Laser-based Kinetic and Spectroscopic Investigations of the Cl_2^--Radical in Aqueous Solution

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The absorption spectra of the Cl_2^- radical anion has been measured in the range of 270 to 725 nm by using a time resolved UV/VIS-broadband diode array absorption spectroscopy experiment. As analysis light source a 400 W halogene lamp and a deuterium lamp were used. To enlarge the sensitivity of the experiment the light beam was folded eight times through the reaction cell by the use of two aluminium coated mirrors in White configuration.

For the spectroscopic investigations as well as for the kinetic investigations Cl_2^- was generated by laser photolysis of peroxodisulfate according to:

$$S_2O_8^{2-} + h\nu\ (\lambda = 248\ nm) \rightarrow 2\ SO_4^-$$

$$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$$

$$Cl + Cl^- \rightleftharpoons Cl_2^-$$

By adding Chloride in large excess (0.1 M) the equilibrium between Cl and Cl_2^- was shifted towards the dichloride radical anion.

For the kinetic investigations the Cl_2^- radical anion has been monitored by long path absorption applying the output of a high power halogene lamp at 340 nm recorded with a monochromator/photomultiplyer combination or, alternatively, long path laser absorption using the 632 nm emission of a HeNe-laser recorded with a photodiode.

In this study the rate coefficients for the reactions of the Cl_2^- radical anion with several sulfur containing organic compounds that are supposed to be oxidation products of dimethyl sulfide were measured. Also the rate coefficients for the reactions of the Cl_2^- radical anion with some aldehydes and nitrogene containing aromatic compounds which are of interest for the aqueous phase of the troposphere were investigated.

The obtained results can be used in modelling studies and though may be helpful for a better understanding of the tropospheric aqueous phase.