

Acceleration of a ground-state reaction by selective femtosecond infrared laser excitation

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Infrared (IR) excitation of vibrations that participate in the reaction coordinate are believed to accelerate an otherwise thermally driven chemical reaction. Attempts of practical realization of this concept have been hampered so far by competing processes leading to sample heating. Here we demonstrate, using femtosecond IR-pump IR-probe experiments, the acceleration of urethane and polyurethane formation due to vibrational excitation of the reactants for 1:1 mixtures of phenylisocyanate and cyclohexanol, and toluene-2,4-diisocyanate and 2,2,2-trichloroethane-1,1-diol, respectively. We determined reaction rate changes upon selective vibrational excitation with negligible heating of the sample and observed an increase of the reaction rate up to 24%. The observation is rationalized using reactant and transition state structures obtained from quantum chemical calculations. We utilized reaction acceleration to write a polyurethane square on sample windows by a femtosecond IR pulse.

New cost-effective methods for synthesis of molecular films or three-dimensional architectures with specific properties are in demand. For example, IR laser induced synthesis of graphene has been demonstrated, utilizing photothermal effects at high temperatures to manufacture films with high electrical conductivity¹. A standard tool in imaging and radiation curing technologies is photopolymerization²⁻⁵. Here, the polymerization reaction is triggered or accelerated by the absorption of visible light. In most cases, this involves photochemistry via excited electronic states²⁻⁵, i.e. with radical formation, dissociation of molecules or via high vibrational overtones⁶⁻¹¹. A reduction of photon numbers and energy would decrease the costs of laser-based methods. This should be possible by controlling thermally driven reactions by a single photon with moderate energy as provided by the IR spectral region.

Many chemical reactions are driven by thermal activation¹²⁻¹⁴. In a simplified picture, a ground-state reaction proceeding from reactants such as phenylisocyanate (PHI) and cyclohexanol (CH-ol) to a product (here cyclohexyl-carbanilate, CC) can be expressed as a transformation on an energy surface from a reactants' energy minimum to a product energy minimum through a transition state (cf. Fig. 1). Thereby, the reaction coordinate (RC) traces the reaction pathway with the lowest energy. Elevated temperatures increase the collision rate and hence the population of vibrational modes of higher energy participating in the RC. Thus, nuclear conformations can be reached that are associated

with the transformation from reactants to the transition state and thermal energy propels the system over the transition state to the product.

While temperature dependence of a chemical reaction in solution provides important information on the reaction rate and activation barrier^{12,13}, details on the RC, on the nuclear conformation, and the dynamics of the reactive complex and its surroundings at the transition state (TS) are hard to obtain for ground state reactions¹⁵.

It is known that coherent excitation pulses can be applied to select and optimize specific molecular reaction pathways. Coherent control strategies were developed for electronic ground and excited states (for reviews, see refs. 16-20). Recently, it was shown that mode specific excitation of vibrations coupled to electron transfer pathways in an excited electronic state can efficiently change the outcome of a reaction^{21,22}.

In contrast, acceleration of thermally driven ground state reactions without heating all molecules is very difficult. Heating the sample results in excitation of vibrational modes according to the Boltzmann distribution. In comparison, direct IR excitation instantaneously populates a specific vibrational mode²³⁻²⁵. Relaxation of the excited mode occurs via intramolecular vibrational energy redistribution (IVR) on a picosecond (ps) time scale and intermolecular vibrational energy relaxation (VER, also called intermolecular energy transfer, IET) into a microvolume around the excited molecule on a longer time scale²⁶⁻³¹. Hence, to distinguish between excitation of RC and heating, time resolved experiments with ultrafast time resolution are necessary. Thus, femtosecond (fs) IR excitation is a promising tool to initiate and track otherwise thermally driven chemical reactions via direct excitation of the RC. However, there are only very few successful experimental realizations of fs IR pulse initiated reactions, which are limited to small molecules undergoing simple unimolecular reactions. For instance, Motzkus et al. demonstrated vibrational ladder climbing enhancing the statistical dissociation yield of Cr(CO)₆ decarbonylation²³. In a pioneering work, the same group also demonstrated nonstatistical dissociation of CH₂N₂, but in gas phase³². Furthermore, Hamm et al. used IR laser pulses to drive the cis-trans-isomerization of HONO in a Kr matrix at 32 K³³. Up to now, IR pulse driven reactions were limited to unimolecular systems in the condensed phase.

In this study, for the first time, we present evidence for acceleration of urethane and polyurethane formation by direct ultrafast IR excitation of the alcohol OH-stretching vibration and the isocyanate NCO-stretching vibration, respectively. At these spectral positions, solvent absorption is negligible.