Laboratory studies on cloud chemistry processes

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Motivation

Atmospheric free radicals are important for the description of many atmospheric processes including chemical conversion processes in clouds, fog, rain and deliquescent particles. Important atmospheric radicals within the tropospheric multiphase system are OH, NO_3, SO_x^- and halogen radicals [1]. However, reactions of these radicals as well as photochemical processes in the aqueous phase are still not fully characterized. Moreover, aqueous phase chemistry can be strongly influenced by atmospheric parameters such as the temperature, the pH and the ionic strength. Since these parameters are highly variable within the atmosphere, the possible influence of them on chemical reactions needs to be investigated. In order to describe the very complex chemistry within clouds different experimental information are necessary. The modeling of multiphase chemical processes requires both purely kinetic data as well as product studies, spectroscopic studies and phase transfer parameters. However, this information are not yet available for important atmospheric reactions and compounds. Recent results from the IfT chemistry department aqueous phase laboratory will be presented in this contribution.
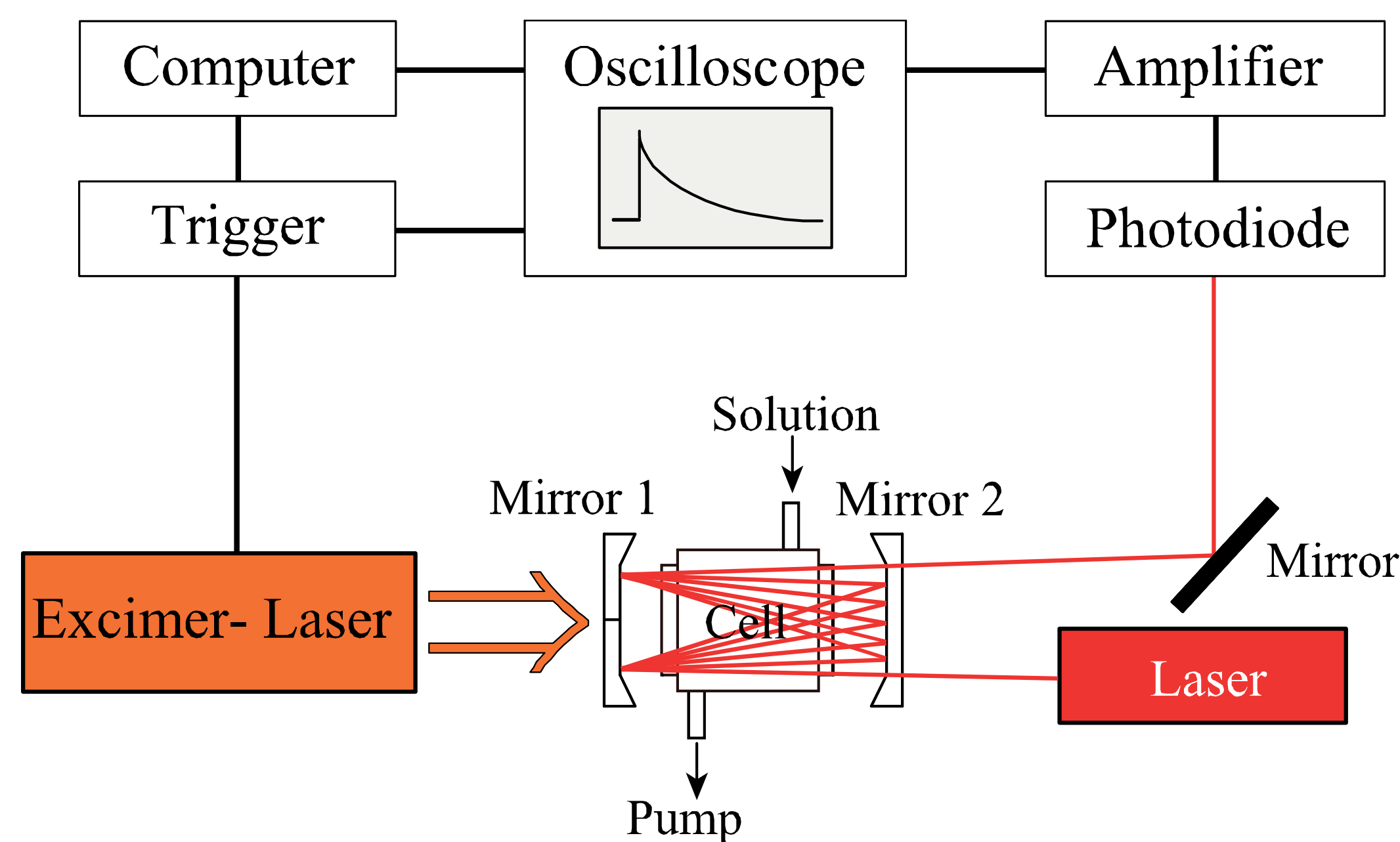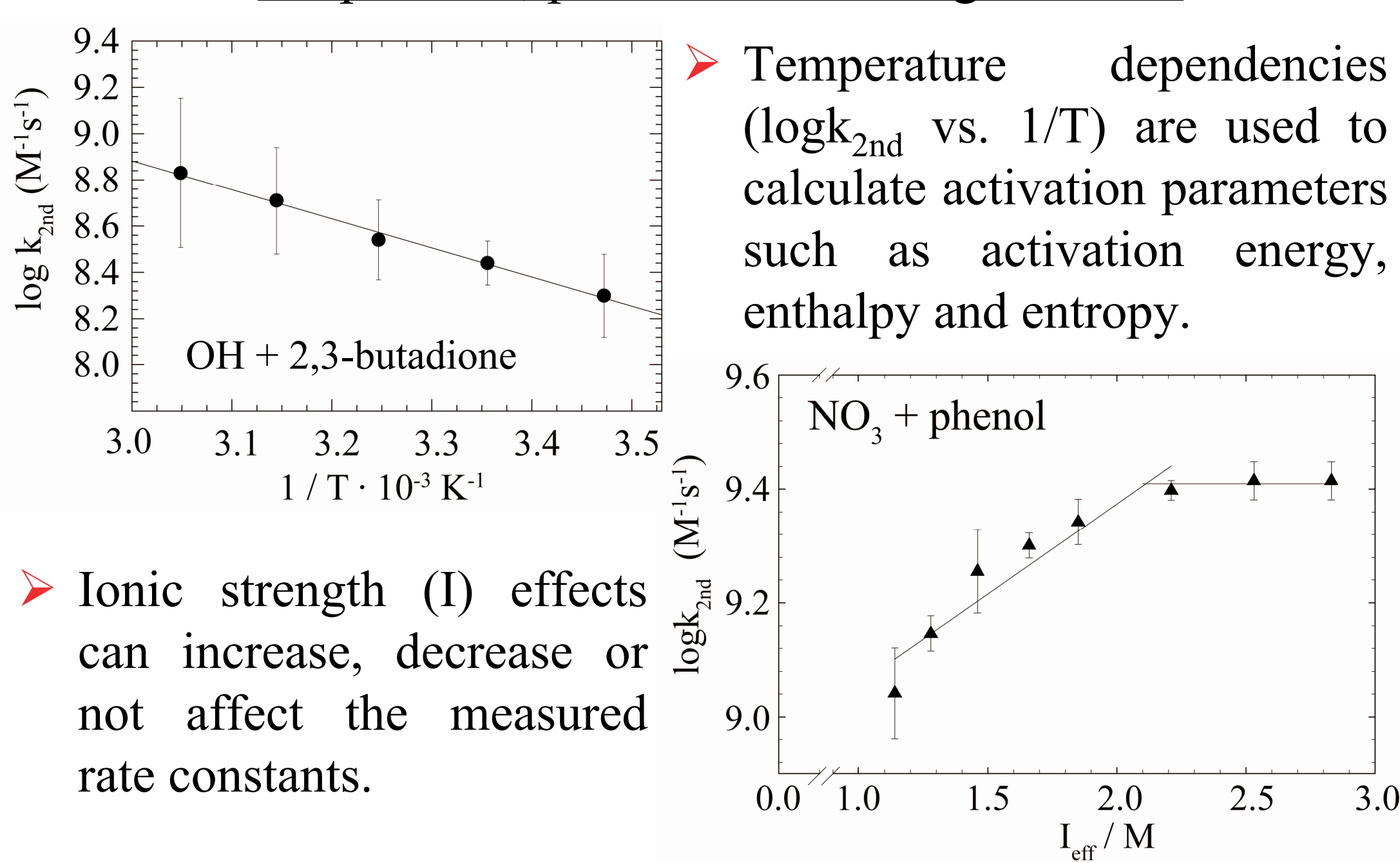
Experimental

Fig. 1: Scheme of the Laser Photolysis Long Path Absorption set-up used for the kinetic investigations.

➤ For the laboratory studies different, slightly modified, Laser Photolysis Long Path Absorption (LP-LPA) setups (Fig. 1) are applied in order to measure and characterize rate constants, photochemical processes and product distributions.

➤ Radical oxidants such as OH, NO_3, SO_4^-, Cl and others are generated within the thermostated reaction cell by excimer laser photolysis of suitable precursor compounds (e.g., $NaNO_3$, H_2O_2, $K_2S_2O_8$, …).

➤ As analytical light sources Hg-Xe lamps, deuterium lamps or different cw-lasers are used.

➤ Dependent on the application different detectors such as photomultipliers, photodiodes, diodearray detectors or CCD cameras are used.

➤ Investigated reactants are mainly oxygenated water-soluble organics such as alcohols, carbonyls, carboxylic acids and aromatics.
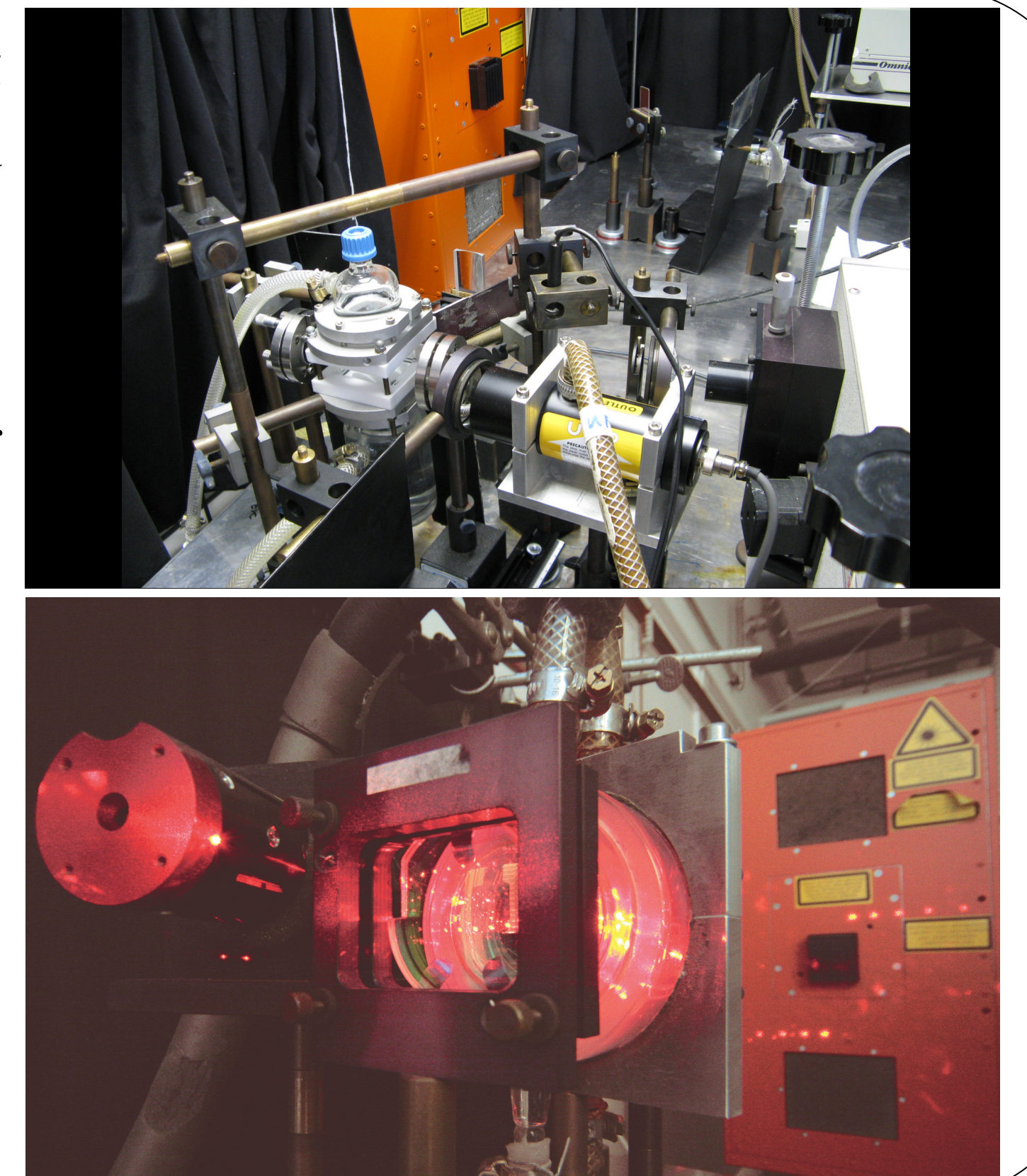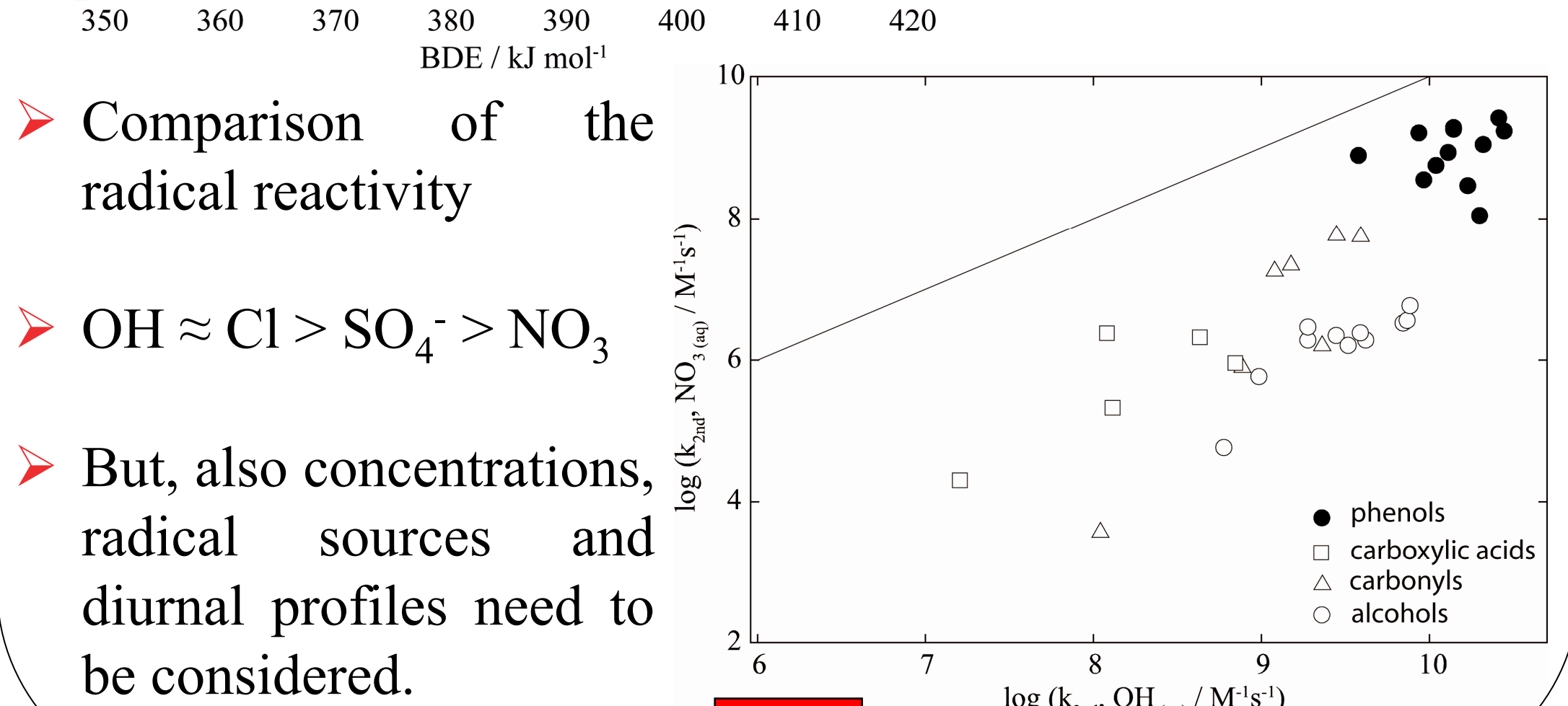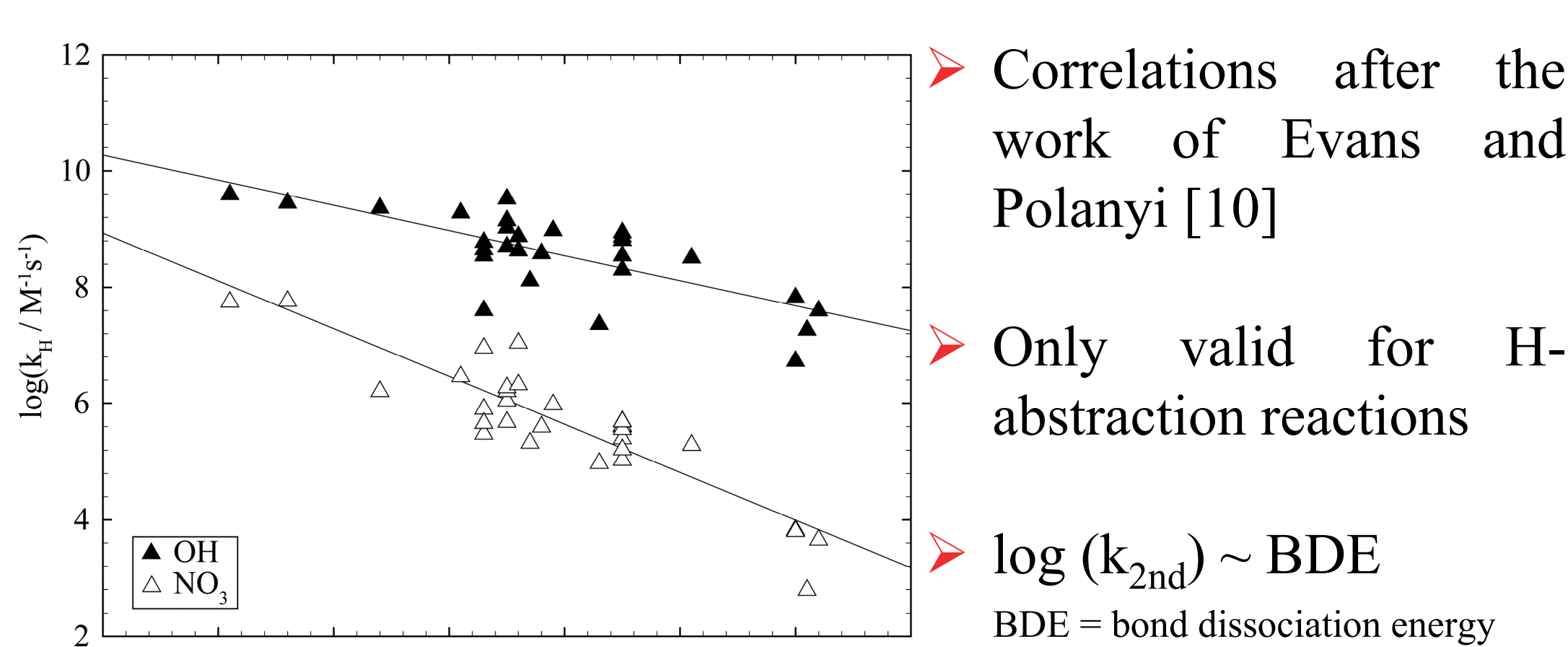
Kinetic studies [1-9]

Measurement of rate constants as well as chracterization of temperature, pH and ionic strength effects
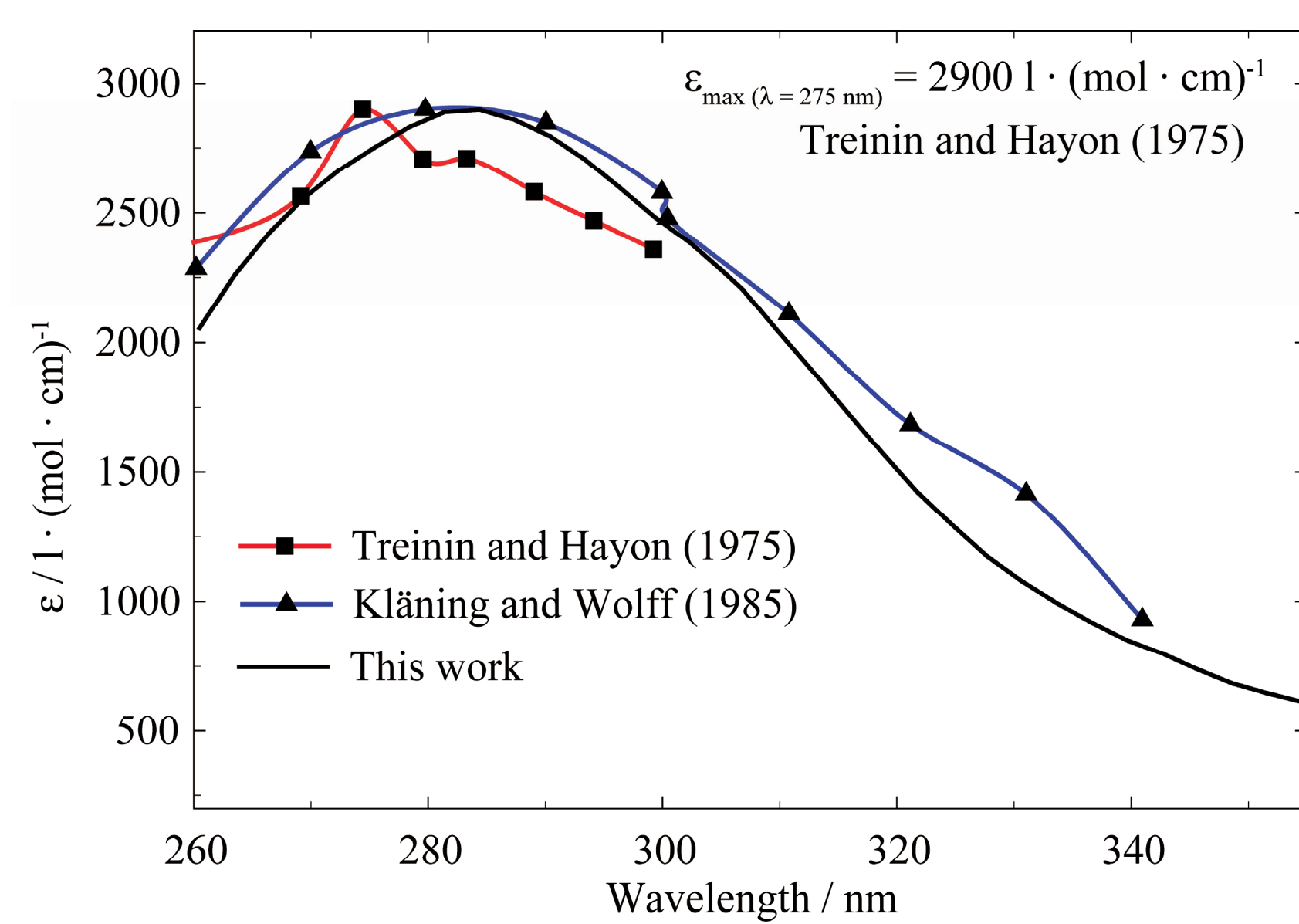
➤ Temperature dependencies ($\log k_{2nd}$ vs. $1/T$) are used to calculate activation parameters such as activation energy, enthalpy and entropy.

➤ Ionic strength (I) effects can increase, decrease or not affect the measured rate constants.

Reactivity correlation to estimate kinetic data not yet measured

➤ Correlations after the work of Evans and Polanyi [10]

➤ Only valid for H-abstraction reactions

➤ $\log (k_{2nd}) \sim$ BDE
BDE = bond dissociation energy

➤ Comparison of the radical reactivity

➤ OH ≈ Cl > SO_4^- > NO_3

➤ But, also concentrations, radical sources and diurnal profiles need to be considered.

Spectroscopic studies [11-13]

Spectroscopic properties of oxidizing reactants (e.g., the Br atom)

$\varepsilon_{max (\lambda = 275 nm)} = 2900\ l \cdot (mol \cdot cm)^{-1}$
Treinin and Hayon (1975)

- Treinin and Hayon (1975)
- Kläning and Wolff (1985)
- This work

Formation of transient reaction products (peroxy radicals)

OH + Butyraldehyde
OH + Propionaldehyde
OH + 2-Hydroxy-3-butanone
OH + Acetone
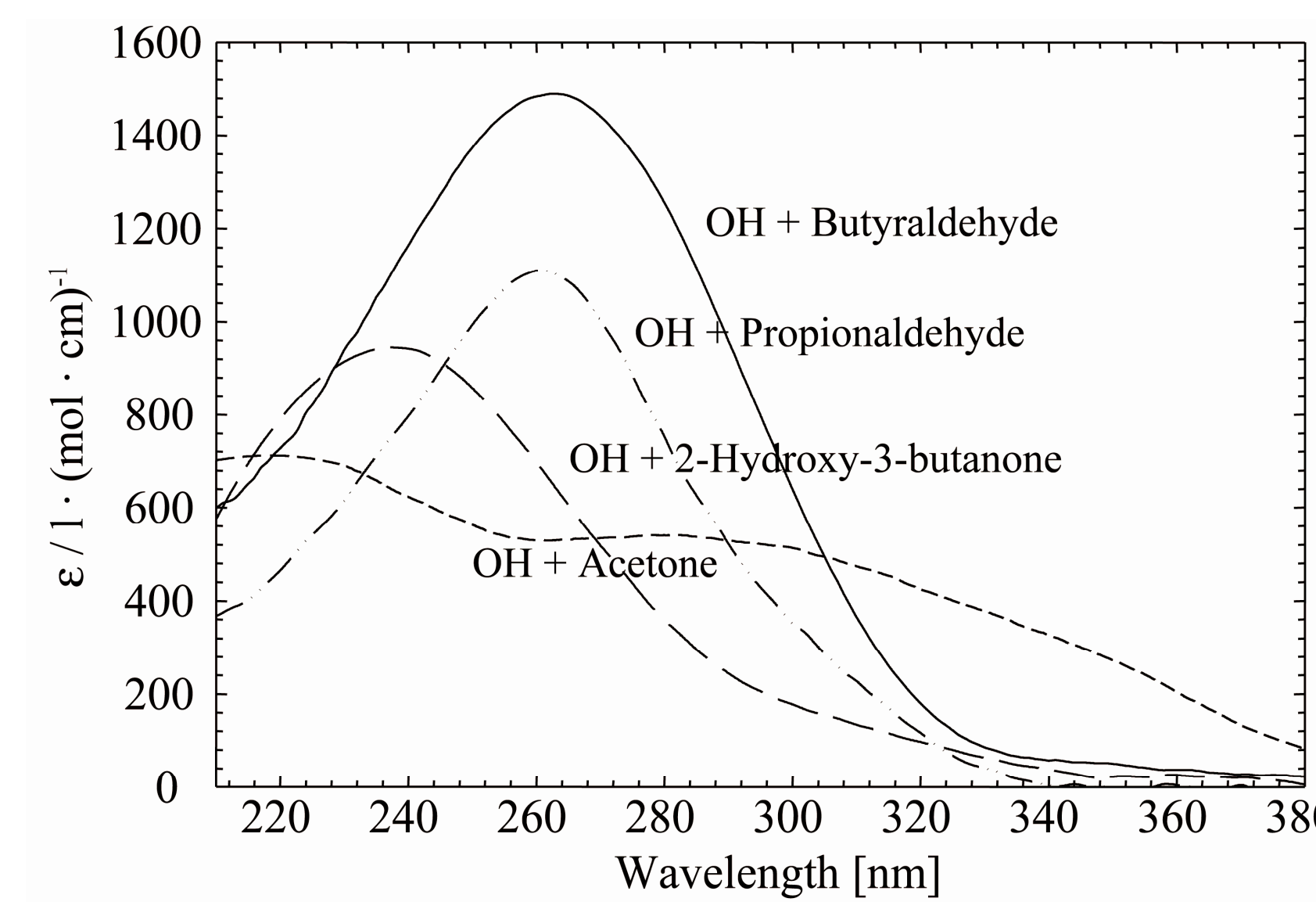
Furthermore, spectroscopic measurements are applied to calculate quantum yields of important photochemical processes such as the photolysis of iron-complexes. These studies will help to characterize the radical production and the fate of important organics (e.g., oxalic acid) and iron at the sea-atmosphere interface, in marine particles and clouds.
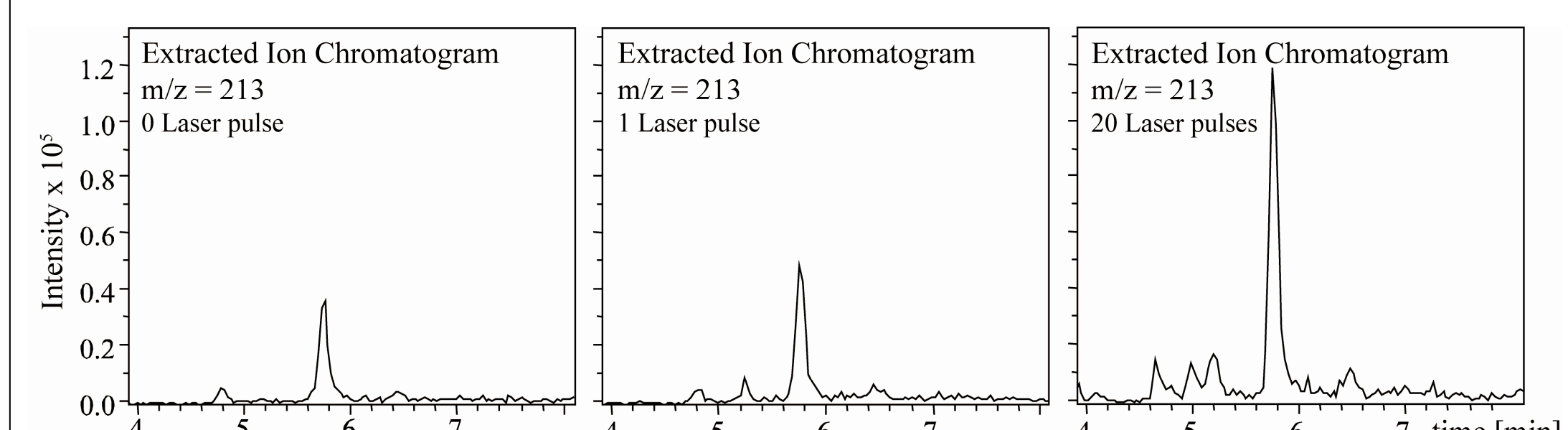
Product studies [14, 15]

Characterization of stable reaction products by HPLC/MS after the oxidation of phenols in aqueous solution

ring retaining products

condensation products

$C_{14}H_{14}O_2$ M = 214 g/mol
$C_{14}H_{14}O_2$ M = 214 g/mol
$C_{14}H_{14}O_2$ M = 214 g/mol
$C_{14}H_{14}O_2$ M = 214 g/mol
$C_{14}H_{12}N_2O_6$ M = 304 g/mol
$C_{14}H_{13}NO_4$ M = 259 g/mol
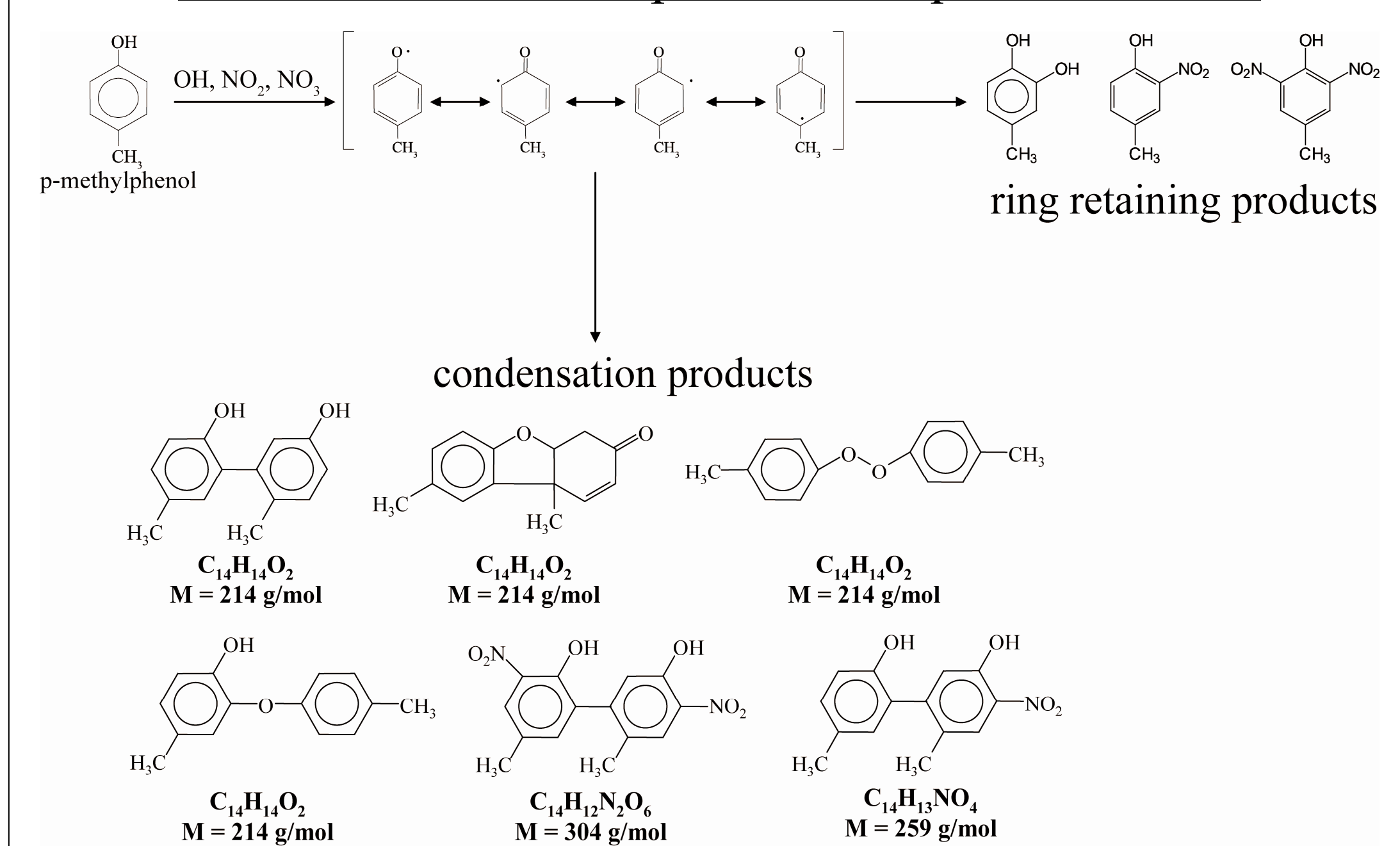
OH + p-methylphenol

➤ Formation of p-methylcatechol

➤ Formation of different condensation products (e.g., M_W = 214 g/mol)

Extracted Ion Chromatogram m/z = 213 0 Laser pulse
Extracted Ion Chromatogram m/z = 213 1 Laser pulse
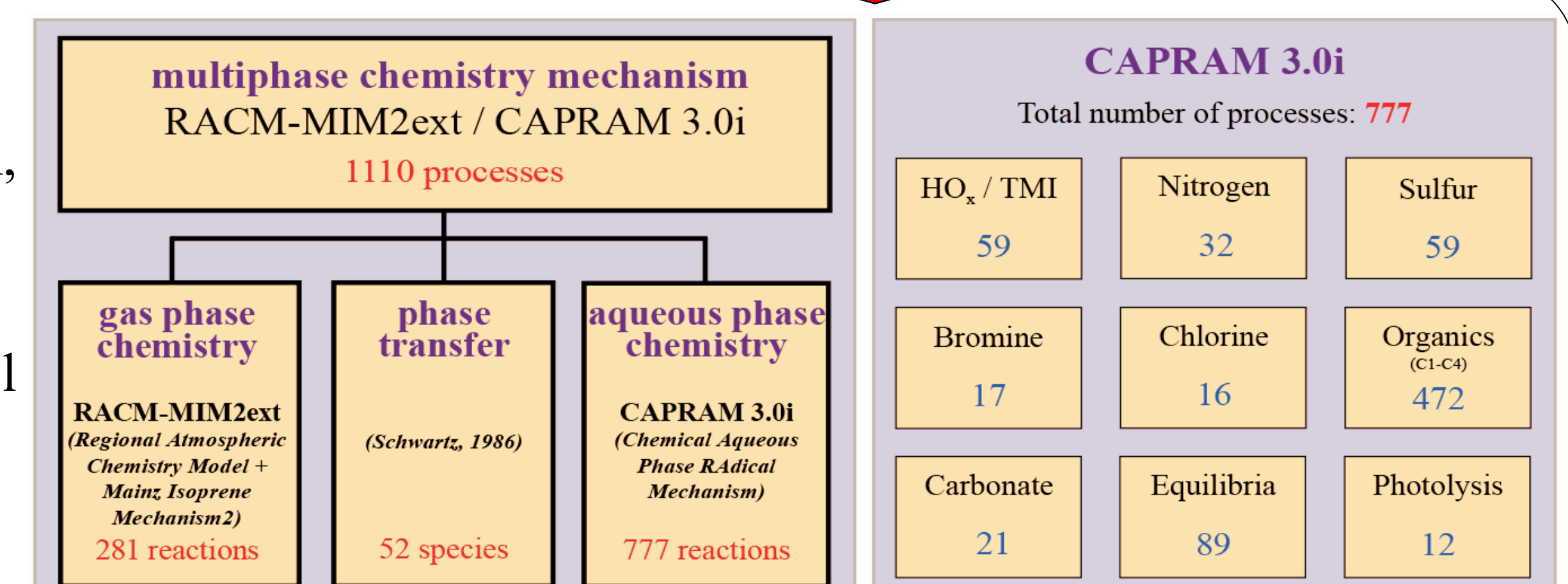Extracted Ion Chromatogram m/z = 213 20 Laser pulses

OH/NO_2/NO_3 + p-methylphenol

➤ Formation of mono- and dinitrophenols

➤ Formation of different (nitrated) condensation products

High molecular weight condensation products from the oxidation of aromatics could be significant part of the organic mass in atmospheric particles.

Aqueous Phase Chemistry Mechanism

➤ CAPRAM 3.0 (**C**hemical **A**queous **P**hase **RA**dical **M**echanism, http://projects.tropos.de/capram; [16])

➤ CAPRAM is currently the most detailed aqueous phase radical mechanism.

➤ This makes CAPRAM an adequate tool for studies of the tropospheric aerosol processing and cloud chemistry processes.

➤ Laboratory data obtained will be used to further extend and improve the mechanism.

➤ For more details concerning CAPRAM mechanism see also Poster **P12.3**.

multiphase chemistry mechanism
RACM-MIM2ext / CAPRAM 3.0i
1110 processes

gas phase chemistry
RACM-MIM2ext
(Regional Atmospheric Chemistry Model + Mainz Isoprene Mechanism2)
281 reactions

phase transfer
(Schwartz, 1986)
52 species

aqueous phase chemistry
CAPRAM 3.0i
(Chemical Aqueous Phase RAdical Mechanism)
777 reactions

CAPRAM 3.0i
Total number of processes: 777

HO_x / TMI 59	Nitrogen 32	Sulfur 59
Bromine 17	Chlorine 16	Organics (C1-C4) 472
Carbonate 21	Equilibria 89	Photolysis 12

References

[1] H. Herrmann, *Chem. Rev.*, 103, 4691, **2003**; [2] B. Ervens et al., *Phys. Chem. Chem. Phys.*, 5, 1811, **2003**; [3] S. Gligorovski and H. Herrmann, *Phys. Chem. Chem. Phys.*, 6, 4118, **2004**; [4] I. Morozov et al., *Int. J. Chem. Kinet.*, 40, 174, **2008**; [5] T. Umschlag et al., *Phys. Chem. Chem. Phys.*, 4, 2975, **2002**; [6] P. Barzaghi and H. Herrmann, *Phys. Chem. Chem. Phys.*, 6, 5379, **2004**; [7] P. de Semainville et al., *Phys. Chem. Chem. Phys.*, 9, 958, **2007**; [8] F. Wicktor et al., *Phys. Chem. Chem. Phys.*, 5, 2562, **2003**; [9] H. W. Jacobi et al., Int. J. *Chem. Kinet.*, 31, 169, **1999**; [10] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 34, 11, **1938**; [11] H. Herrmann, *Phys. Chem. Chem. Phys.*, 9, 3935, **2007**; [12] K. Parajuli, Dissertation, University of Leipzig, **2007**; [13] J. Hesper, Dissertation, University of Leipzig, **2003**; [14] P. Barzaghi and H. Herrmann, *Phys. Chem. Chem. Phys.*, 4, 3669, **2002**; [15] D. Hoffmann, Dissertation, University of Leipzig, **2007**; [16] H. Herrmann et al., *Atmos. Environ.*, 39, 4351, **2005**