

Decoding the role of heat in plasmon-driven coupling reactions: the case of nitrothiophenol

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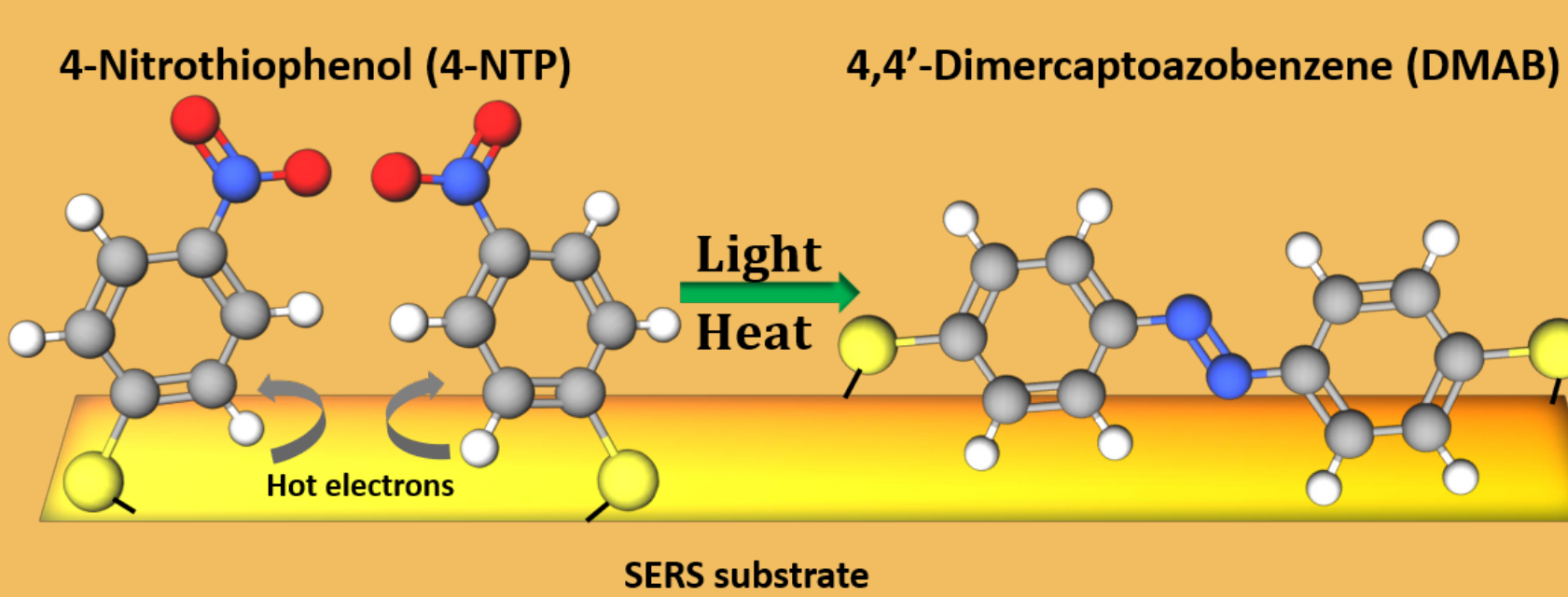
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Summary

Today, the reaction rates of many plasmon-driven reactions is rather low. In particular the reaction times of the technologically highly relevant coupling reactions is often in the range of tens to hundreds of seconds. In order to increase the rates, it is important to not only understand the mechanism that initialises the reaction, but also the factors limiting it.

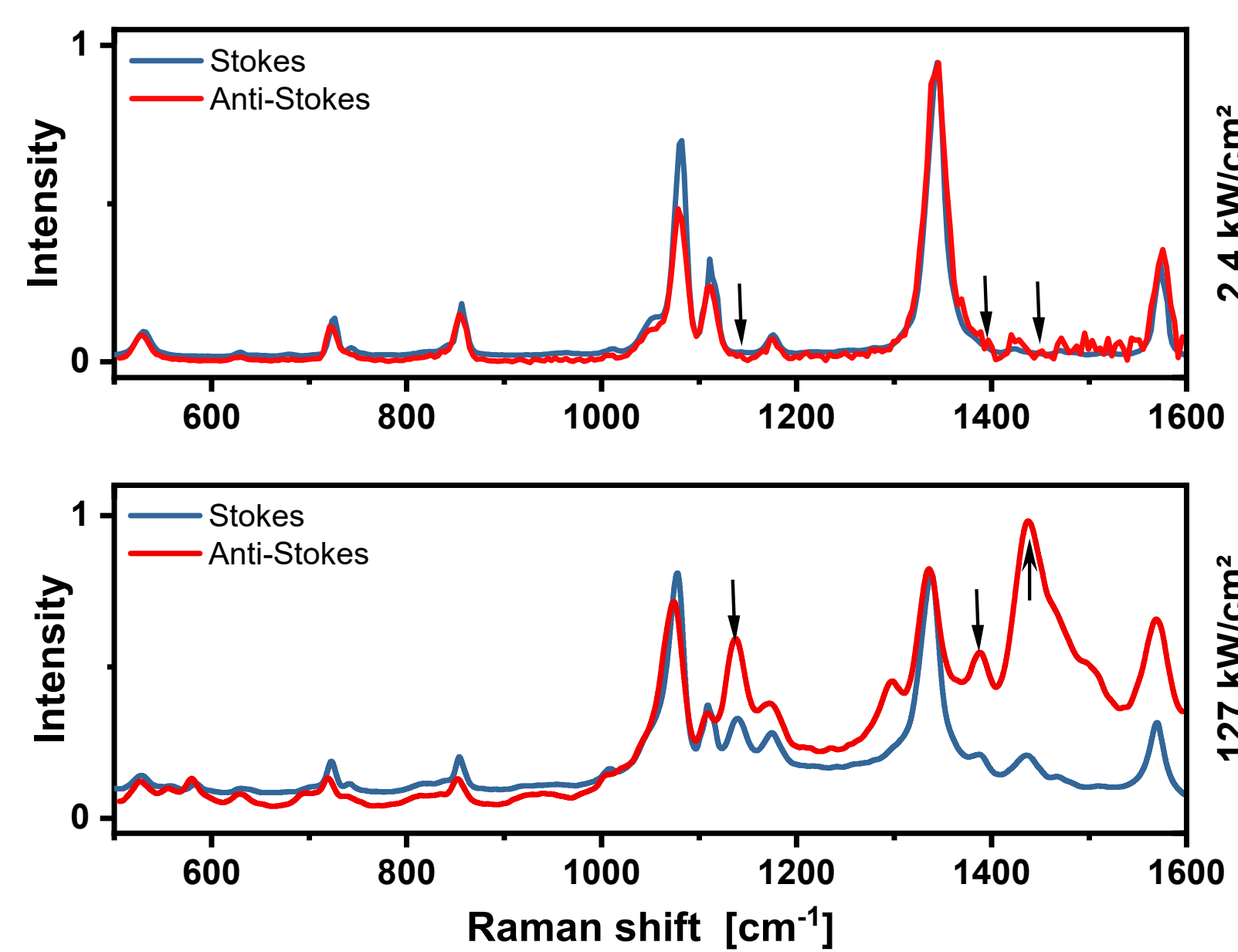
Here we investigate on the role of heat on the kinetics of a classical plasmon-driven N=N coupling reaction: the dimerization of 4-nitrothiophenol (4-NTP) to 4,4'-dimercaptoazo-benzene (DMAB). Initially, we determined the temperature of Au nanoparticles, reactants, and product molecules. The observed temperature increase of up to 350 K under reaction conditions already imply a non-negligible role of heat in this reaction. Moreover, a comparison of the 4-NTP dimerization to the dimerization of the more flexible 4-Nitrobenzylmercaptan (4-NBM) clearly indicates that the dimerization and not the electron-driven activation step limits the reaction. Finally, by comparing the dependence of the 4-NTP dimerization kinetics on external heating with its dependence on light intensity, we demonstrate that as soon as the reactants can be activated, the over-all reaction is



Plasmonic Heating

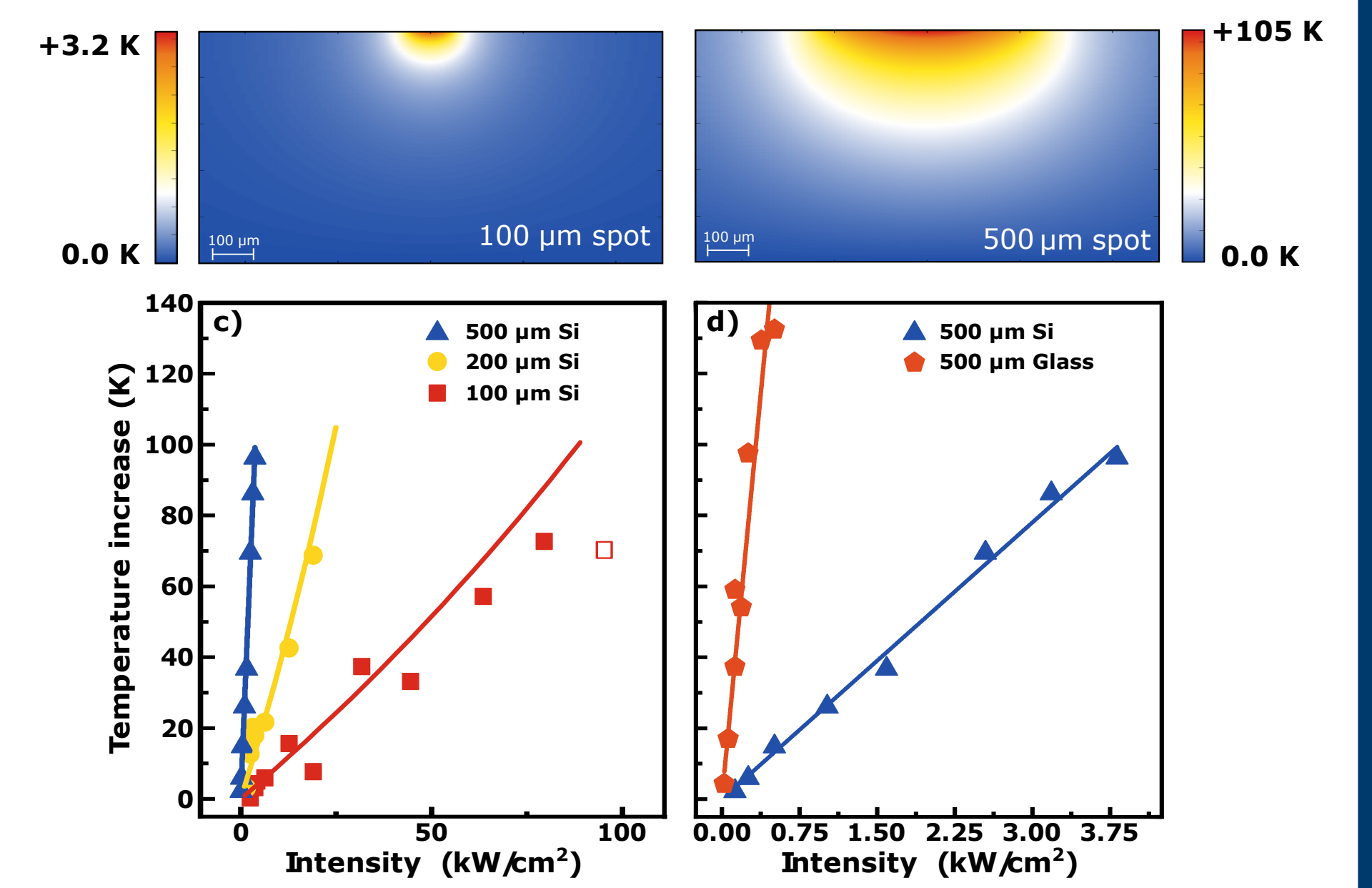
Measuring the particle heating directly is a non-trivial task. We used two methods: Raman thermometry allows to determine the temperature of the reactants and particles. XRD is a more direct measurement of the particle temperature.

Raman Thermometry [1]



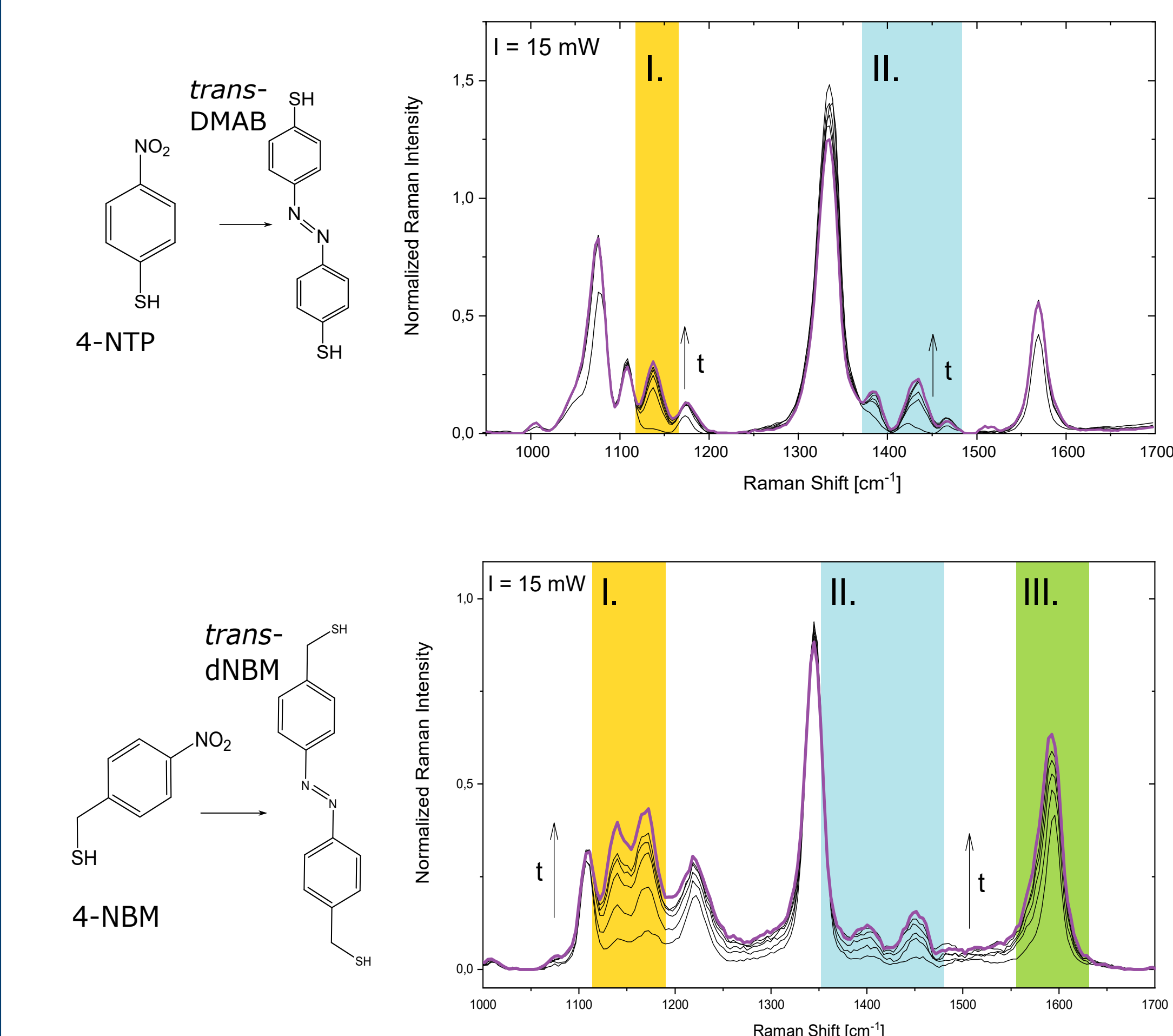
Raman thermometry (comparing Stokes and Anti-Stokes scattering) showed a clear temperature increase of $T = 200$ K for the reactant and 350 K for the product at high laser intensities. At low intensities no increase was found. The particle temperature was estimated at about 150 K.

X-Ray Diffraction [2]



Similar particle temperatures were determined by XRD measurements. Here we also investigated an often overlooked effect: the particle temperature not only depends on the laser intensity, but also on spotsizes and substrate properties, such as heat conductivity.

Rate Determining Step [3]



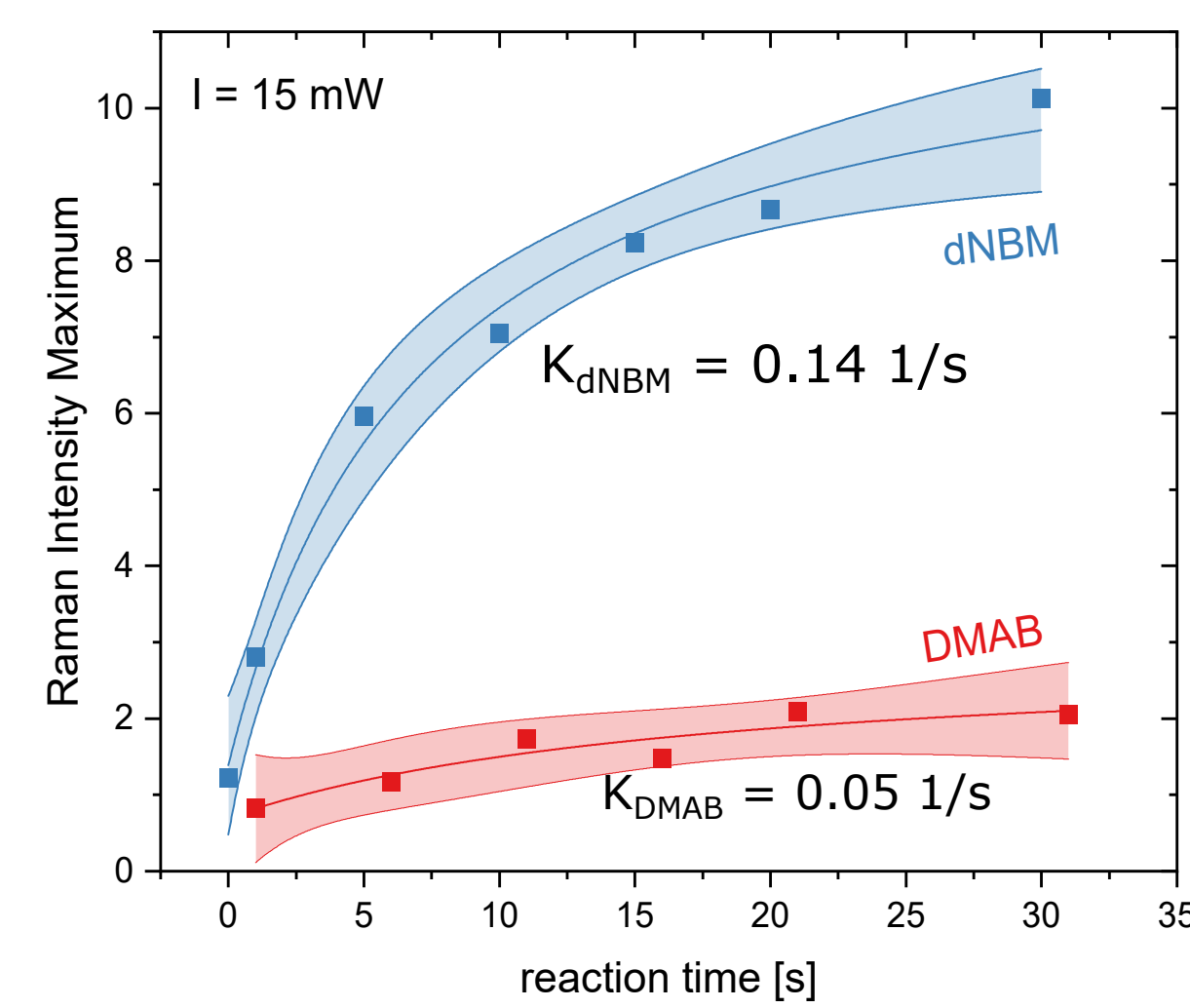
The 4-NBM molecule is functionally similar to 4-NTP, but possess an additional methylene group that gives it a higher flexibility but also removes it further from the gold surface. Thus compared to 4-NTP electron injection should be hindered, while the coupling process will improve.

Comparing the reaction kinetics at the characteristic product wavenumber of 1130 cm^{-1} shows a 2x higher reaction rate for 4-NBM. Thus not the activation but the coupling step limits the coupling of 4-NTP.

The lower rate of 4-NTP can be understood in the sense that only a part of the consumed reactants couple to form the DMAB product, such that on average 4 reactant molecules form one product. For 4-NBM nearly all reactant molecules convert to the dimer product and the conversion factor is accordingly around 2.

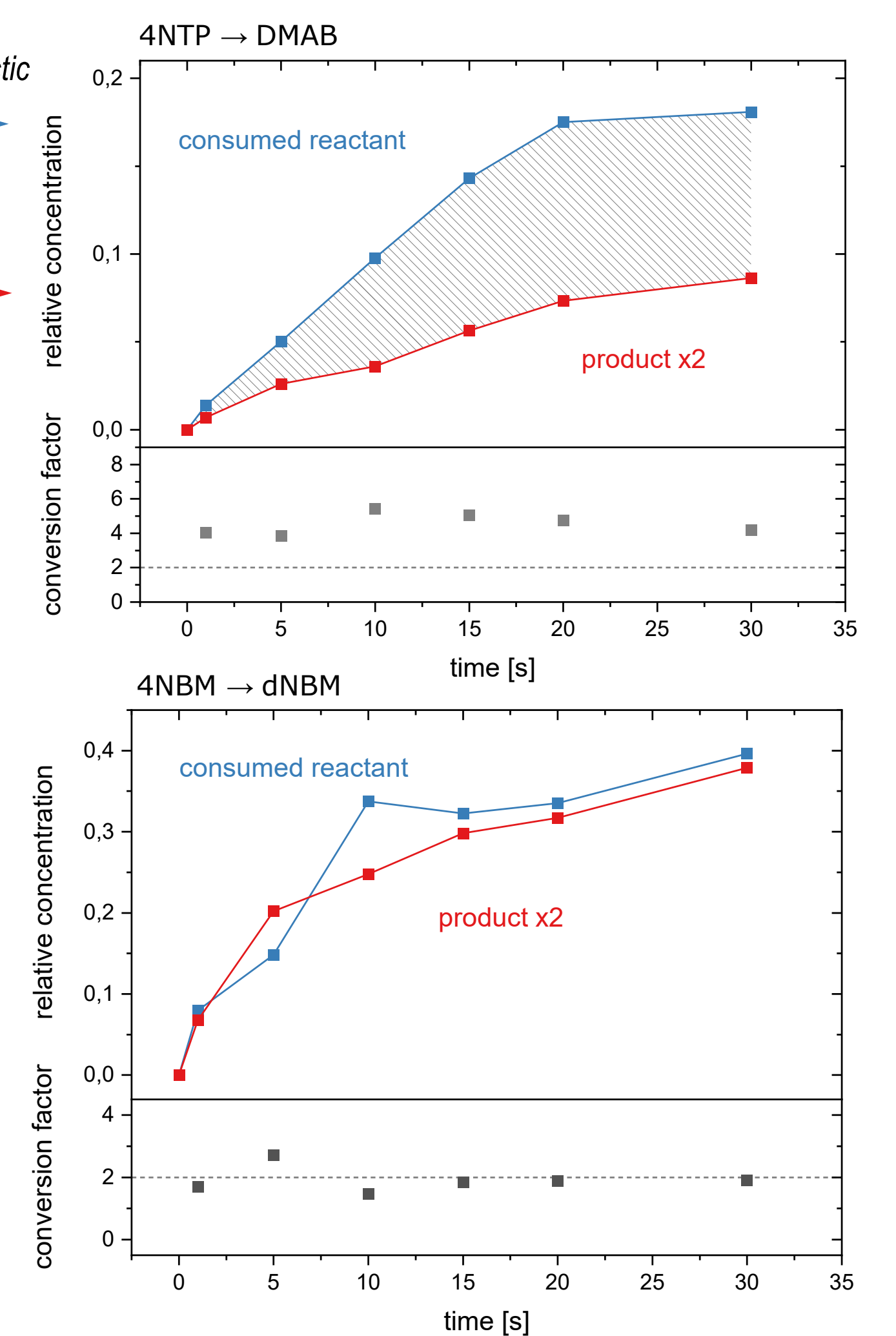
The consumed reactant is determined from the characteristic reactant peak at 1350 cm^{-1} .

The product is normalized to the maximum product signal obtained from the fitting.



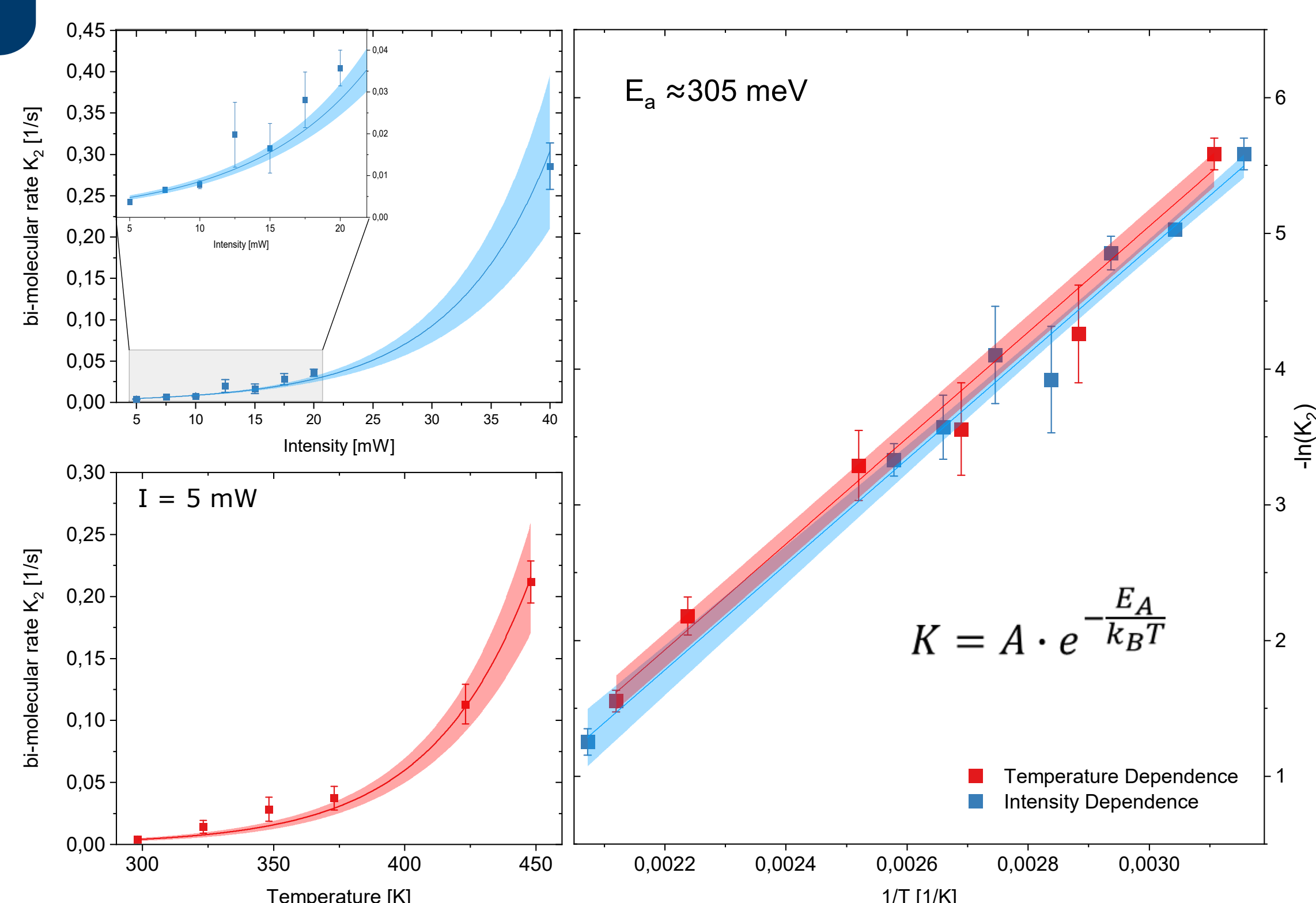
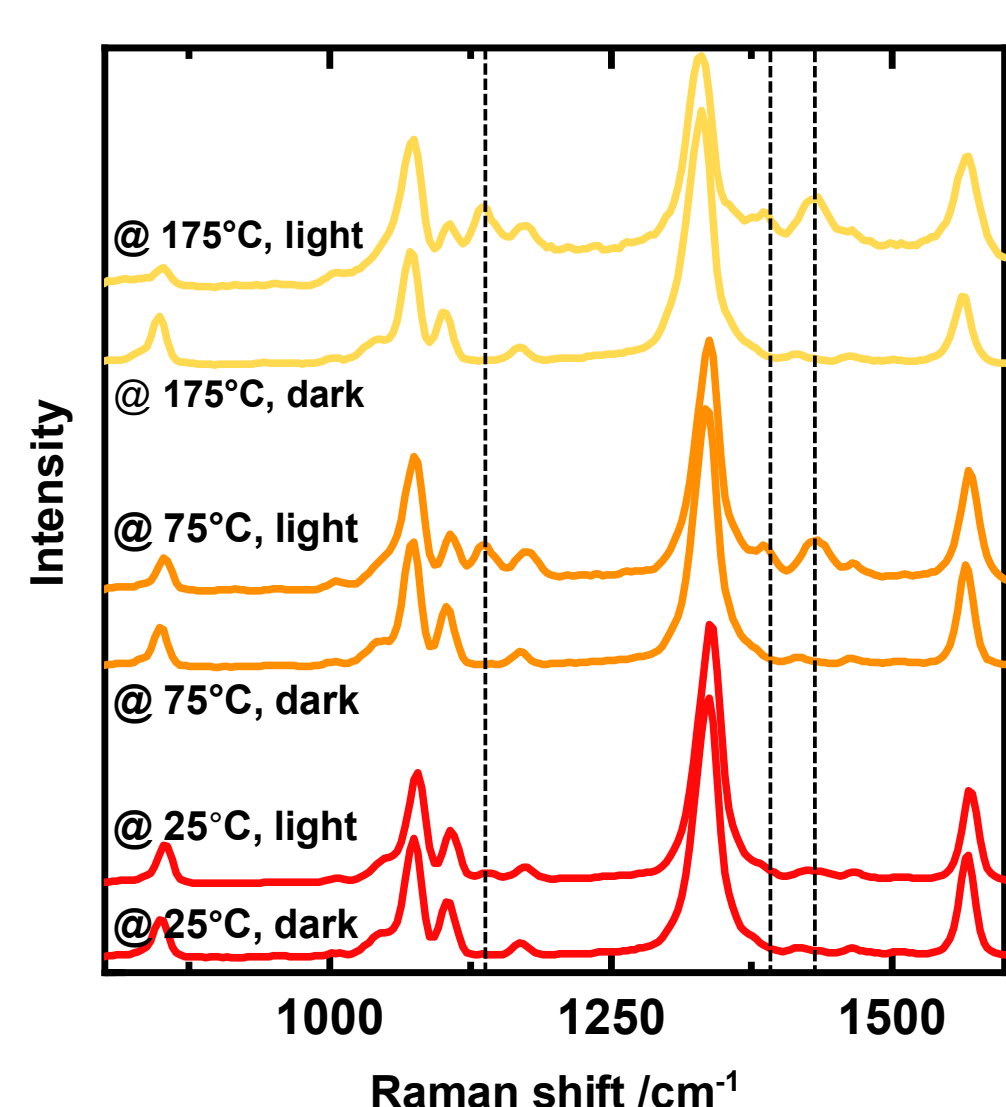
$$I_p(t) = \frac{1}{2} \cdot \sigma_p \cdot \frac{[R]_{0,dim}^2 k_2 t}{1 + [R]_{0,dim} k_2 t} = \sigma_p \cdot \frac{K_2 t}{1 + K_2 t}$$

Fitting of the reaction kinetics was performed according to a bi-molecular reaction model.



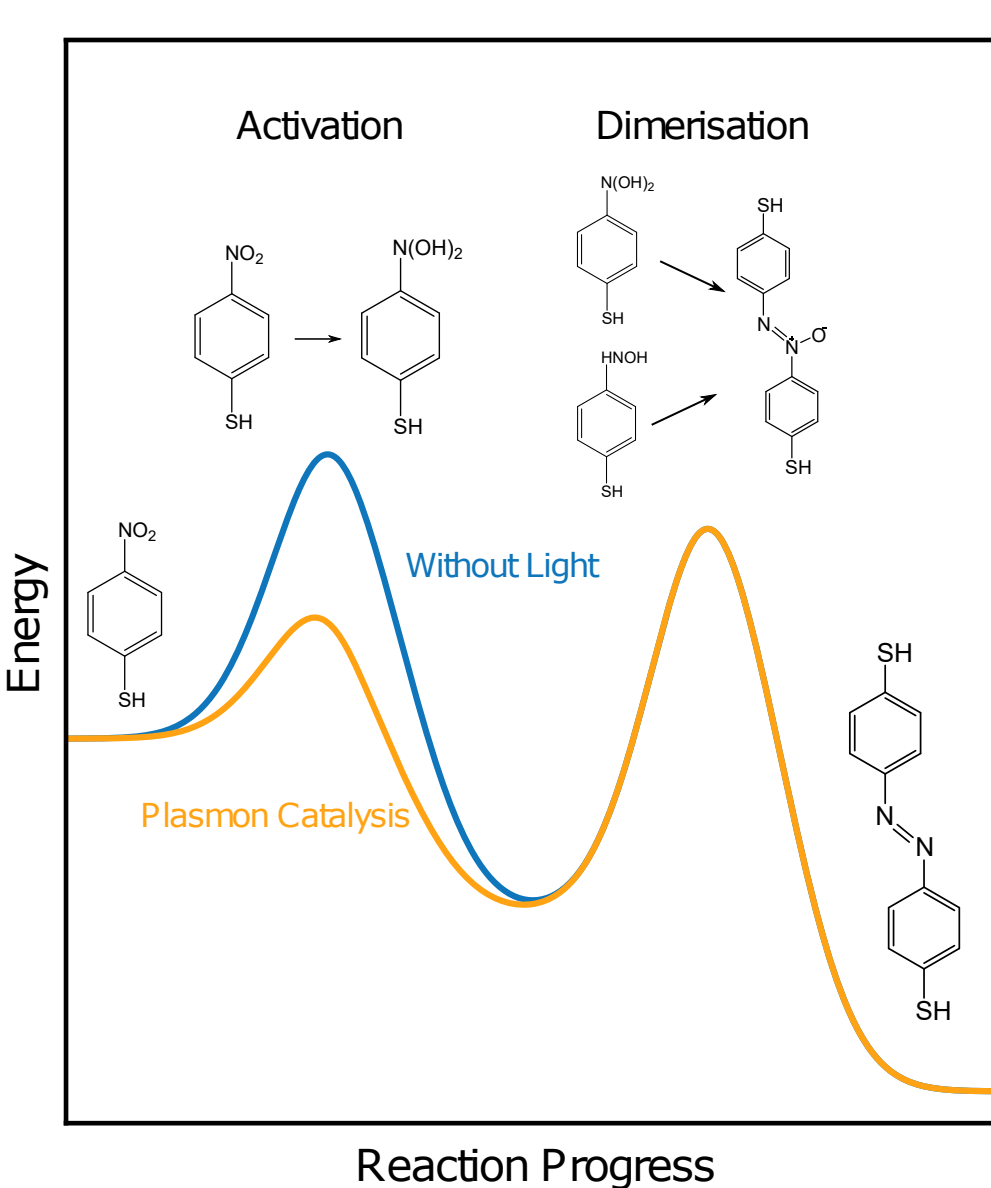
Intensity and Heat [4]

The reaction is clearly activated by light, as no product could be observed by heating the sample for 30 min under dark conditions, while with light immediately (<1 s) a product peak appears. On the other hand, a clear increase of the rate with temperature under light conditions can be seen.



The reaction rate follows a similar exponential trend, if the temperature or the intensity are increased. Indeed if the plasmonic heating measured by Raman thermometry is taken into account, the resulting Arrhenius plots show the same activation energy determined by plasmonic heating and external heating of the substrate. We therefore conclude that the reaction rate is only determined by the reaction temperature.

Discussion



From our investigation we conclude that this plasmon-driven dimerization can be seen as a tandem reaction, with at least two significant reaction barriers. Without excitation, the high reaction barrier connected to the initial activation prevents the reaction. The plasmon excitation reduces this first barrier. The reaction becomes subsequently limited by the dimerization step. The nanoparticle excitation also assists this step, by plasmon induced heating.

In summary, we show that both the injection of energetic electrons, and plasmonic heating play a significant role in plasmon induced coupling reactions. In particular, complex reactions can be limited by later steps, in which case an optimization of the number of energetic electrons does not lead to an improvement of the overall-reaction process. This has to be kept in mind for all further optimization steps in the future development of plasmon driven chemistry.

[1] Sarhan, Koopman et al., *The importance of plasmonic heating for the plasmon-driven photodimerization of 4-nitrothiophenol*, Sci. Rep. 9, 3060, 2019

[2] Sarhan, Koopman et al., *Scaling Up Nanoplasmon Catalysis: The Role of Heat Dissipation*, JPCC, 123, 9352, 2019

[3] Koopman, Sarhan, et al., *The role of the coupling in plasmon-driven dimerization reactions*, writing in progress

[4] Koopman, Sarhan, et al., *Decoding the intensity-dependence of plasmon-driven coupling reactions: the case of nitrothiophenol-dimerization*, writing in progress