Time-resolved combined XAS and UV-Vis applied to the study of the cerium catalysed BZ reaction

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Abstract. X-ray absorption spectroscopy has been applied to the study of the Belousov-Zhabotinsky reaction. Ultraviolet-visible spectroscopy has been used as the reference spectroscopic technique. The extent of the reaction has been followed continuously by acquiring the X-ray absorption at specific photon energies during the process. Oxidation states as well as local structural data of the cerium catalyst and the bromine reactant species during self sustained chemical oscillations have been determined.

1. Introduction

The Belousov-Zhabotinsky (BZ) reaction [1, 2] is the most prominent model reaction for self-sustained chemical oscillations. The basis for the description of the reaction pathways and kinetics has been described [3].

X-ray absorption spectroscopy (XAS) provides invaluable insight into the electronic structure and short range geometrical order of condensed matter. Not only to well ordered crystalline materials, it has been also applied to the study of disordered or nanostructured systems, i.e. catalysts, amorphous, glasses or liquids. For many years this method has been combined with other experimental techniques (microscopy, ultraviolet-visible (UV-Vis), infrared (IR) or Raman spectroscopy) to obtain a full picture of the structure on different length scales and resolved in time [4].

After the initiation of the BZ reaction, the concentration of constituents oscillates between different states, either in terms of oxidation or molecular states. The analysis of spectra as well as of electrical potential during the reaction has allowed a detailed analysis of the reaction mechanism. The overall chemistry can be described by process T without regard for the detailed organic chemistry [5].

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\text{BrO}_3^- + 3\text{RH} + \text{H}^+ \rightarrow 2\text{ROH} + \text{RBr} + \text{H}_2\text{O} \quad (T)
\]

The organic moiety R is oxidized. Cerium ions are used to catalyse the reaction. The process T describes the overall chemistry but not the detailed evolution of the reaction. Today many species, reactions and overall reaction models are reported [6]. The reaction remains after initiation far from chemical equilibrium for many hours. After an induction period, self-sustained chemical oscillations are observed. The oscillation period of the BZ reaction is typically in the seconds to minutes range.

2. Experimental

The experiment reported here has been performed at the ANKA-XAS beamline at the absorption edges Ce L₃ and Br K. XAS and UV-Vis spectroscopy have been applied using a specifically designed
in-situ cell. To monitor the compositional and structural changes in the reaction, quick scan mode XAS was employed together with a time scan mode at fixed monochromatic photon energy.

2.1. Sample and sample environment
The chemicals Ce(NO$_3$)$_3$·6H$_2$O, C$_3$H$_4$O$_4$ (malonic acid), KBrO$_3$ were used as received and dissolved in 1 M acidic solution (H$_2$SO$_4$) using deionised water. The sample solution was kept in a stirred batch reactor. The chemical solution was pumped into the sample cell for combined XAS and UV-Vis experiments using a gear pump and thin tubes. The small inner aperture of the tubes and high pumping speed assured the concurrence of chemical reaction states in both vessels.

Glass fibre optics was applied connecting the sample cell to the grating/diode array based Ocean Optics UV-Vis spectrometer. The X-ray beam is transmitted through kapton windows and a nominal solution thickness of 5 mm.

The liquid acidic solutions have been mixed and filled into the batch reactor and into the programmable syringe pump. During the experiment S1 stored in the batch reactor was continuously pumped through the sample cell. In order to initiate the reaction, a defined quantity S2 was added to S1 in the batch reactor using the syringe pump. The stirred batch reactor was purged with helium.

Table 1: The composition of the solutions S1 and S2 in the initial state after mixing is summarized.

| Experiment | Solution S1 | Solution S2 |
|------------|-------------|-------------|
| Ce L$_3$ edge | 0.05 mol/l Ce(NO$_3$)$_3$·6H$_2$O and 0.4 mol/l C$_3$H$_4$O$_4$ | 0.06 mol/l KBrO$_3$ |
| Br K edge | 0.06 mol/l KBrO$_3$ | 0.002 mol/l Ce(NO$_3$)$_3$·6H$_2$O and 0.04 mol/l C$_3$H$_4$O$_4$ |

2.2. XAS set-up
X-ray absorption spectroscopy data (in transmission and fluorescence mode) were taken at the XAS beamline at ANKA. The synchrotron is operated at 2.5 GeV energy and typical electron currents of 100 to 200 mA. The bending magnet beamline is equipped with a Si(111) double crystal monochromator together with ion chambers and a Ge multi-element fluorescence detector. Typically time scan mode at fixed photon energy with a time resolution of 0.2 s has been applied, interrupted by QEXAFS scans (typically 30 s scan time) during reaction and step by step EXAFS scans of stable states. EXAFS spectra of a set of reference compounds in solid and liquid state were acquired for the Ce L$_3$ edge as well as the Br K edge.

2.3. UV-Vis set-up
UV-Vis spectra were measured using an Ocean optics USB200 device. The spectral range comprises 178 to 874 nm wavelength. The data were corrected for background and dark signal. A single spectrum is taken by averaging five spectra which are acquired in 1.2 s. During the BZ reaction changes are observed in the spectral range of 250 to 450 nm. The UV absorption in cerium oxides is generated by a charge-transfer transition between O2$p$ and Ce 4$f$ bands [7]. The increasing absorption is attributed to the oxidation of Ce$^{3+}$ to Ce$^{4+}$.

3. Results and discussion
The time dependent variation of the catalyst species has been measured at the Ce L$_3$ edge and the absorption of the reactant species at the Br K edge.

3.1. Time resolved experiment at the CeL$_3$ edge
The Ce L$_3$ edge XAS of Ce$^{3+}$ (4$f^0$) in hydrated cerium samples shows a strong resonance absorption line at the photon energy of 5.728 keV. The near edge structure of Ce$^{4+}$ (4$f^0$) of solid CeO$_2$ powder is considerably different with two less pronounced maxima at 5.732 and 5.739 keV. The resonance
absorption features have been studied in detail in order to deduce valence states of rare earth elements dissolved in liquids [8] as well as in solids [9, 10]. The observed XANES of the BZ solution is characteristic for Ce$^{3+}$. The small change of the white line intensity during the reaction (as seen in the inlet plot) indicates that only a small amount of the trivalent ions is oxidized to Ce$^{4+}$. It has been estimated that the molar ratio Ce$^{3+}$/Ce$^{4+}$ during all phases of the BZ reaction should be larger than 0.99.

3.2. Time resolved experiment at the Br K edge

The spectra at the K absorption edge of bromine vary strongly as a function of Br oxidation state. The spectra of solid KBrO$_3$ and of this substance dissolved in water are characterized by a white line.

Fig. 2 left: Br K edge XANES of Br-containing solutions prior to mixing and at the two different stages of the reaction. The strong white line typical for BrO$_3^-$ ions (black line, feature B) before initiation of the reaction is steadily damped during the course of the reaction. The final state spectrum (blue line) is characteristic for bromine bound to an organic moiety. Right: Temporal variation of the white line (blue line and blue diamonds) at the photon energy of 13.4725 keV (feature B) displayed together with the temporal variation of the UV-Vis absorption (dark red line) during the course of the BZ reaction. The reaction has been initiated at $t_i = 39645$ s. During the gaps of the time scan mode the QEXAFS spectra have been acquired.
The strong white line typical for bromate BrO\(_3^-\) ions corresponding to the reference spectrum of KBrO\(_3\) in solution characterises the initial spectrum (fig. 2, see also [11]). Upon reaction the white line (feature B) is damped and shifts to higher photon energy, two shoulders prior to the white line and at the post edge develop (feature A and C, fig. 2).

The white line at the photon energy 13.473 keV is used for the acquisition of time scans. During the course of the reaction the intensity of the white line steadily decreases (fig. 2 right). The final state spectrum (fig. 2 left, blue spectrum) is characteristic for bromine bound to an organic moiety. The spectrum resembles a spectrum of CHBr\(_3\) [12]. The quick consumption of bromate ions is also supported by the EXAFS analysis. The analysis of the intermediate state sample reveals only a weak coordination peak at the Br-O position, implying that a mixture of multiple Br species may coexist. The final product of Br shows two weak but distinct peaks with the first peak very different from Br-O coordination. The two peaks can be assigned to Br-C and Br-Br coordination shells. The result implies the reaction with malonic acid to form brom-malonic acid, indicating that the reaction of brome with malonic acid leads to a product that is a multiply halogenated carbohydrate. A Br-Br shell at a distance of 3.22 Å with a coordination number 1.8 is determined. The formation of multiply halogenated compounds during the BZ reaction has been reported [13].

4. Conclusions
A detailed analysis revealed that fast temporal variations observed in the UV-Vis signal correspond to the oscillatory variations in the X-ray absorption. The absorption determined with the two experimental techniques during the course of the reaction shows a well defined frequency as well as phase relationship. With the oxidation of Ce\(^{3+}\) a reduction of bromine ions should take place at the same time. The oxidation of cerium ions lead to an increased UV-Vis absorption, as does the reduction of bromine ions leads to an increase of the X-ray absorption signal of the white line at the Br K edge. The acquisition of the X-ray absorption signal interlaced with QEXAFS spectra allowed the determination of kinetic as well as structural data of the catalyst and one of the reactant species.

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