Electronic supplementary information to "X-ray absorption in homogeneous catalysis reasearch: The iron-catalyzed Michael addition reaction by XAS, RIXS and multi-dimensional spectroscopy" by M. Bauer* and C. Gastl

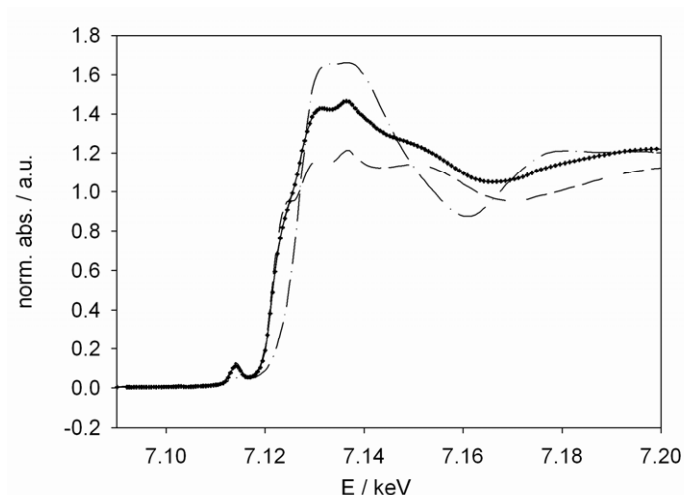## Deeper insights into the active species by RIXS and HERFD-XANES spectroscopy

Figure SI1: Result of the LC-XANES fit (dotted line) of the spectrum of $FeCl_3 \cdot 6\,H_2O$ (**2**) in **1** (solid line) with the references $[FeCl_4]^-$ (**9**) (dashed line) and $[Fe(\mathbf{1}\text{-}H)_2(H_2O)_2]^+$ (dotted dashed line).

The role of chloride as catalyst poison and iron sink

Table SI1: Molar fractions (F) of $[FeCl_4]^-$ and $[Fe(\mathbf{1}\text{-}H)_2(H_2O)_2]^+$ in solutions containing 0 to 3.5 equivalents Cl^- [Cl], as obtained by LC-XANES fit and optical absorption spectroscopy.

Reference	0 eq. Cl^-	0.5 eq. Cl^-	1 eq. Cl^-	1.5 eq. Cl^-	2 eq. Cl^-	2.5 eq. Cl^-	3 eq. Cl^-	3.5 eq. Cl^-	Regression function
$[FeCl_4]^-$ LC-XANES	0.00	0.182	0.189	0.284	0.506	0.604	0.755	0.818	F = 0.245(±0.015)·[Cl]-0.011 (±0.030)
$[FeCl_4]^-$ UV/Vis	0.00	0.140	0.230	0.280	0.450	0.620	0.770	0.840	F = 0.260(±0.014)·[Cl]-0.023 (±0.028)
$[Fe(\mathbf{1}\text{-}H)_2(H_2O)_2]^+$ LC-XANES	1.00	0.817	0.817	0.716	0.494	0.396	0.245	0.182	F = -0.249(±0.019)·[Cl]+1.016 (±0.038)
$[Fe(\mathbf{1}\text{-}H)_2(H_2O)_2]^+$ UV/Vis	1.00	0.860	0.770	0.720	0.550	0.380	0.230	0.160	F = -0.260(±0.014)·[Cl]+1.023 (±0.028)

XAFS and Raman *operando* studies

Local structure (EXAFS)

Table SI2: Structural parameters from fitting the EXAFS spectra of the first 150 minutes of the reaction of 2-oxocyclopentanecarboxylate (**1**) with methyl viny ketone, catalyzed by $Fe(ClO_4)_3 \cdot 9\ H_2O$ (**3**)[a].

Sample	Abs-Bs	N(Bs)	R / Å	σ / Å	Fit index[b]	Filter / Å E_f / eV
3 in 1	Fe-O	6[c]	2.01 ± 0.02	0.092 ± 0.009	16.01	1.0 – 3.0
	Fe-C	4[c]	2.87 ± 0.03	0.100 ± 0.010		4.38
after 0 min.	Fe-O	6[c]	2.03 ± 0.02	0.100 ± 0.010	18.99	1.0 – 3.0
	Fe-C	4[c]	2.88 ± 0.03	0.112 ± 0.011		3.67
after 30 min.	Fe-O	6[c]	2.03 ± 0.02	0.102 ± 0.010	17.53	1.0 – 3.0
	Fe-C	4[c]	2.90 ± 0.03	0.112 ± 0.011		3.17
after 60 min.	Fe-O	6[c]	2.04 ± 0.02	0.102 ± 0.010	20.15	1.0 – 3.0
	Fe-C	4[c]	2.90 ± 0.03	0.112 ± 0.011		3.16
after 90 min.	Fe-O	6[c]	2.03 ± 0.02	0.102 ± 0.010	19.57	1.0 – 3.0
	Fe-C	4[c]	2.90 ± 0.03	0.112 ± 0.011		3.21
after 120 min.	Fe-O	6[c]	2.05 ± 0.02	0.102 ± 0.010	17.45	1.0 – 3.0
	Fe-C	4[c]	2.90 ± 0.03	0.112 ± 0.011		3.22
after 0 min.	Fe-O	6[c]	2.05 ± 0.02	0.105 ± 0.010	21.95	1.0 – 3.0
	Fe-C	4[c]	2.90 ± 0.03	0.112 ± 0.011		3.33

[a]Amplitude reducing factor (AFAC) = 0.8. [b]Quality of fit [c]Coordination numbers were fixed, all other parameters were iterated.
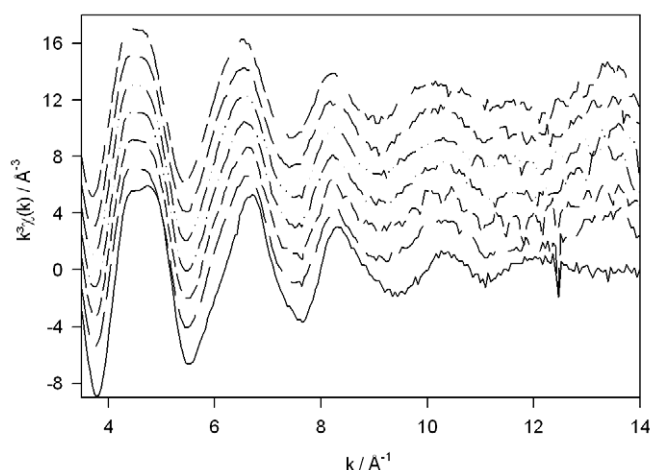

Figure SI2: Successive unfiltered $k^3 \cdot \chi(k)$ functions recorded in course of the reaction of oxocyclopentanecarboxylate (**1**) with methyl vinyl ketone catalyzed by $Fe(ClO_4)_3 \cdot 9\ H_2O$ (**3**): 0 min. (long dashed line), 30 min. (short dashed line), 60 min. (dotted dashed line), 90 min. (double dotted dashed line), 120 min. (medium dashed line) and 150 min. (short long short dashed line) after the addition of methyl vinyl keton. The solution of only $Fe(ClO_4)_3 \cdot 9\ H_2O$ (**3**) in **1** is shown as solid line.

Results of *in-operando* Raman studies

The kinetic data was plotted according to the following equations of integrated rate laws. The starting concentration $[A_0]$ was neglected in order to make the analyses more simple. Nonetheless, this procedure does not affect the conclusions about the reaction order and rate constant.

0. order: $[A] = -k_0 t + [A_0]$ $\Rightarrow$ plot: Int(v)-t

1. order: $\ln[A] = -k_1 t + \ln[A_0]$ $\Rightarrow$ plot: ln[Int(v)]-t

2. order: $\dfrac{1}{[A]} = k_2 t + \dfrac{1}{[A_0]}$ $\Rightarrow$ plot: [Int(v)]$^{-1}$-t

3. order: $\dfrac{1}{[A]^2} = k_3 t + \dfrac{1}{[A_0]^2}$ $\Rightarrow$ plot: [Int(v)]$^{-2}$-t

First inspection showed, that the data could not be fitted in total by a simple model. Therefore, the data was analyzed in two sections, i.e. in the time intervals from 0-100 min. and from 100-200 min. The results for both the ν(C=C) and ν(C=O) mode are in very good agreement in the first section (0 – 105 min.), where the R-factor strongly indicates a reaction order of two.

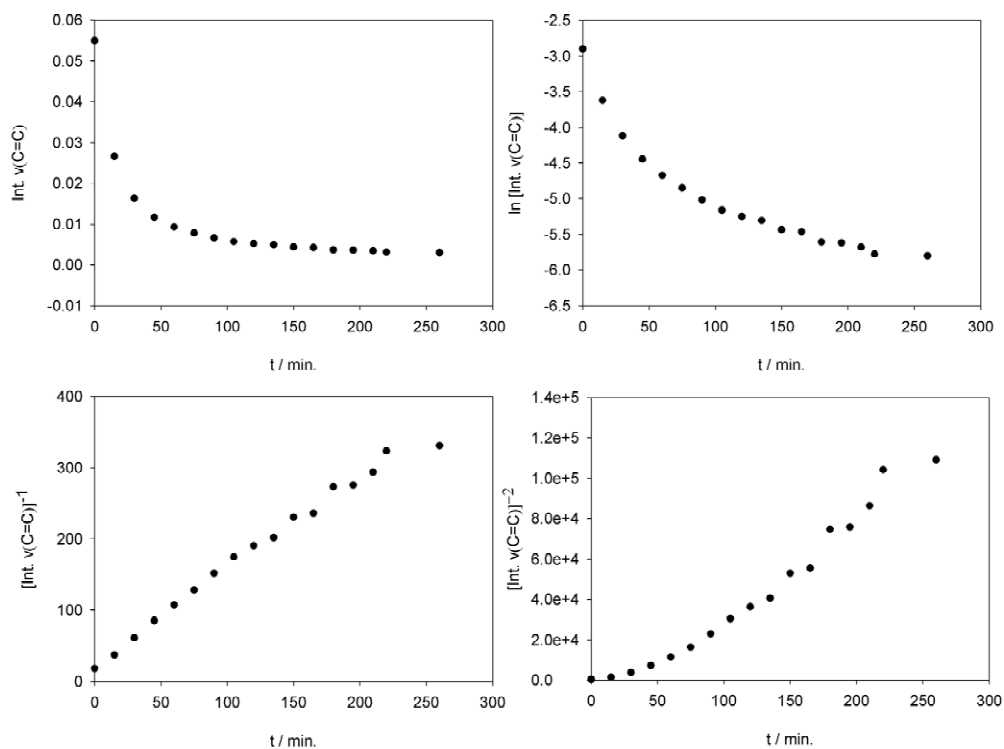**Figure SI3:** Time dependent intensities of the C=C streching band at 1619.5 cm^{-1}, plotted in accordance with the integrated velocity laws of 0. order (top left), 1. order (top right), 2. order (bottom left) and 3. order (bottom right).
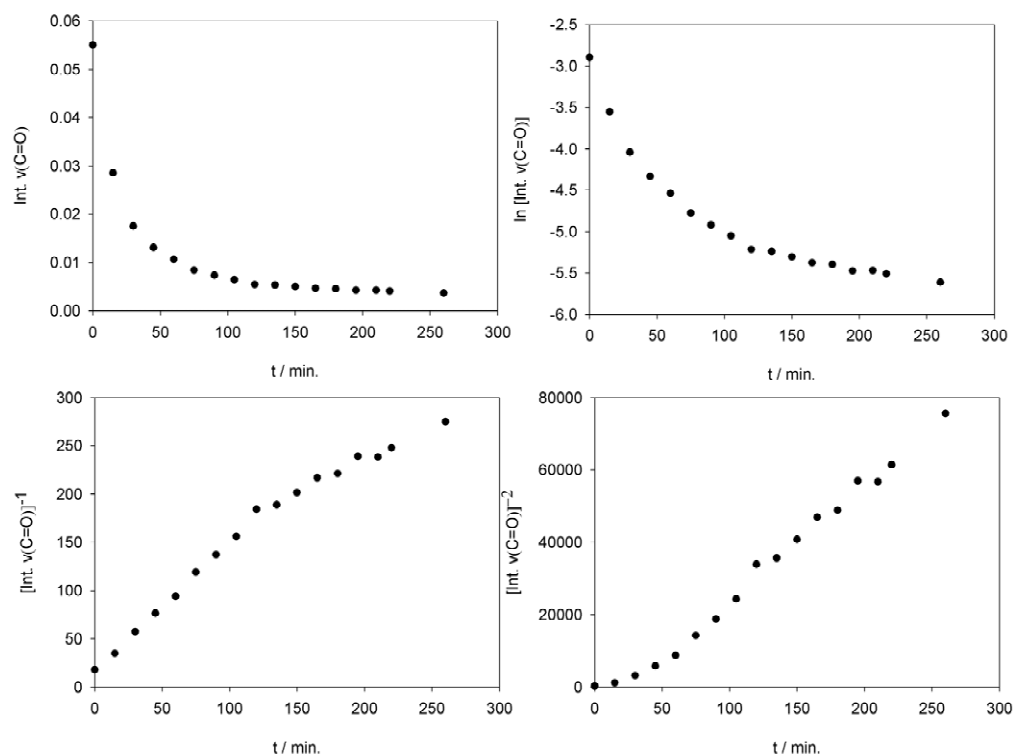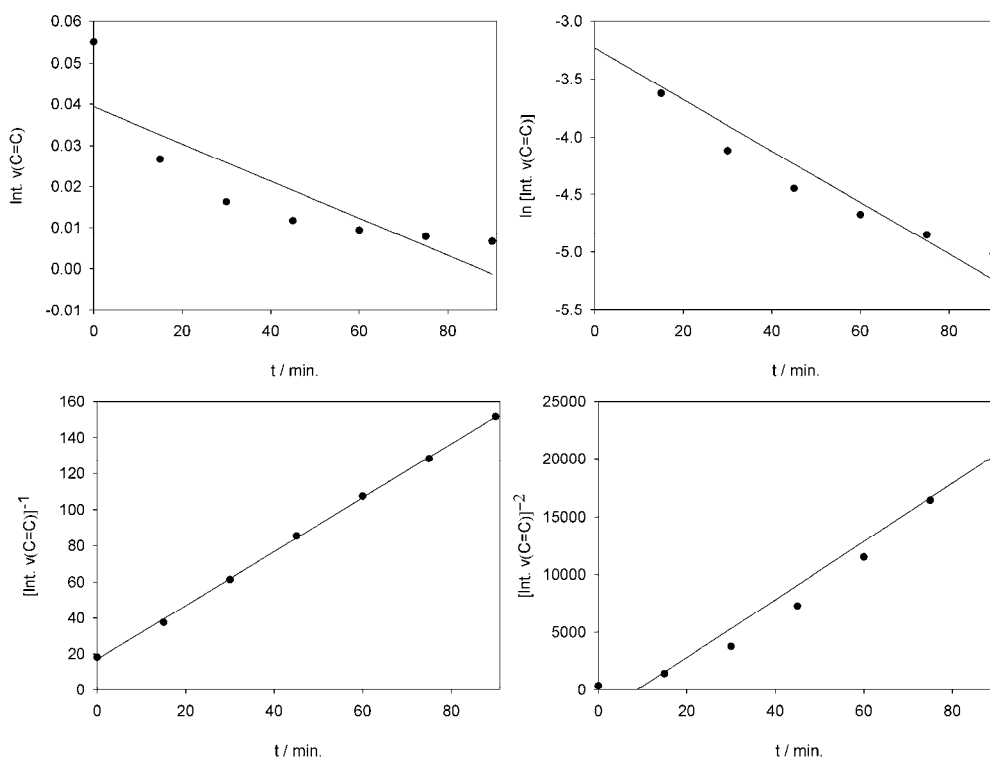
Figure SI4: Time dependent intensities of the C=O streching band at 1680.1 cm^{-1}, plotted in accordance with the integrated velocity laws of 0. order (top left), 1. order (top right), 2. order (bottom left) and 3. order (bottom right).
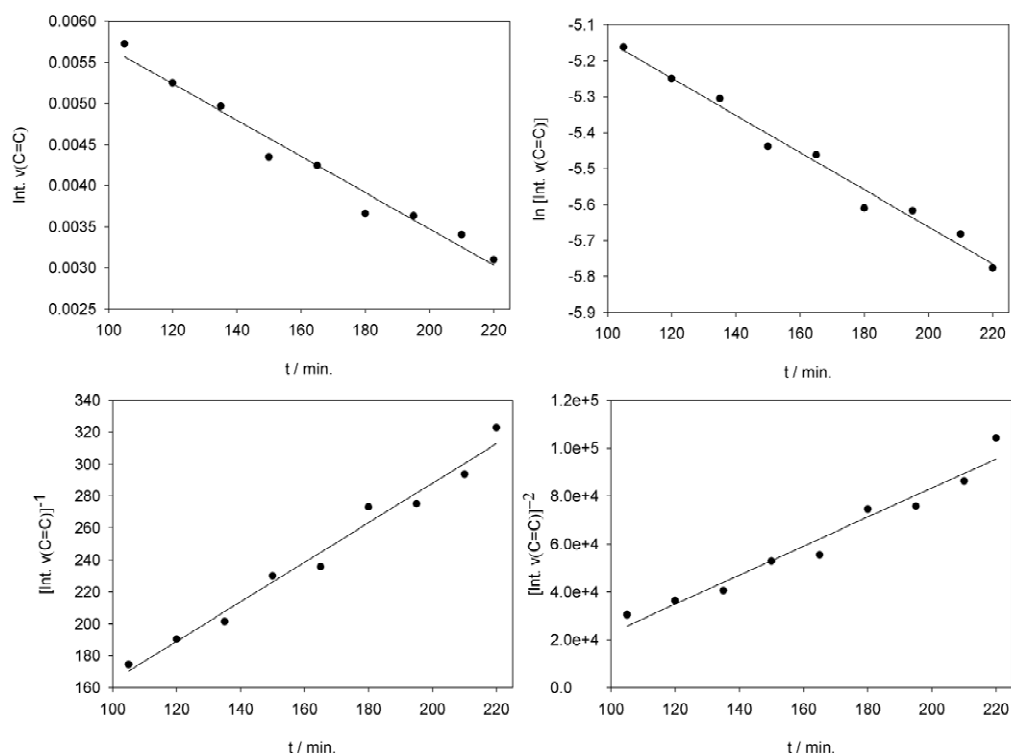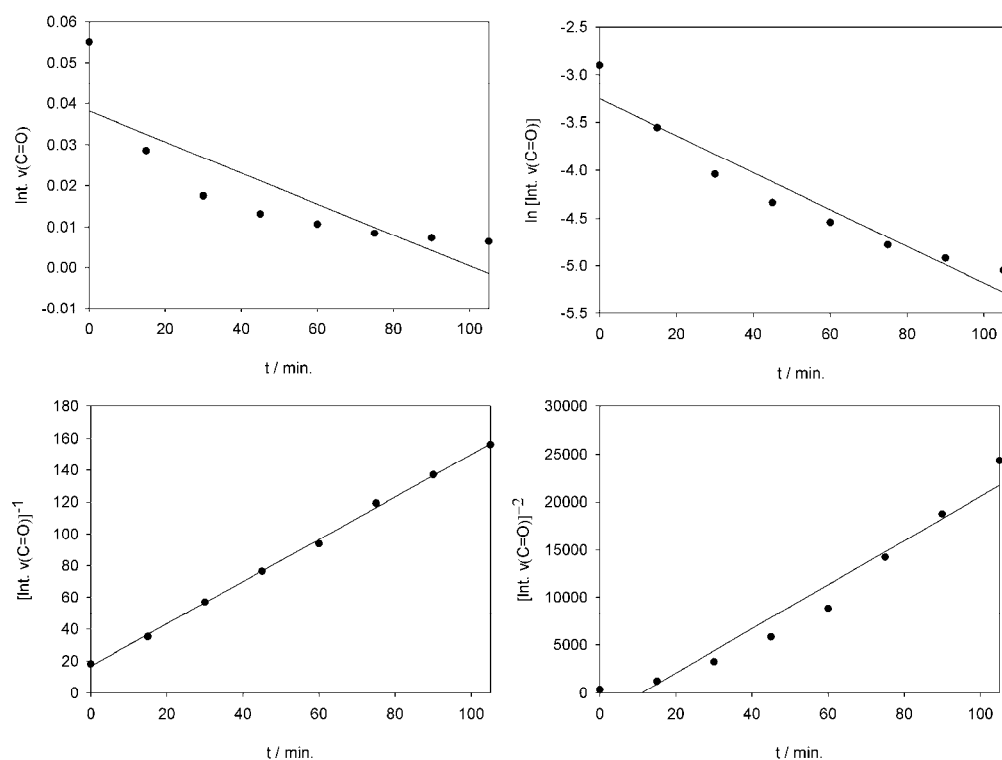
Figure SI5: Results of a linear least square fit (solid line) of the kinetic data of the $\nu(C{=}C)$ mode at 1619.5 cm^{-1} in the time intervalls 0-105 min. (four graphs on top) and 105-220 min. (four graphs at bottom). The regression functions and R-factors are given in table SI3.

Figure SI6: Results of a linear least square fit (solid line) of the kinetic data of the ν(C=O) mode at 1680.1 cm^{-1} in the time intervals 0-105 min. (four graphs on top) and 120-220 min. (four graphs at bottom). The regression functions and R-factors are given in table SI3.
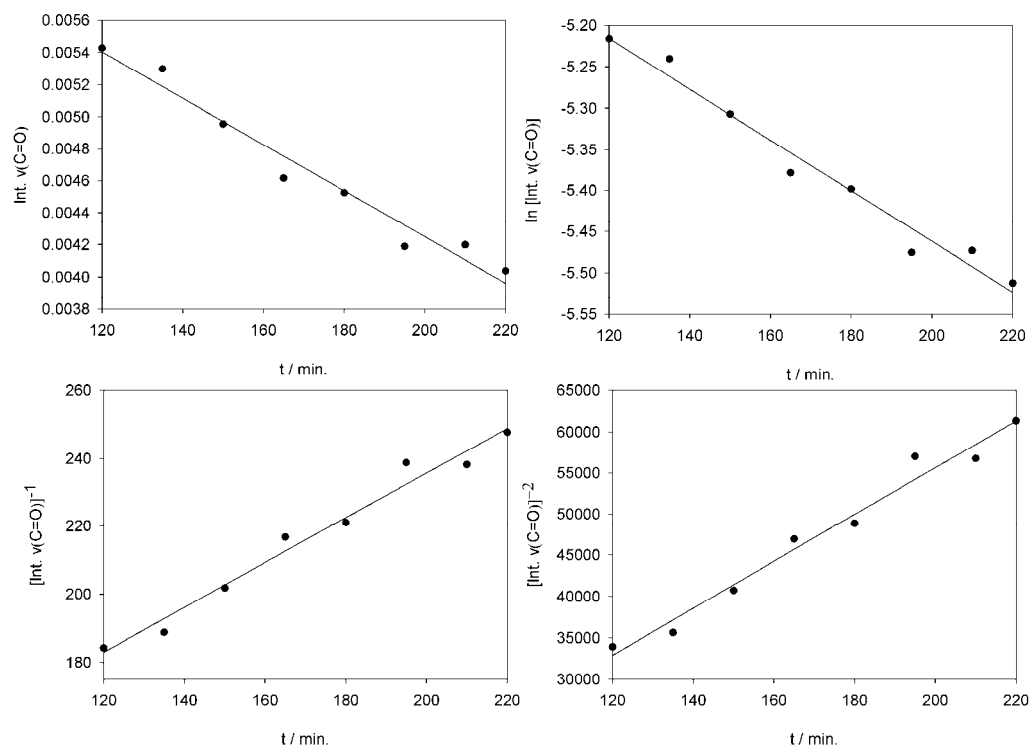
Table SI3:

Table SI3: Fit results of a linear least-square approximation of the kinetic data for the ν(C=C) and ν(C=O) streching modes.

vibration	time window	0. order	1. order	2. order	3. order
ν(C=C)	0 – 105 min.	R = 0.849 y = -0.0005x + 0.039	R = 0.960 y = -0.0223x – 3.230	**R = 0.999** y = 1.493x + 17.025	R = 0.975 y = 251.49x – 2218.06
ν(C=C)	105 – 220 min.	R = 0.986 y = -2.2·10^{-5}x + 0.008	R = 0.991 y = -0.0052x – 4.628	R = 0.989 y = 1.238x + 40.445	R = 0.979 y = 606.572x – 37926.77
ν(C=O)	0 – 105 min.	R = 0.843 y = -0.0004x + 0.038	R = 0.960 y = -0.0193x – 3.254	**R = 0.999** y = 1.332x + 16.637	R = 0.974 y = 231.347x – 2553.76
ν(C=O)	105 – 220 min.	R = 0.983 y = -1.4·10^{-5}x + 0.007	R = 0.986 y = -0.0031x – 4.847	R = 0.987 y = 0.659x + 103.810	R = 0.988 y = 284.335x – 1218.81

A three-dimensional *operando* set-up for combined XAFS, Raman and UV/Vis studies
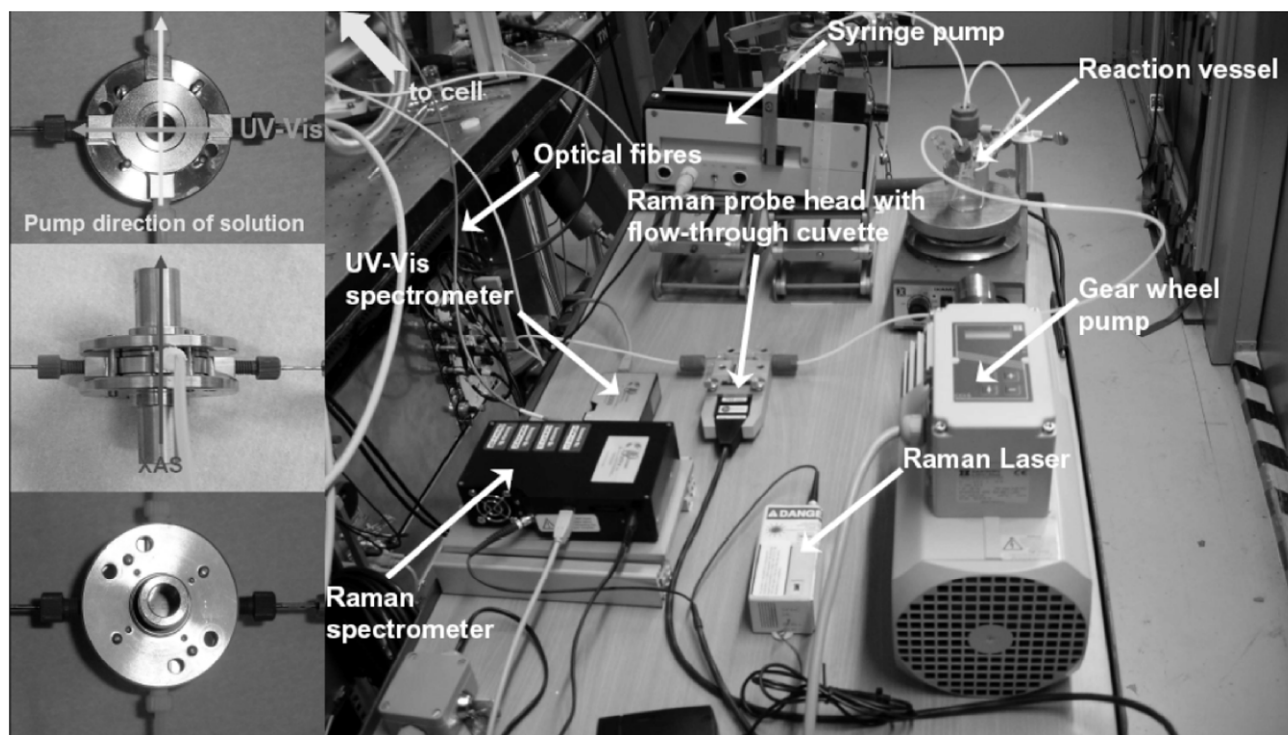
Figure SI7: Realization of the 3-dimensional spectroscopic *operando* set-up at the beamline ANKA-XAS. All important components are marked in the right picture, they are explained in the text. The left three pictures show the measurement cell, where the XAFS and UV/Vis spectra are recorded simultaneously. Details of this cell are given in the text.