

Spectroscopic set-up for simultaneous UV-Vis/(Q)EXAFS *in situ* and *in operando* studies of homogeneous reactions under laboratory conditions

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A novel experimental set-up for *in operando* studies of homogeneous catalyzed reactions under laboratory conditions has been developed and tested. It combines time-resolved X-ray absorption spectroscopy with UV/Vis spectroscopy. The reaction solution is stirred in a vessel and pumped in a circle by a peristaltic free gear-wheel through a measurement cell. The X-ray and UV/Vis beams probe the same sample volume of the cell orthogonally. Reactants can be added to the reaction mixture in the course of the measurements and a defined gas atmosphere can be adjusted up to a pressure of 10 bar. The *in situ* reduction of cerium(IV) ammonium nitrate to cerium(III) by isopropanol is studied as a test reaction with quick-XANES and UV/Vis measurements with a time resolution of 60 s and 1 s, respectively.

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1. Introduction

In operando spectroscopic techniques are suitable for studying homogeneous and heterogeneous catalysts in real time under working conditions (Beale *et al.*, 2005). These techniques are nowadays frequently used to obtain mechanistic insight into the active site of the catalyst and the related reaction mechanism (Clausen *et al.*, 1993; Couves *et al.*, 1991; Rastogi *et al.*, 1998). Over the past several years, new instrumental developments combining two or three *in operando* spectroscopic techniques simultaneously have emerged, offering ample opportunities to reach a better understanding of many relevant catalytic systems (Brückner, 2005; Beale *et al.*, 2006). The crucial advantage of such combinations is the fact that multiple spectroscopic data are obtained from a catalytic system under identical reaction conditions. Ideally, the spectrometer device is inserted into the reactor vessel used in laboratory procedures (Tinnemans *et al.*, 2006).

While, in the case of heterogeneous catalyzed reactions (solid–gas and solid–liquid), several set-ups for the simultaneous combination of different spectroscopic methods are known from the literature, *e.g.* XAFS–XRD (Shannon *et al.*, 1997; Couves *et al.*, 1991; Clausen *et al.*, 1993; Grunwaldt *et al.*, 2000), dispersive XAFS–IR (Newton *et al.*, 2004) and dispersive XAFS–Raman–UV/Vis (Beale *et al.*, 2005), to the best of our knowledge, approaches to study homogeneous catalyzed

reactions by XAFS, UV/Vis and Raman spectroscopy are very rare (Tromp, 2004; Tromp *et al.*, 2003; Brios *et al.*, 2005; Kervinen *et al.*, 2005), and existing set-ups are aimed at studying reactions with a subsecond time resolution, resulting in limitations to studying reactions of more complex procedures under laboratory conditions. Nevertheless, the combination of XAFS and UV/Vis is of particular relevance for investigations of important homogeneous catalytic reactions (Bauer *et al.*, 2005; Feth *et al.*, 2003).

Intrinsically, the stopped-flow set-up presented by Tromp (2004) and Tromp *et al.* (2003), which combines dispersive-XAFS with UV/Vis spectroscopy, is limited to fast reactions, and no stirring and no addition of reactants is possible after starting the measurements. On the other hand, so-called immersion probe heads were used by Briois *et al.* (2005) and Kervinen *et al.* (2005) to record Raman and UV/Vis spectra of a reaction solution simultaneously, also with a time resolution of the order of 1 s. But here, as well, neither stirring nor addition of reactants is foreseen.

With the present work, this ‘design gap’ is aimed to be bridged by reproducing a laboratory set-up at an X-ray absorption beamline. By definition, such a set-up requires mixing, which limits the reasonable time resolution to the duration of the mixing process. The proposed set-up is therefore useful in combination with quick-EXAFS (QEXAFS) measurements with a time resolution from some

seconds to a few minutes. Faster reactions require procedures as mentioned above (Tromp *et al.*, 2003; Briois *et al.*, 2005; Kervinen *et al.*, 2005). In this work, a reaction vessel is used, where adding reactants, stirring and mixing is carried out, while the X-ray absorption spectroscopy (XAS) and UV/Vis spectra are recorded in a spatially separated measurement cell. Both compartments are connected to each other by a gear wheel pump, which pumps the reaction mixture from the vessel through the cell. A detailed description of the technical design will be given in this work, together with a first test study as proof of principle.

2. Experimental

2.1. X-ray absorption measurements

X-ray absorption experiments at the cerium L_3 -edge (5.724 keV) were carried out at the XAS beamline at the Ångströmquelle Karlsruhe (ANKA) in the QEXAFS mode using a double-crystal fixed-exit monochromator (DCM). Owing to the combined movement of the Bragg axis with the two linear drives, the stability of the beam height is maintained within 40 μm . The DCM was detuned to 65% of the maximum intensity using a D-MOSTAB (Struck, Hamburg). The data from all detectors are read out by pure software triggering of spec, which enables the readout of all detectors, including the digital detector electronics of XIA. This enables measurements in transmission mode and in fluorescence mode. The measurements were carried out in transmission mode at ambient temperatures. Oxford X-Spec ionization chambers of length 30 cm were used. The first ionization chamber was filled with 450 mbar nitrogen, the second and third with 900 mbar nitrogen. The QEXAFS scan was performed for all scans between 5.68 and 5.8 keV. The measurement time per point was 0.05 s, the time per complete scan was 60 s. The reference substance cerium(III) acetylacetonate $\text{Ce}(\text{acac})_3$ was placed before the third chamber for re-calibration of all spectra.

In order to prove the quality of the QEXAFS spectra, solid-state spectra of cerium ammonium nitrate $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (CAN) and cerium acetylacetonate $\text{Ce}(\text{acac})_3$ (acac = 2,4-pentadione) were measured in the QEXAFS and step-by-step mode. The spectra are compared in Fig. S11 (electronic supplementary information).¹ The QEXAFS spectra are of high quality and no differences to the step-by-step mode can be observed in the XANES region.

Data acquisition of the investigated solution was carried out using the experimental set-up, described in §3. A solution of CAN in isopropanol was measured in order to record the time-dependent reduction of Ce(IV) to Ce(III) by isopropanol by means of quick-XANES and UV/Vis spectroscopy.

Data analysis started with normalization of the quick-XANES spectra using the program *WINXAS* (Ressler, 1997). Evaluation of the QEXAFS kinetic data was performed by linear combination (LC)-XANES fit (Ressler, 1997). CAN

was used as Ce(IV) reference and the solution of CAN in isopropanol, which was left for four days to ensure complete reduction, as reference for Ce(III). The spectra of both references were linearly fitted to the experimental, but energy-corrected, spectra. Using this method, the molar fraction of Ce(III) and Ce(IV) can be determined independently.

2.2. UV/Vis measurement

UV/Vis measurements were performed with an Ocean Optics USB2000 spectrometer (Ocean Optics, 2007), described in §3. The recording time per individual spectrum was 10 ms; ten spectra were averaged after every 0.5 s. The total acquisition time therefore amounts to about 0.7 s per averaged spectrum, giving a total number of approximately 52000 spectra during a reaction of around 10 h. Kinetic data were obtained by recording the absorbance at 513 nm and the wavelength where the absorbance amounts to the value 0.5.

2.3. Materials

All chemicals were used as received. Oxygen-free isopropanol was prepared by the freeze-pump-though technique and stored under argon. A solution of 0.055 mol l⁻¹ Ce(IV) was prepared by dissolving 900 mg (1.6 mmol) of CAN, purchased from SigmaAldrich, in 30 ml isopropanol. Measurements were carried out under argon atmosphere.

3. Technical design

In the following chapters, the technical data and design details of the set-up used for the two-dimensional spectroscopic *in operando* studies of homogeneous catalytic reactions are presented. Fig. 1 shows a scheme of the developed set-up. Laboratory-like conditions are achieved by separating the vessel in which the reaction is carried out from the measurement cell. The reaction vessel consists of a five-neck flask. Two necks are used to lead a controlled gas stream through the reaction vessel. The reactants are added through a third neck with a syringe pump. The remaining necks are the outlet and inlet for the reaction solution. The vessel is placed on a magnetic stirrer. The reaction mixture is pumped with a gear wheel pump of adjustable power from the vessel to the measurement cell, where XAS and UV/Vis spectra were recorded simultaneously.

3.1. Measurement cell

UV/Vis spectra were measured simultaneously with XAFS spectra using a fibre optic technique in a specialized measurement cell. Several cells for combining UV/Vis spectroscopy with the following other techniques have been reported: diffuse reflectance spectroscopy (Bailes & Stone, 1991), difference spectroscopy (Ahl *et al.*, 1988) and variable- and low-temperature spectroscopy (Blackburn *et al.*, 1988; Sanyal *et al.*, 1993; Hartl *et al.*, 1994; Andréa *et al.*, 1986).

In addition, there exist several examples of specialized XAS cells, e.g. for high-temperature measurements (Inui *et al.*, 2001; Kuroda *et al.*, 1989; Kampers *et al.*, 1998; Pettiti *et al.*, 1999),

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: KV5073). Services for accessing these data are described at the back of the journal.

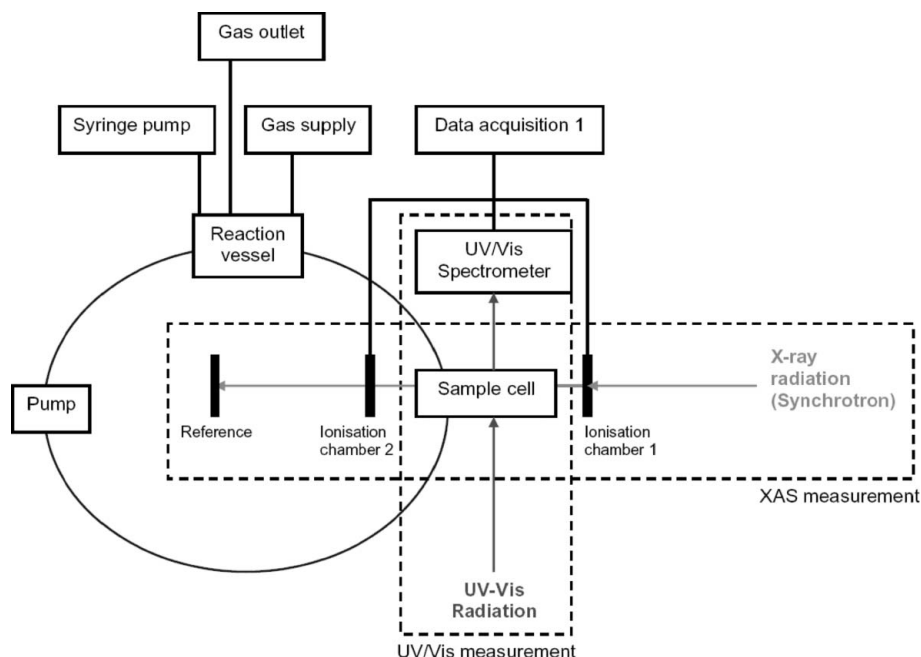


Figure 1 Schematic presentation of the *in operando* set-up for the simultaneous two-dimensional spectroscopic investigations of homogeneous catalytic reactions. The individual components are explained in the text.

in situ catalytic studies (Odzak *et al.*, 2001; Schneider *et al.*, 2000; Grunwaldt *et al.*, 2001; van Bokhoven *et al.*, 1999), combination with electrochemistry (Cognigni *et al.*, 2001; Dewald, 1991) and for corrosive or air-sensitive compounds (Sánchez Marcos *et al.*, 1994; Munez-Páez *et al.*, 1995). Weber *et al.* (1998) have described an XAS cell that is suitable for measurements of air-sensitive compounds at low temperature in fluorescence mode. Furenlid *et al.* (1990a,b) have used a glass cell for electron paramagnetic resonance, optical absorption, and XAS measurements on oxidation and reduction reactions with a nickel porphyrin complex at room temperature.

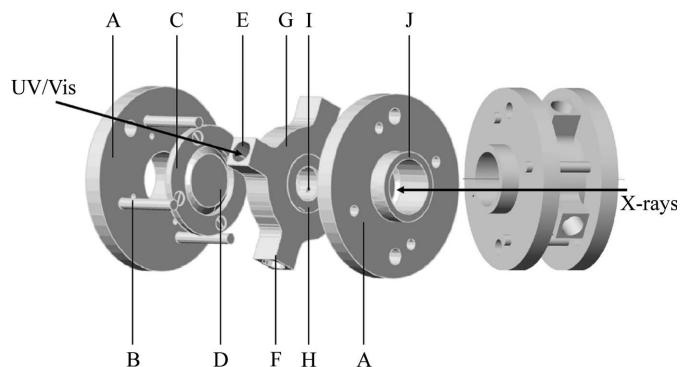


Figure 2 Left: components of the measurement cell for combined XAFS-UV/Vis studies: (A) mounting disc for the spacer; (B) pins to fix the spacer; (C) ring disc fixing the Kapton windows (D); (E) inlet for the optical fibres; (F) inlet for the reaction solution pumped through the cell; (G) spacer of variable thickness; (H) sealing of the cell; (I) drill hole; (J) tube with screw thread. Right: the complete cell.

The cell presented in this work and sketched in Fig. 2 permits a continuous flow rate of the reaction mixture by pumping with a programmable pump. In the cell, the X-ray beam and the UV/Vis beam probe the same volume.

All the parts of the cell used are made of stainless steel. The main part of the cell is the spacer (G), which is mounted between two discs (A) and fixed by four pins (B). Design details of the spacer are given in the electronic supplementary information (Fig. S12). A set of spacers of thickness between 4 and 20 mm enables an adjustment of the X-ray path length. Kapton windows (D) are fixed to the discs (A) with thin ring-discs (C) by four Torx screws. The windows are tightened by the threads of a cylindrical tube (J). These tubes press the Kapton window against the sealing (H), made of Viton and Teflon. The cell was tight up to a pressure of 10 bars. The spacer (G) contains two pairs of inlet and outlet of 1/4" outer diameter (E and F) and a drill hole (I) of 1/16" diameter leading into the cell. One pair (F) is used to pump the reaction solution through the cell, the other pair (E) for the optical fibres of the UV/Vis spectrometer. The distance between the ends of the optical fibres defines the path length of the UV/Vis spectroscopy and is variable between 0 and 10 mm. Pressure-tight connection of the solution supply and optical fibres to the cell is achieved by Tefzel fingertight fittings with PTFE ferrules. Photographs of the cell with labelling of the different parts are shown in Fig. 3.

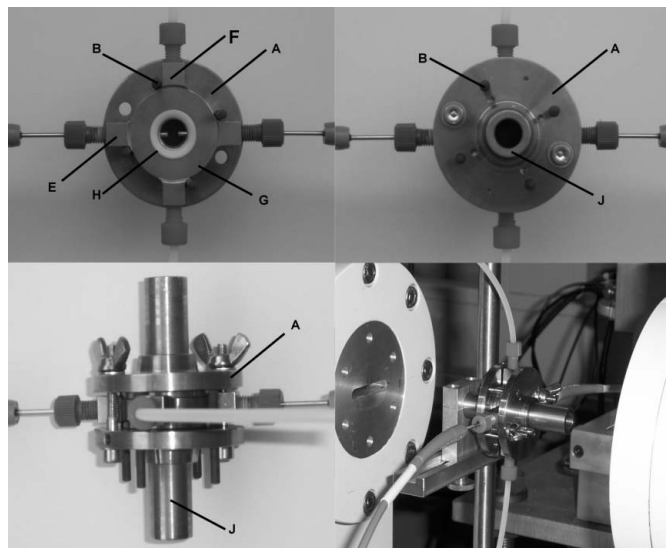


Figure 3 Photographs of the cell mounted at the ANKA-XAS beamline (bottom left), with all parts labelled according to Fig. 2.

3.2. UV/Vis spectrometer

An Ocean Optics USB2000 UV/Vis spectrometer of dimensions $9 \times 6 \times 34$ mm and weight 190 g with fibre optic, as shown in Fig. S13 of the electronic supplementary information (Ocean Optics, 2007), was used. The incoming beam enters the spectrometer *via* a connector (1) and passes a slit (2) with an entrance aperture of $50 \mu\text{m}$ and a spectral resolution of 2.5 nm FWHM. The filter (3) limits the radiation to the pre-determined wavelength regions. The collimating mirror (4) focuses the light onto a grating (5) of groove density $600 \text{ lines mm}^{-1}$, which defines a wavelength region of 250–800 nm. The light reflected from the grating (5) is focused by a mirror (6) and a collection lens (7), and recorded by a CCD detector (8). A Sony ILX511 linear silicon CCD array detector with 2048 pixels and a signal-to-noise ratio of 250:1 are used with an integration time between 3 ms and 65 s.

The light emitted from a DT-Mini-GS deuterium–halogen source in the spectral range 200–1700 nm is transmitted by a FIA-P400-SR $400 \mu\text{m}$ optical fibre of length 2 m with chemical-resistant ferrule end-piece directly into the solution. An identical fibre collects the transmitted beam.

3.3. Pump

The pump has to be chemically resistant and the pump rate must be adjustable over a wide range. Several peristaltic pumps were tested, but the peristaltic structure of the flux, even of very small amplitude, is immediately detectable in the EXAFS spectra. The instability of the X-ray windows causes oscillations of the X-ray path length. Gear wheel pumps do not show this effect. A very robust one, with high chemical resistance and a velocity range of 10–4500 r.p.m., is a magnet-coupled gear wheel pump, model 1M-J/6/D-S/Y/Q, produced by GatherIndustrie. The following materials were used, in order to ensure chemical resistance and broad applicability. The pump body was made of stainless steel 1.4404, the shaft of hardened stainless steel 1.4571. Gear wheels consisted of nickel alloy, slide bearing of Sb-impregnated carbon; Teflon jacketed Viton O-ring sealings were applied. The pump head was entered through $1/4$ " NPT core thread connections. The 230 VDC power unit provided a velocity range of 10–4500 r.p.m. The flow rate for the solvents isopropanol and water were determined experimentally in the range 10–900 r.p.m. and are depicted in Fig. 4.

In the set-up used at the ANKA-XAS beamline the length of the chemically inert Teflon tube between the reaction vessel and the XAFS-UV/Vis cell is 50 cm with an inner diameter of $1/16$ ". Thus the volume of the liquid in the tube is about 1 ml. This volume is transported within 0.25–2 s. Since a QEXAFS scan typically requires 60 s, the transport from the reaction vessel to the cell causes no loss of information.

3.4. Syringe pump

A syringe pump (Dr Lehky Lambda VIT-FIT) with a driving force of maximal 30 N was used. Its main advantage is that different syringes run with this type and the driving velocity can be chosen in 0 and 999 increments. The char-

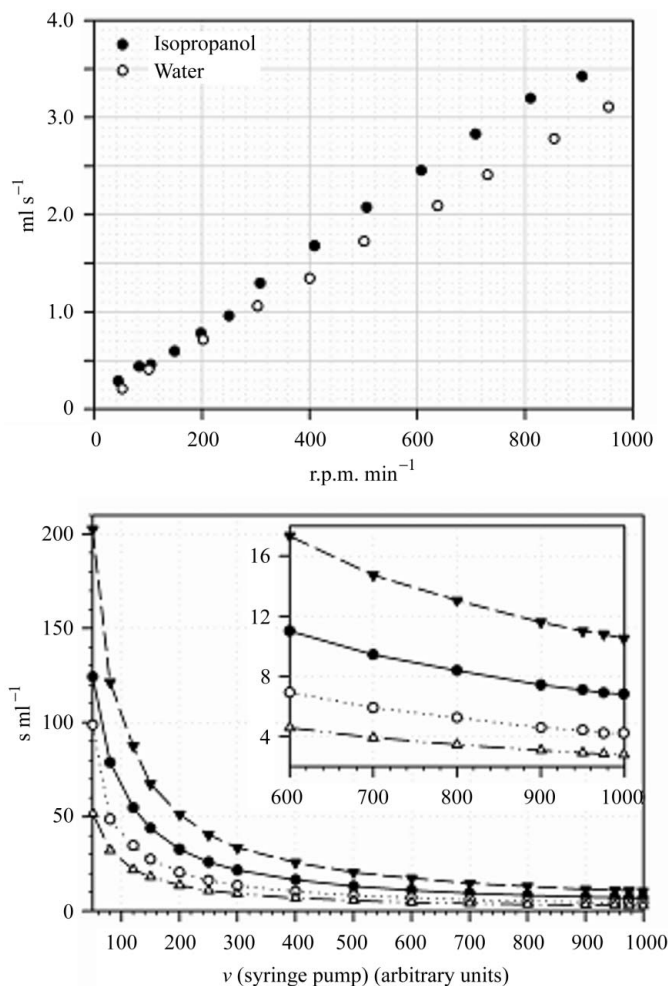
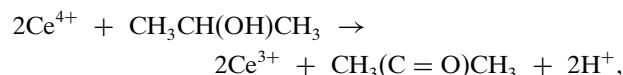


Figure 4
Top: experimental calibration curve of the gear wheel pump for isopropanol and water, obtained under identical experimental conditions as for the kinetic studies. Bottom: characteristic function of the capacity of the syringe pump. Open triangles: 20 ml syringe; open circles: 10 ml syringe; filled circles: 5 ml syringe; filled triangles: 2 ml syringe. The inset shows an enlargement of the most commonly used driving speed range.

acteristic functions of four typical types of syringes (2, 5, 10 and 20 ml) were recorded and are also depicted in Fig. 4.

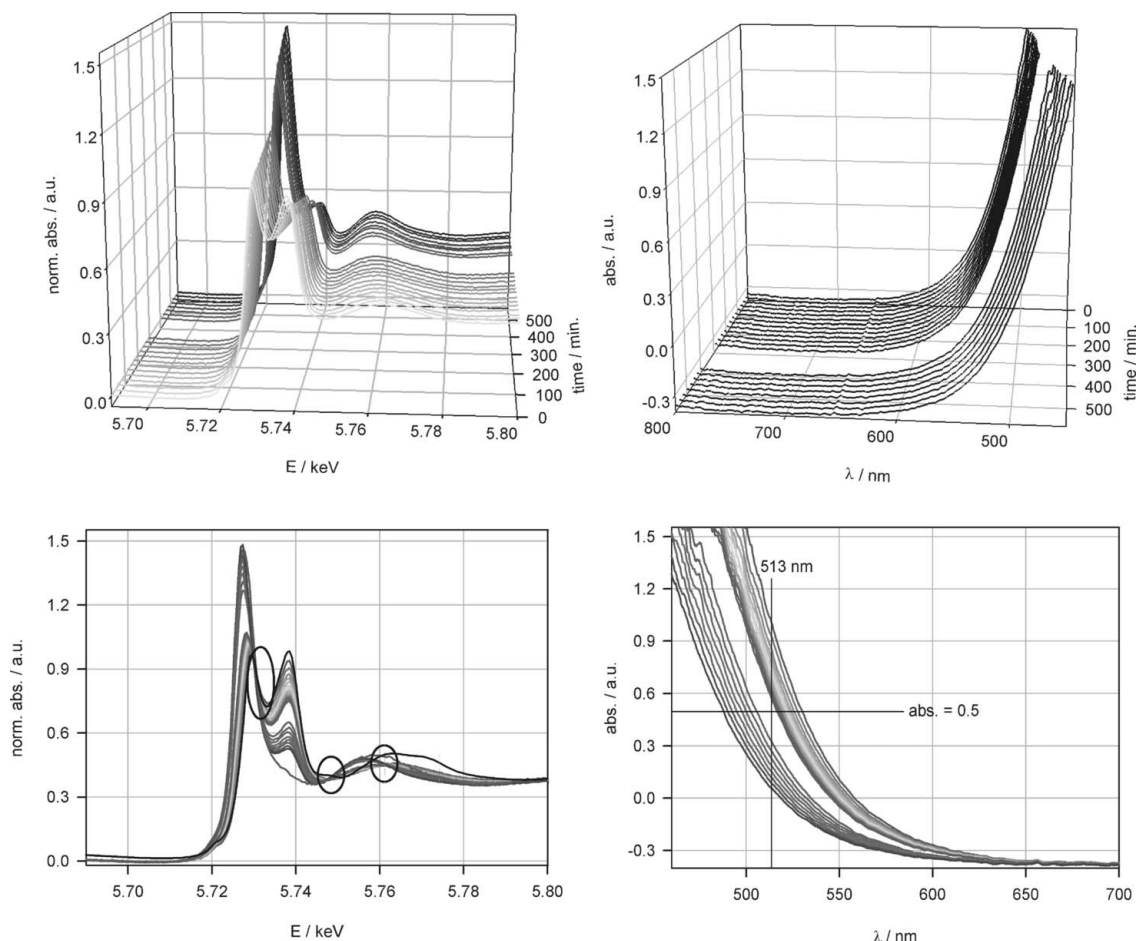
4. Test study: the reduction of cerium ammonium nitrate in *i*PrOH

The reduction of Ce(IV) to Ce(III) in *i*PrOH, according to the following reaction,



was selected as the test reaction for the two-dimensional spectroscopic *in operando* set-up. In order to avoid reoxidation, the whole set-up was flushed with argon and an argon pressure of 1 bar was applied during the measurements.

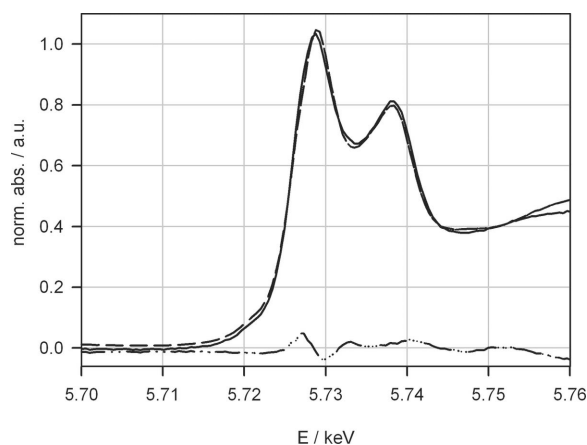
Fig. 5 shows the XANES and UV/Vis spectra recorded for the first 500 min of the reaction. The acquisition time of one XANES spectrum amounts to 60 s. UV/Vis spectra were


Figure 5

Left: time-resolved XANES spectra of the reduction of Ce(IV) by isopropanol in three-dimensional (top) and two-dimensional (bottom) representation. In the bottom picture, the Ce(IV) (maximal resonance at 5.738 keV) and Ce(III) (no resonance at 5.738 keV) reference spectra used in the LC-XANES fit are shown as black and dark grey curves, respectively. Ovals highlight the isosbestic points. The gap in the spectra is due to an interruption of the X-ray beam during injection of electrons into the storage ring. Right: time-resolved UV/Vis spectra in three-dimensional (top) and two-dimensional (bottom) representation.

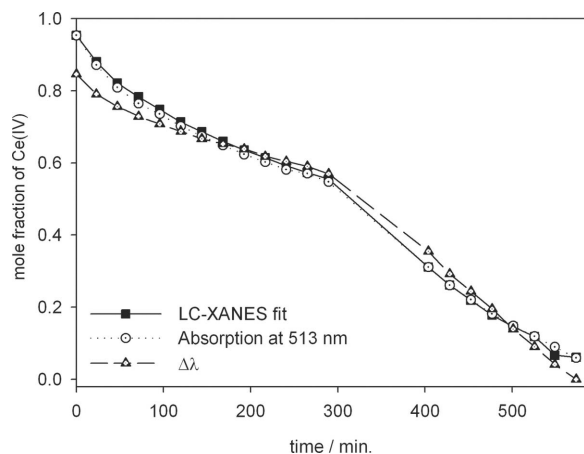
recorded every 0.7 s. The existence of three isosbestic points in the XANES spectra, marked in Fig. 5 by ovals, indicates that no intermediates are formed (Briois *et al.*, 2005). Thus each spectrum should be a weighted linear combination of Ce(III) and Ce(IV) spectra, which could be shown by principal component analysis (Jackson, 1991). In order to determine the Ce(IV)/Ce(III) composition in the course of the reaction, the initial Ce(IV) and the final Ce(III) reference spectrum were fitted to the experimental spectra. As can be seen in Fig. 6, the quality of the fit is very high.

Because only the Ce(IV) species are coloured, any point of the measured UV/Vis spectra can in principle be used to determine the kinetics of the reaction. The absorbance at a wavelength of 513 nm as well as the wavelength at which the adsorption amounts to 0.5 were monitored. In the latter case, the wavelength of the solution after four days was subtracted from all spectra, and the difference value used as a measure of the Ce(IV) fraction. With this method, only relative kinetic data can be obtained, but they can provide a cross-check for the absolute determination of the Ce(IV) fraction, namely the absorbance at 513 nm and the LC-XANES fit. The kinetic functions show very good agreement and are given in Fig. 7.


Figure 6

Example of a typical LC-XANES fit with defined Ce(IV) and Ce(III) references. The experimental spectrum is shown as a solid line, the linear combination of both references as a dashed line. Additionally, the residual function after subtraction of the linear combination from the experimental spectrum is shown (double-dotted dashed line).

The regression functions to the kinetic data, deduced from the XANES and UV/Vis spectra, respectively, are $\text{Ce(IV)} = -0.015(\pm 0.000)t + 0.907(\pm 0.012)$ and $\text{Ce(IV)} =$


Figure 7

Individual kinetic functions of the Ce(IV) species during the reduction of Ce(IV) by isopropanol as obtained by simultaneous XANES (squares) and UV/Vis measurements (circles: absorption at 513 nm; triangles: wavelength at an absorption of 0.5). The values of $\Delta\lambda$ were rescaled to the Ce(IV) XAS plot for better comparability. The gap between 300 and 400 min is due to the injection of electrons into the synchrotron storage ring.

$-0.015(\pm 0.0003)t + 0.922(\pm 0.011)$ and indicate an order of the reaction of zero.

The ordinate intersection point is not zero due to the fact that the solution of CAN has to be prepared prior to the start of the measurement. Since the regression functions are almost identical, the approach of fitting the XANES spectra with only two references is confirmed. The two methods should differ if a third cerium compound is formed during the reaction.

5. Conclusion

A special experimental set-up for two-dimensional spectroscopic investigations of homogeneous catalyzed reactions by simultaneous QEXAFS and UV/Vis measurements has been designed. The essential unit of the set-up is a measurement cell that can be generally used owing to variable path lengths of the optical and X-ray beam, which probe an identical volume. The periphery of the set-up allows laboratory conditions to be mimicked, as they are applied in preparative organic chemistry and catalysis. In contrast to previous set-ups, one or more reactants can be added in the course of the reaction under defined gas atmosphere and stirring is possible. This makes the presented set-up more suitable for investigations of preparative sophisticated reactions, which need to be carried out either under inert or reactant gas atmosphere. With this set-up, very important classes of reactions, such as iron- or palladium-catalyzed cross-coupling reactions that are sensitive to moisture or air, can be studied over the complete reaction time in the future.

As a test reaction, the kinetics of the reduction of cerium(IV) to cerium(III) in isopropanol was studied. The order of this reaction is zero.

Owing to a further enhancement of the beam stability during the Q-XAFS scan at the ANKA-XAS beamline, newer measurements will have even better quality. However, owing to the easy portable technical parts implemented in the set-up,

it can be used at any synchrotron radiation facility. Its application is of course not limited to the Q-XAFS technique, but can also be used for longer studies by normal EXAFS measurements.

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References

- Ahl, P. L., Stern, R. J., Düring, D., Mogi, T., Khorana, H. G. & Rothschild, K. J. (1988). *J. Biol. Chem.* **263**, 13594–13601.
- Andréa, R. R., Luyten, H., Vuurman, M. A., Stufkens, D. J. & Oskam, A. (1986). *Appl. Spectrosc.* **40**, 1184–1190.
- Bailes, M. & Stone, F. S. (1991). *Mater. Chem. Phys.* **29**, 489–501.
- Bauer, M., Kauf, Th., Christoffers, J. & Bertagnolli, H. (2005). *Phys. Chem. Chem. Phys.* **7**, 2664–2670.
- Beale, A. M., van der Eerden, A. M. J., Jacques, S. D. M., Leynaud, O., O'Brian, M. G., Meneau, F., Nikitenko, S., Bras, W. & Weckhuysen, B. M. (2006). *J. Am. Chem. Soc.* **128**, 12386–12387.
- Beale, A. M., van der Eerden, A. M. J., Kervinen, K., Newton, M. A. & Weckhuysen, B. M. (2005). *Chem. Commun.* pp. 3015–3017.
- Blackburn, N. J., Strange, R. W., Farooq, A., Haka, M. S. & Karlin, K. D. (1988). *J. Am. Chem. Soc.* **110**, 4263–4272.
- Bokhoven, J. A. van, van der Eerden, A. M. J., Smith, A. D. & Koningsberger, D. C. (1999). *J. Synchrotron Rad.* **6**, 201–203.
- Briois, V., Lützenkirchen-Hecht, D., Villain, F., Fonda, E., Belin, S., Griesebock, B. & Frahm, R. (2005). *J. Phys. Chem. A*, **190**, 320–329.
- Brückner, A. (2005). *Chem. Commun.* pp. 1761–1763.
- Clausen, B. S., Grabaek, L., Steffensen, G., Hansen, P. L. & Topsoe, H. (1993). *Catal. Lett.* **20**, 23–36.
- Cognigni, A., Ascone, I., Zamponi, S. & Marassi, R. (2001). *J. Synchrotron Rad.* **8**, 987–989.
- Couves, J. W., Thomas, J. M., Waller, D., Jones, R. H., Dent, A. J., Derbyshire, G. E. A. & Greaves, G. N. (1991). *Nature (London)*, **354**, 465–468.
- Dewald, H. D. (1991). *Electroanalysis*, **3**, 145–155.
- Feth, M. P., Bolm, C., Hildebrand, J. P., Köhler, M., Beckmann, O., Bauer, M., Ramamonjisoa, R. & Bertagnolli, H. (2003). *Chem. Eur. J.* **9**, 1348–1359.
- Furenliid, L. R., Renner, M. W. & Fajer, J. (1990a). *Rev. Sci. Instrum.* **61**, 1326–1327.
- Furenliid, L. R., Renner, M. W., Smith, K. M. & Fajer, J. (1990b). *J. Am. Chem. Soc.* **112**, 1634–1635.
- Grunwaldt, J.-D., Kappen, P., Hammershøi, B. S., Tröger, L. & Clausen, B. S. (2001). *J. Synchrotron Rad.* **8**, 572–574.
- Grunwaldt, J. D., Molenbroek, A. M., Topsoe, N. Y., Topsoe, H. & Clausen, B. S. (2000). *J. Catal.* **194**, 452–460.
- Hartl, F., Luyten, H., Nieuwenhuis, H. A. & Schoemaker, G. C. (1994). *Appl. Spectrosc.* **48**, 1522–1528.
- Inui, M., Matsusaka, T., Ishikawa, D., Sakaguchi, Y., Hong, X., Kazi, M. H. & Tamura, K. (2001). *J. Synchrotron Rad.* **8**, 767–769.
- Jackson, J. E. (1991). *A Users Guide to Principal Component Analysis*. New York: John Wiley and Sons.
- Kampers, F. W. H., Mass, T. M. J., van Grondelle, J., Brinkgreve, P. & Koningsberger, D. C. (1998). *Rev. Sci. Instrum.* **60**, 2635–2638.
- Kervinen, K., Korpi, H., Mesu, J. G., Soulimani, F., Repo, T., Rieger, B., Leskela, M. & Weckhuysen, B. M. (2005). *Eur. J. Inorg. Chem.* pp. 2591–2599.
- Kuroda, Y., Maeda, H. & Morimoto, T. (1989). *Rev. Sci. Instrum.* **60**, 3083–3085.
- Munez-Páez, A., Gil, M., Martínez, J. M. & Sánchez Marcos, E. (1995). *Physica B*, **208–209**, 241–242.
- Newton, M. A., Jyoti, B., Dent, A. J., Fiddy, S. G. & Evans, J. (2004). *Chem. Commun.* pp. 2382–2383.
- Ocean Optics (2007). *Ocean Optics Product Catalogue*. Ocean Optics, Dunedin, FL, USA.

- Odzak, F., Argo, A. M., Lai, F. S., Gates, B. C., Pandya, K. & Feraria, L. (2001). *Rev. Sci. Instrum.* **72**, 3943–3945.
- Pettiti, I., Gazzoli, D., Inversi, M., Valigi, M., De Rossi, S., Ferraris, G., Porta, P. & Colonna, S. (1999). *J. Synchrotron Rad.* **6**, 1120–1124.
- Rastogi, S., Goossens, J. G. P. & Lemstra, P. J. (1998). *Macromolecules*, **31**, 2983–2998.
- Ressler, T. (1997). *J. Phys. IV*, **7(C2)**, 269–270.
- Sánchez Marcos, E., Gil, M., Martínez, J. M., Munez-Páez, A. & Sánchez Marcos, A. (1994). *Rev. Sci. Instrum.* **65**, 2153–2154.
- Sanyal, I., Karlin, K. D., Strange, R. W. & Blackburn, N. J. (1993). *J. Am. Chem. Soc.* **115**, 11259–11270.
- Schneider, S., Bazin, D., Dubuisson, J. M., Ribbens, M., Sonnevile, H., Meunier, G., Garin, F., Maire, G. & Dexpert, H. (2000). *J. X-ray Sci. Technol.* **8**, 221–230.
- Shannon, I. J., Maschmeyer, T., Sankar, G., Thomas, J. M., Oldroyd, R. D., Sheehy, M., Madill, D., Waller, A. M. & Townsed, R. P. (1997). *Catal. Lett.* **44**, 23–27.
- Tinnemans, S. J., Mesu, J. G., Kervinen, K., Visser, T., Nijhuis, T. A., Beale, A. M., Keller, D. E., van der Eerden, A. M. J. & Weckhuysen, B. M. (2006). *Catal. Today*, **113**, 3–15.
- Tromp, M. (2004). PhD Thesis, Utrecht University, Utrecht, The Netherlands.
- Tromp, M., Sietsma, J. R. A., van Bokhoven, J. A., van Strijdonck, G. P. F., van Haaren, R. J., van der Eerden, A. M. J., van Leeuwen, P. W. N. M. & Koningsberger, D. C. (2003). *Chem. Commun.* pp. 128–129.
- Weber, S., Ostafin, A. E. & Norris, J. R. (1998). *Rev. Sci. Instrum.* **69**, 2127–2129.