

Laboratory studies on the oxidation of small organics in aqueous solution by OH radicals

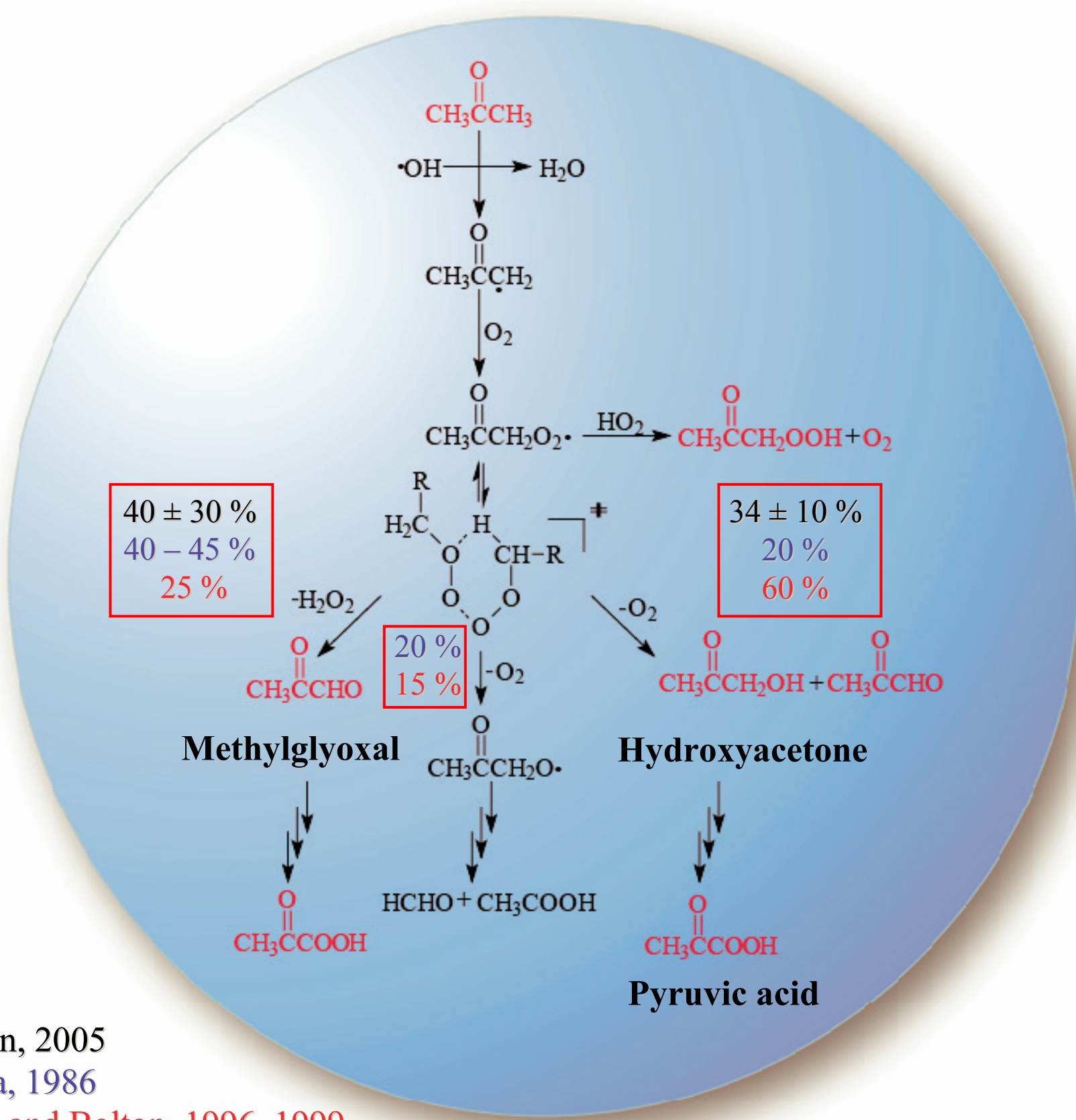
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Motivation

Carbonyl compounds in the atmosphere are mainly produced by oxidation of hydrocarbons. Due to their photo reactivity in the lower troposphere, carbonyl compounds play an important role in the production of atmospheric free radicals and photooxidants. Oxidation reactions of water soluble organic compounds in the atmospheric aqueous phase (cloud droplets, fog, rain, deliquescent particles) can be as fast as in the gas phase,



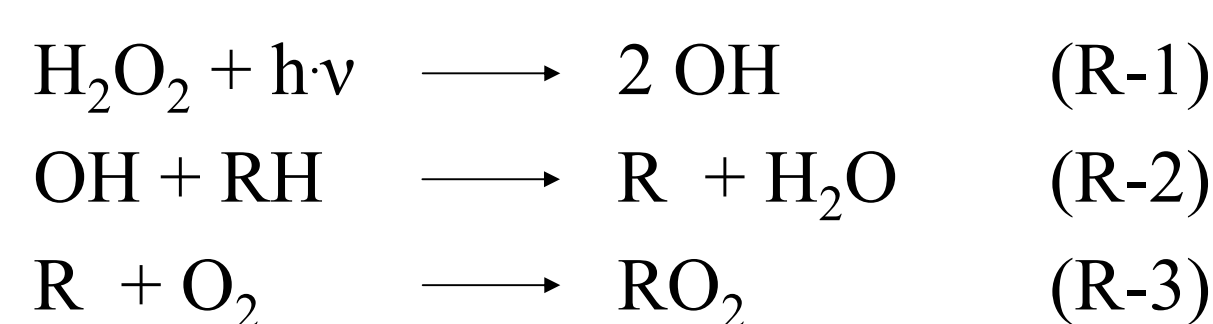
but lead to different reaction products or different product distributions. Figure 1 shows the state of the art reaction scheme of the degradation of acetone in aqueous solution, but there are significant differences within the data from the literature. The objective of this work is to identify and characterize the various transient species formed in the oxidation of carbonyl compounds such as acetone. This characterization is necessary to measure rate constants of elementary reaction steps in the course of the degradation process. The spectroscopic and kinetic information will allow to clarify issues in the acetone chemistry and gives better understanding of the atmospheric fate of carbonyl compounds.

Poulain, 2005
Zegota, 1986
Stefan and Bolton, 1996, 1999

Figure 1: Reaction scheme of acetone in the aqueous phase.

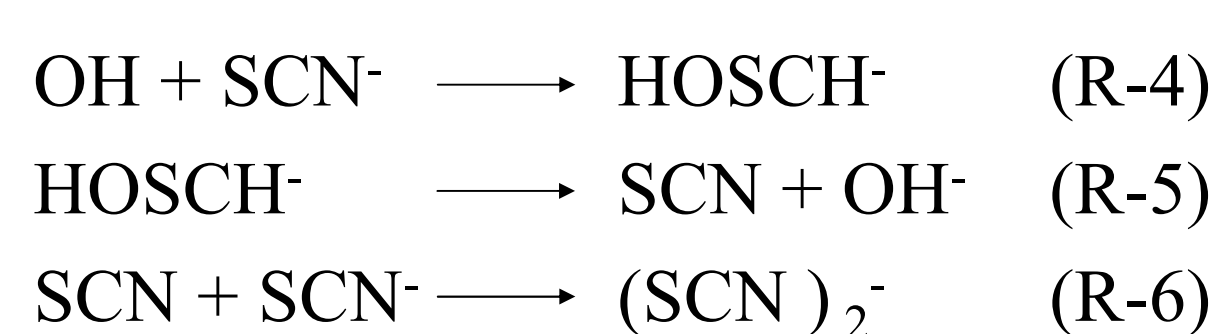
Experimental

For spectroscopic investigation of the peroxy radicals in the oxygen saturated aqueous solution a laser photolysis long path absorption setup (LPA-PA) was used (Figure 2). The hydroxyl radicals were generated directly in the reaction cell by the photolysis of hydrogen peroxide at $\lambda = 248$ nm (R-1). The OH radicals react with the carbonyl compounds via H-atom abstraction mechanism (R-2). As will be shown, the oxygen reacts with the alkyl radicals converting them into the corresponding peroxy radicals (R-3).



With this technique time resolved spectra (at different delay times after the excimer laser pulse) of the reactants and products can be recorded.

The accuracy of flash photolysis dosimetry is important for determining values of the extinction coefficient ϵ for the peroxy radicals which are required for the rate constants of their recombination. Since OH radical absorbs rather weakly, and only in the deep UV region of the spectrum, the direct measurement of the OH radical concentration is difficult. In order to characterize the dose of excimer laser energy inside the cell, the well known thiocyanate system (R-4) - (R-6) (Chin and Wine, 1992) was used. The $(\text{SCN})_2^-$ radical anion absorbs strongly at $\lambda = 475$ nm and extinction coefficient of $\epsilon = 7600 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 2).



The Lambert-Beer's Law was applied with $\epsilon((\text{SCN})_2^-)$ to calculate the initial OH concentration. The value of the energy inside the measuring cell was calculated with $\epsilon(\text{H}_2\text{O}_2) = 25.65 \pm 1 \text{ M}^{-1} \text{ cm}^{-1}$, $\Phi = 1$ (Hunt and Taube, 1952) and the OH radical initial concentration. This energy was used to calculate the radical concentration in the peroxy radical system.

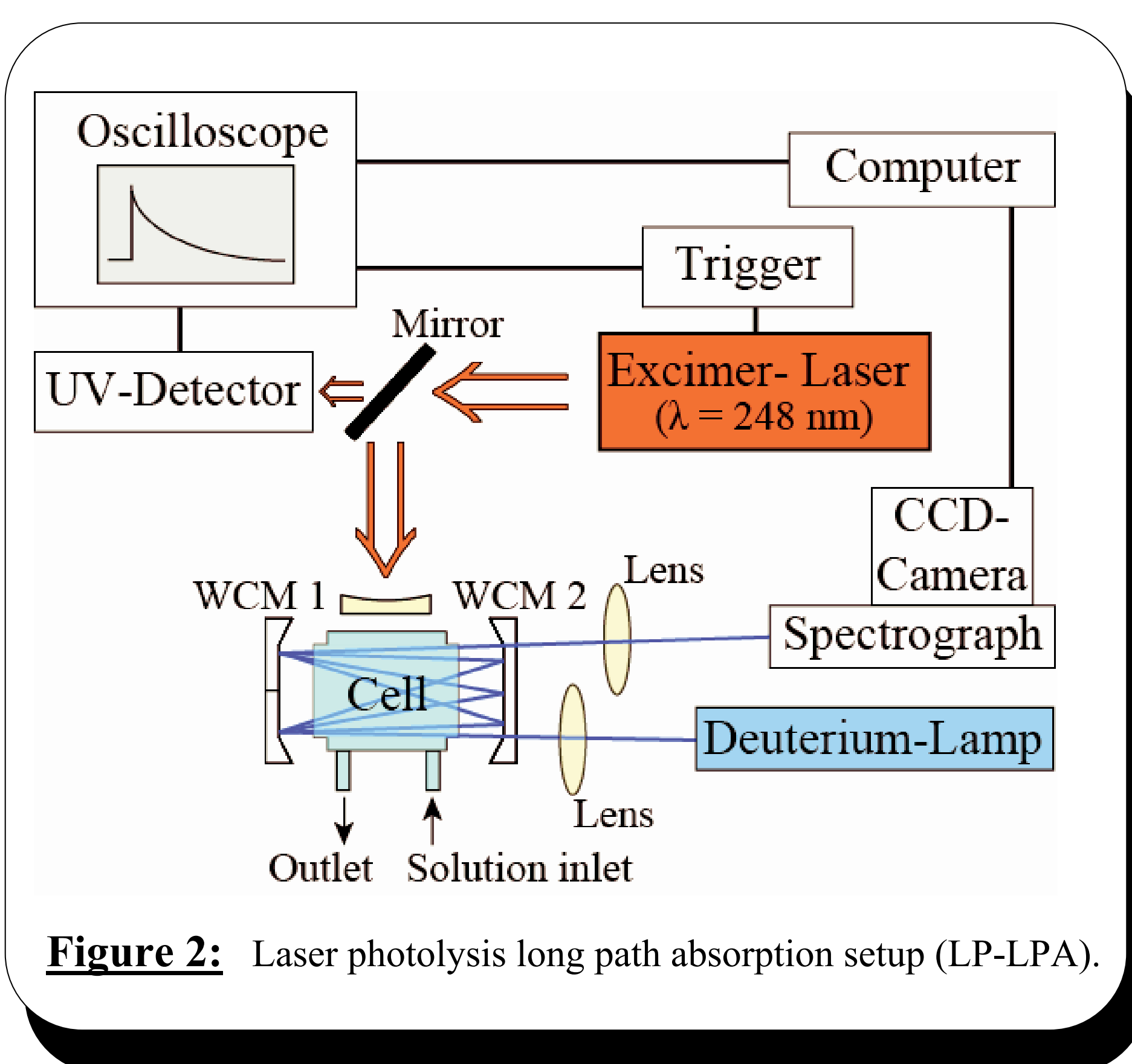


Figure 2: Laser photolysis long path absorption setup (LP-LPA).

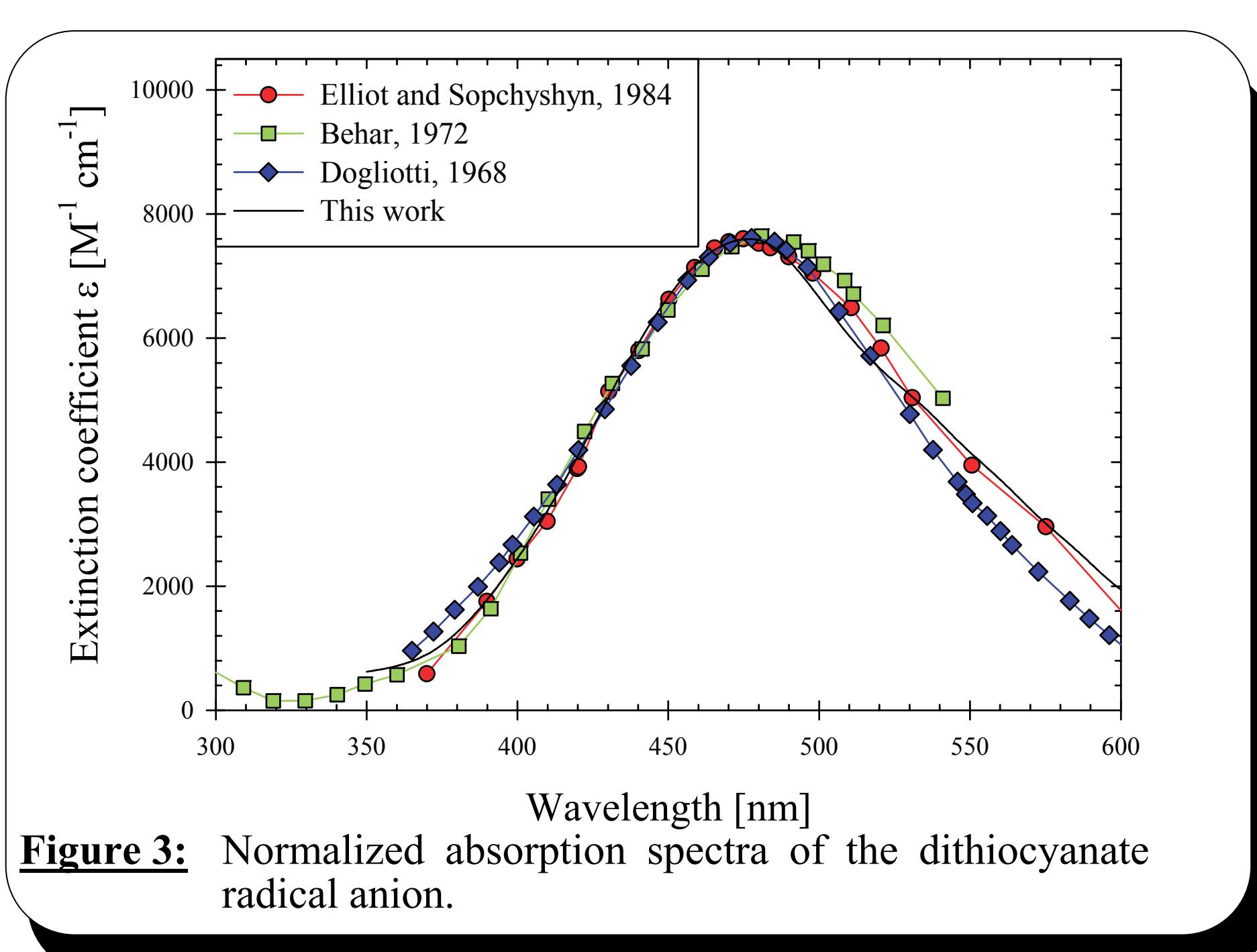


Figure 3: Normalized absorption spectra of the dithiocyanate radical anion.

Modelling

The peroxy radical concentration has been calculated by using a GEPASI model. This model (37 Reactions) takes into account the HO_x side reaction of the reaction cell. The most important reactions are shown in Figure 3.

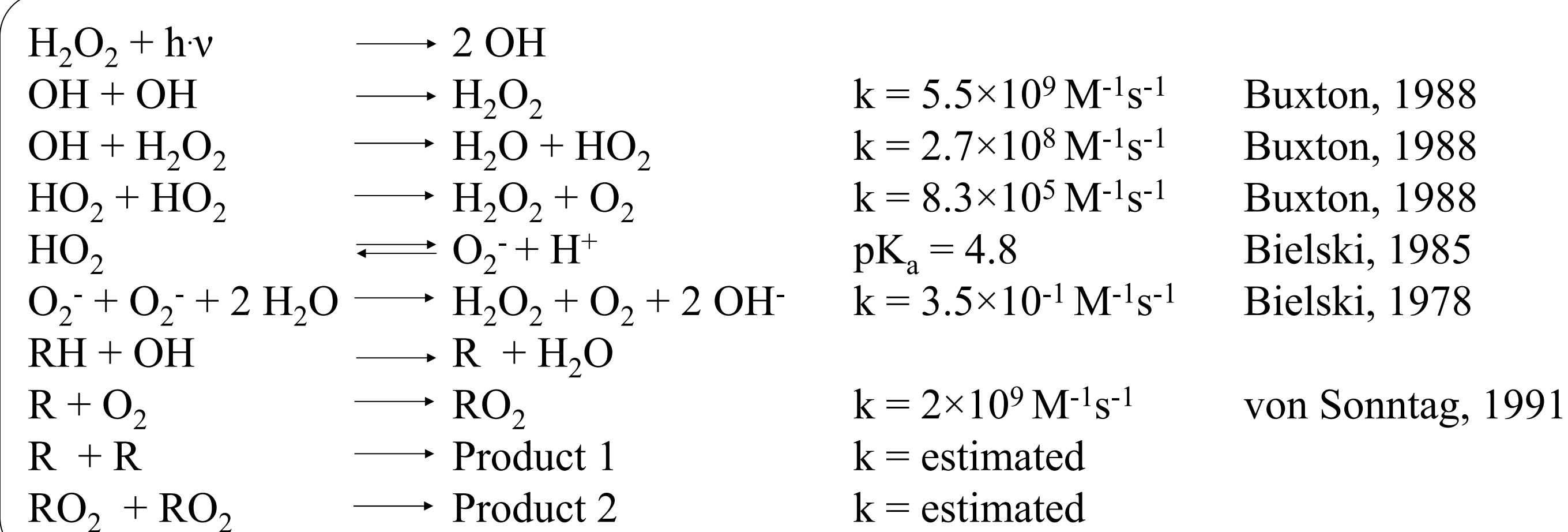


Figure 3: Main reactions of the GEPASI model

Spectroscopic studies

Spectroscopic investigations are done in order to study the formation of transients (organic peroxy radicals) and to characterize the spectroscopic properties of the reactants and organic peroxy radicals. In Figure 5 – 7 the spectra of the organic peroxy radical of the following parent carbonyl compounds (a) acetone, (b) hydroxyacetone and (c) methylglyoxal are shown. In the case of the acetonylperoxy radical the resulting spectrum is in a good agreement with the absorption spectrum obtained by Zegota, 1986. On the other hand the gas phase spectrum published by Cox et al., 1990 indicates that the extinction coefficient of the acetonylperoxy radical should be lower. The data for the transients from hydroxyacetone (Figure 6) and methylglyoxal (Figure 7) are currently not available in the literature.

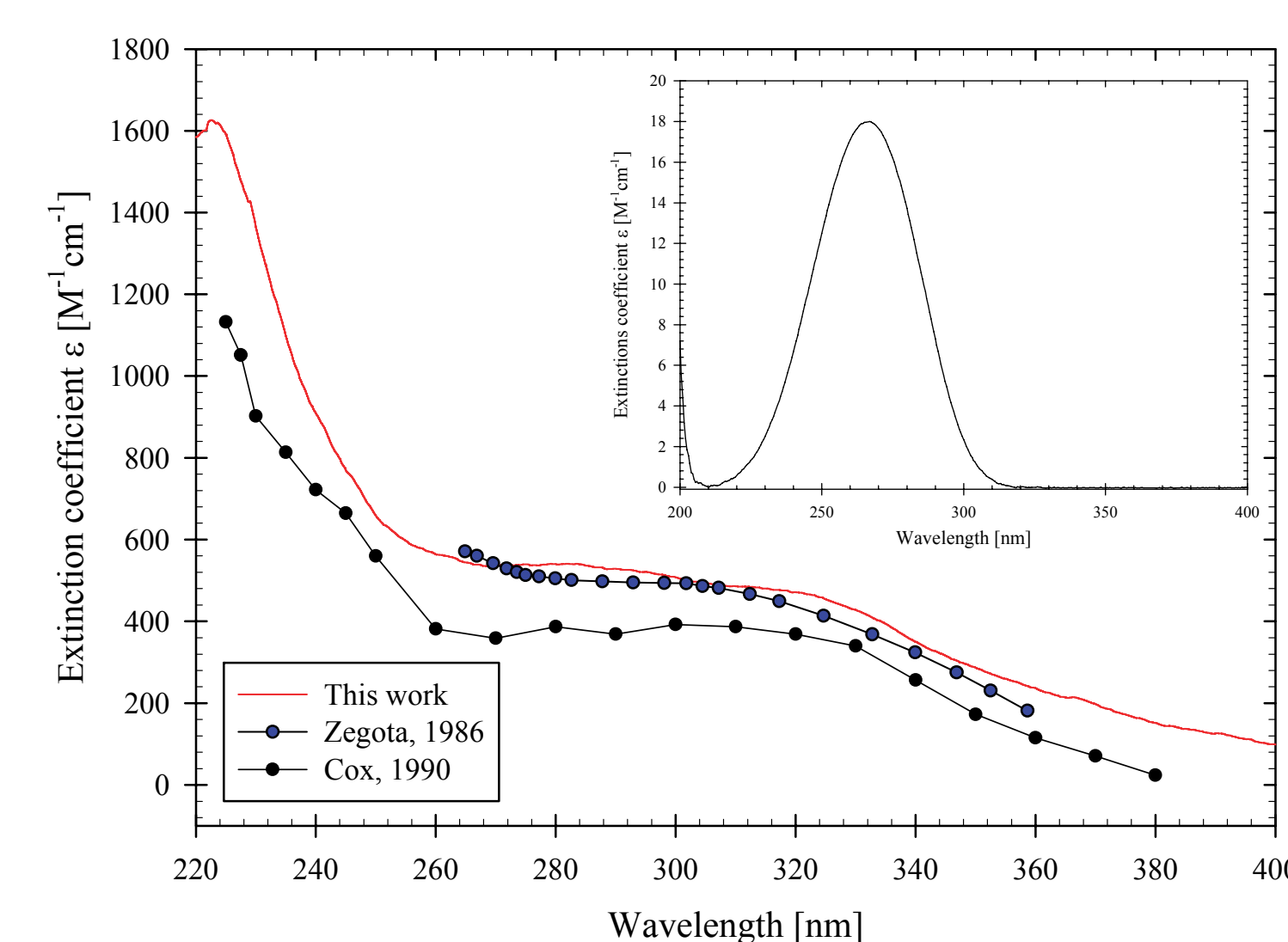


Figure 4: Spectrum of the observed peroxy radical measured in a oxygen saturated solution containing $6 \times 10^{-4} \text{ M}$ acetone and $2 \times 10^{-4} \text{ M}$ hydrogen peroxide. The spectrum was taken $45 \mu\text{s}$ after the pulse. The spectrum of acetone is shown in the inset.

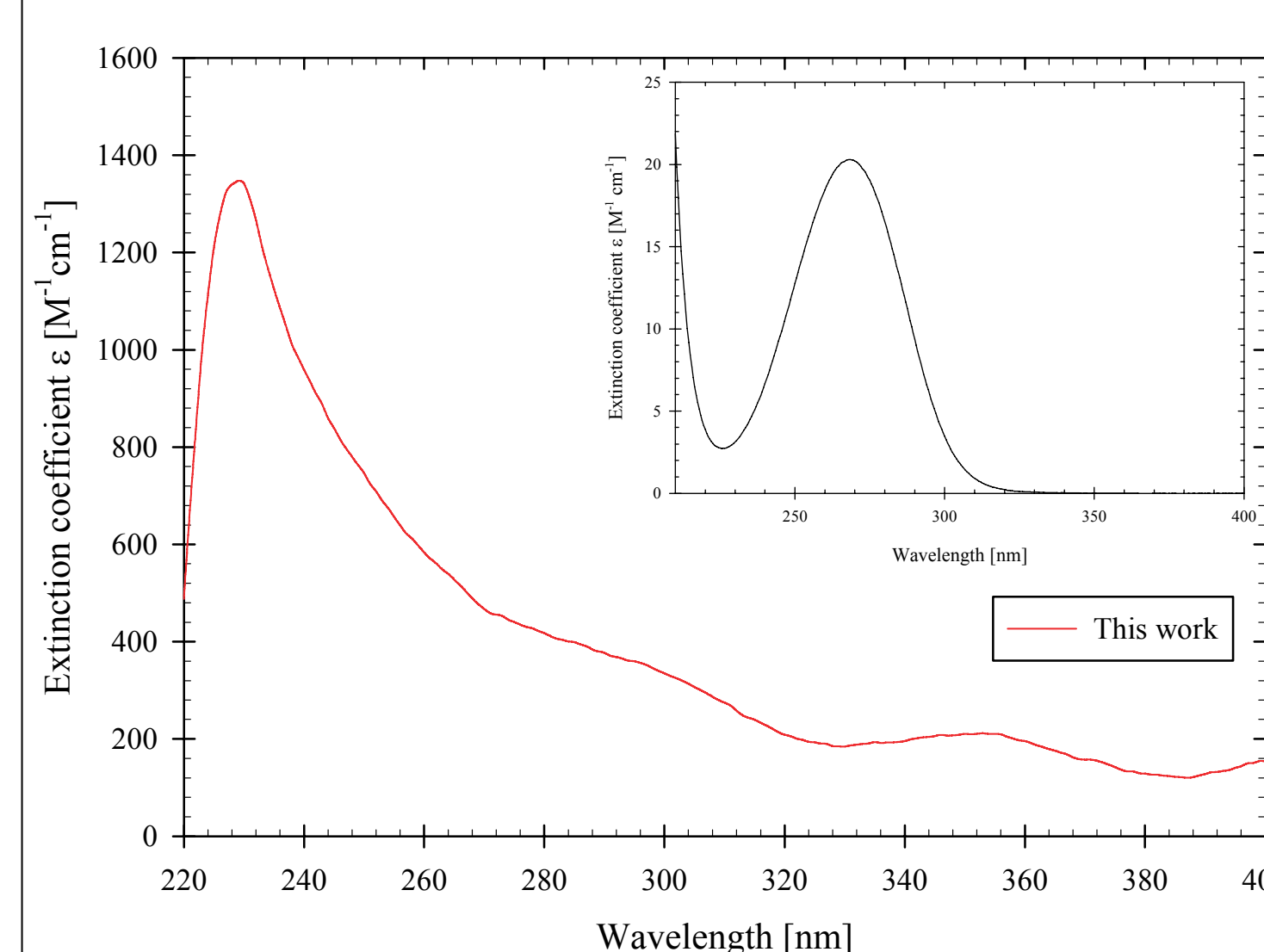


Figure 5: Spectrum of the observed peroxy radical measured in a oxygen saturated solution containing $6 \times 10^{-4} \text{ M}$ hydroxyacetone and $2 \times 10^{-4} \text{ M}$ hydrogen peroxide. The spectrum was taken $15 \mu\text{s}$ after the pulse. The spectrum of hydroxyacetone is shown in the inset.

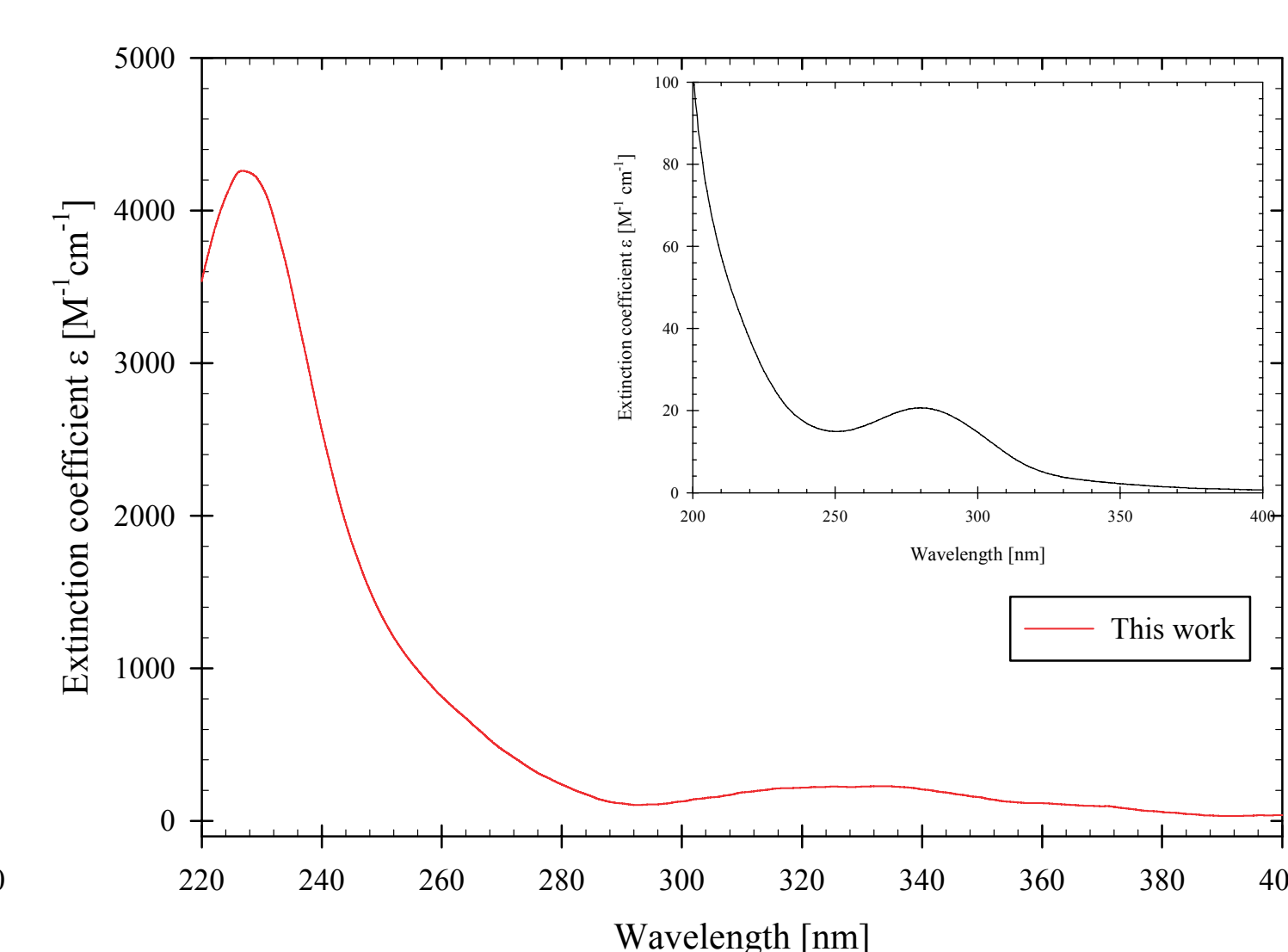


Figure 6: Spectrum of the observed peroxy radical measured in a oxygen saturated solution containing $6 \times 10^{-4} \text{ M}$ methylglyoxal and $2 \times 10^{-4} \text{ M}$ hydrogen peroxide. The spectrum was taken $15 \mu\text{s}$ after the pulse. The spectrum of methylglyoxal is shown in the inset.

Summary and Outlook

Spectroscopic investigations were performed in order to study the formation of transients (organic peroxy radicals) and to characterize the spectroscopic properties of the reactants and organic peroxy radicals. To accomplish the aim of this study the following tasks must be successfully completed: A) Stepwise identification and quantification of the OH driven oxidation products. B) Kinetic studies on the recombination reactions of organic peroxy radical in aqueous phase. C) Validation of the oxidation pathway with continued irradiation experiments under tropospheric aqueous phase conditions.

Acknowledgement

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References

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