants phenylisocyanate (PHI) and cyclohexanol (CH-ol) dissolved in tetrahydrofuran were performed. Here, we excited the relatively strong and well isolated OH stretching vibration of CH-ol, and observed vibrational dynamics in the spectral range of 1730 cm⁻¹. We assign these to intramolecular vibrational interactions, which should be stronger than those due to intermolecular couplings.

Despite the presence of intermolecular interactions and polymerization reactions the intermolecular coupling is weak and we need to improve the signal to noise ratio substantially to be able to cleanly confirm it.

[1] V. Kozich, A.A. Ahmed, F. Kössl, O. Kühn, K. Heyne, Nat. Chemistry (2016) (submitted).

[2] V. Kozich, A. Moguilevski, K. Heyne, Opt. Commun. **285**, 4515 (2012).

[3] H. Helbing and P. Hamm, J. Opt. Soc. Am. **28**, 171 (2011).