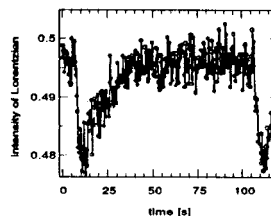


Study of the Belousov-Zhabotinsky chemical oscillator using time-resolving x-ray absorption spectroscopy

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The Belousov-Zhabotinsky (BZ) reaction is the metal-ion catalyzed bromination of malonic acid in aqueous acidic media. The concentration oscillations of the catalyst that occurred in the IM sulfuric acid aqueous solution with 400 mM malonic acid, 57 mM $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and 60 mM KBrO_3 have been followed using time-resolving x-ray absorption spectroscopy. The intensity of the white line at the Ce L_{III} edge proved to be mainly sensitive to the 3+ state of the cerium ion and a peak behind to the 4+ state. The optical transmission has been acquired in parallel in order to correlate the colour changes from transparent to yellow with the changes at the L_{III} edge.

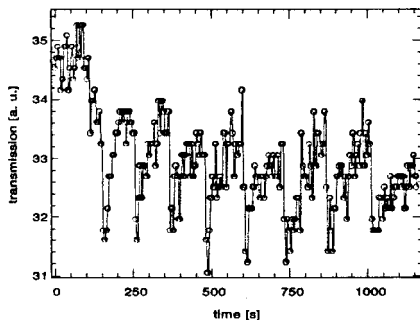


Fig. I Optical transmission after mixing the bromate solution into the Ce/malonic acid solution. The transmission breakdown corresponds to a colour change from transparent to yellow.
(bz063.opt)

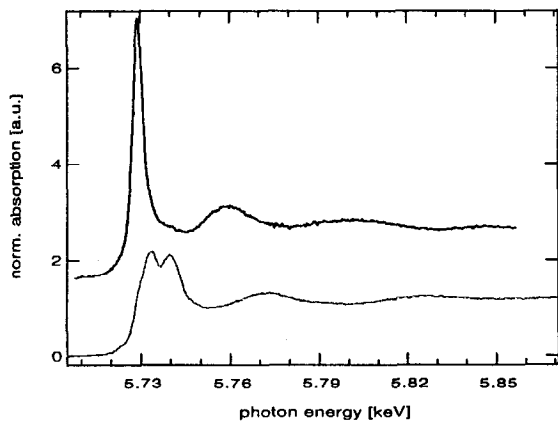


Fig. 2 Normalized absorption spectra of the BZ solution (above, blue, Ce^{3+}) and the CeO_2 powder reference sample (below, red, Ce^{4+}). (63, Ceo2.mes, calibration using the 2 features and the 1st EXAFS oscillation of the CeO_2 spectrum, a+mx, a-5.6611, m = 0.0002)

File 63, time resolved measurement

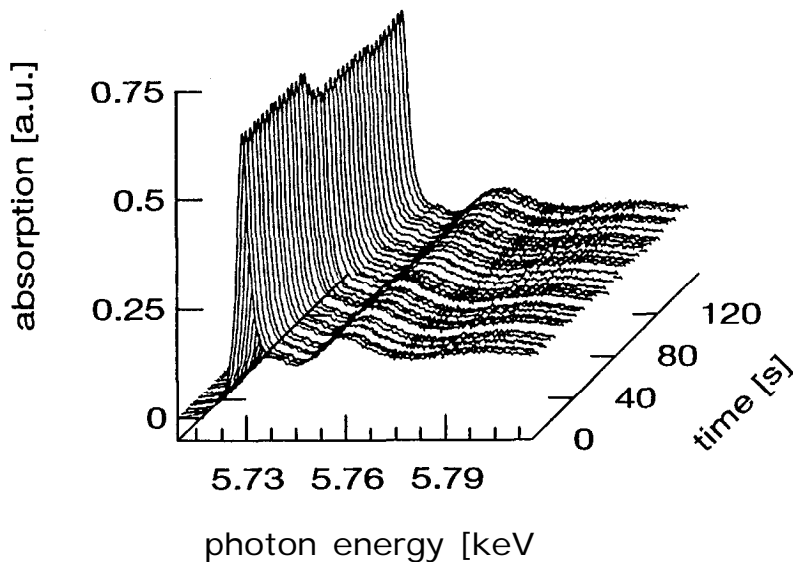


Fig. 3 Evolution of the XANES at the Ce L_{III} edge during the initial phase of the oxidation of Ce^{3+} with BrO_3^- and a breakdown oscillation ($t = 90$ s) in aqueous solution (57 mMol Ce).

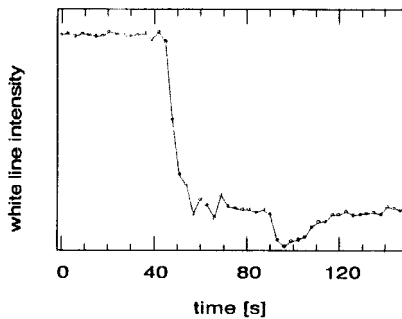


Fig. 4 Variation of the white line intensity with time using a single Lorentian fit of Fig.3 data. The intensity reduction at about 40 s occur at filling the bromate solution into the **Ce/malonic** acid solution and the first breakdown oscillation is visible at 90 s. Time resolution 4 s, exposure time **1s** (file 63-l.dxa. deglich. spectrum number 10 to 58)

Fit using 2 Lorentian curves and a mod. arctan

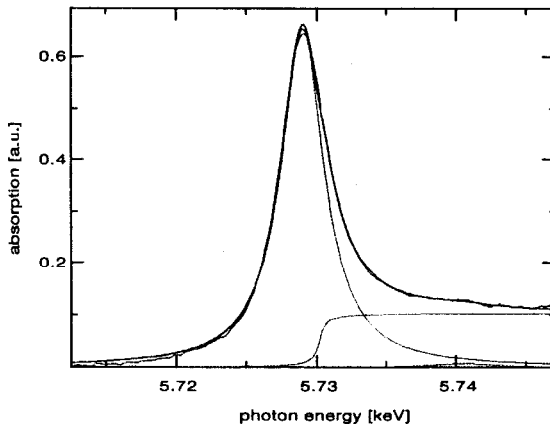


Fig. 5 fit functions for the XANES analysis, 2 Lorentians, 1 mod. arctan. The first Lorentian is assumed to be mainly proportional to the Ce(III) concentration, the 2nd Lorentian to the Ce(IV) concentration. Intensity variations point towards concentration variations.

(63-l .dxa, 5.7125 to 5.7471 keV,

Fit parameter, 2nd column:

Lorentzian 1

Height : 0.6541 +- 0.0449, Position : 5.1289 +- 0 fixed, FWHM : 0.00185+- 1.03E-11

4th cumulant: 1 +- 0 fixed

Lorentzian 2

Height : 0.0071 +- 0.0004, Position : 5.74053 +- 0 fixed, FWHM : 0.00302 t - 0 fixed

4th cumulant: 1 t - 0 fixed

mod. ATangens

Height : 0.1029 +- 0.0048, Position : 5.7301 +- 0 fixed)

results

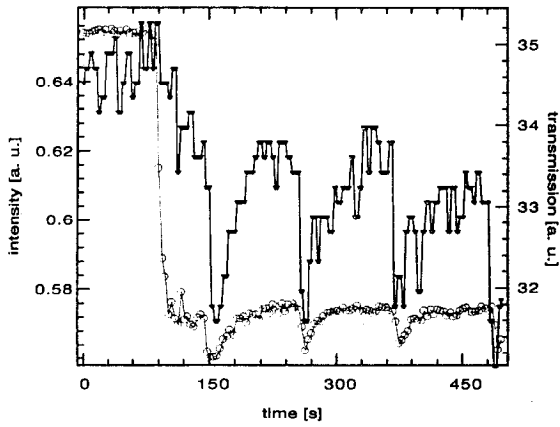


Fig. 6 White line intensity (circles) and optical transmission (triangles) of the first 500 s. (file 63.par, aus 63_1.dxa).

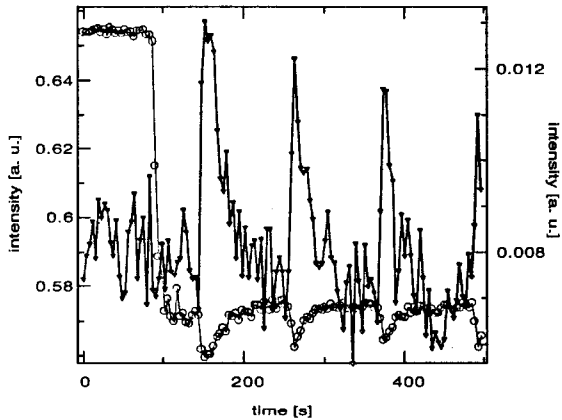


Fig. 7 as above, with intensity of 2nd Lorentian (triangles)

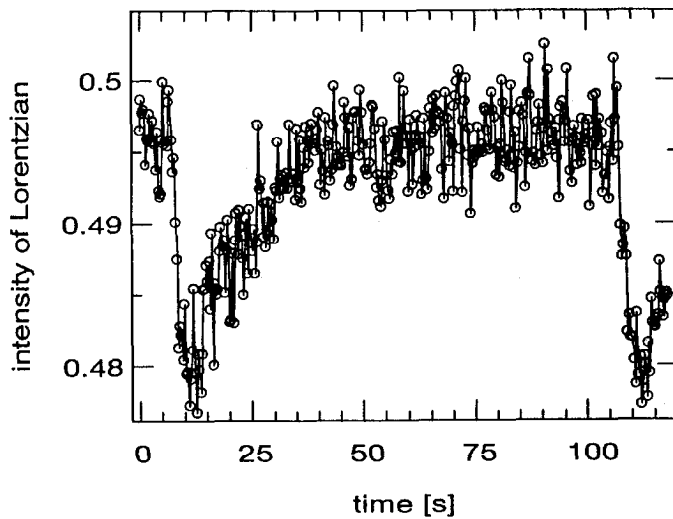
file 73 fast measurement

Fig. 8 Lorentzian fitted to the prominent white line, variation with time. time resolution 0.3 s, one single oscillation
(3 files added 73_1, 73_11, 73_12.par)