Supplementary Information for:

" Development and exploration of a new methodology for the fitting and analysis of XAS data ".

Mario Ulises Delgado Jaime and Pierre Kennepohl*

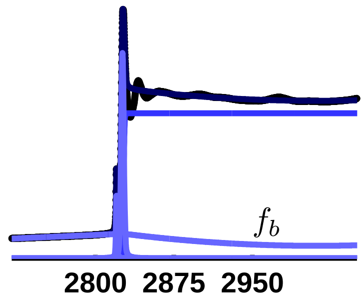
The University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada. E-mail: pierre@chem.ubc.ca

Figure S1. Evaluation function (***f***) for the fitting of the long-range data set on the Cl K-edge XAS spectrum of $(NEt_4)_2CuCl_4$.

$$f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)$$

$$C_G = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1/ln2}\right)\right]$$

$$C_L = \frac{1}{2}\arctan\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1}\right) + \frac{1}{\pi}$$



$$f_{p_1,p_2} = I_{2,3} \cdot I_1 * (G_{2,3} \cdot F_{G_{p_1,p_2}} + (1 - G_{2,3}) \cdot L_{p_1,p_2})$$

$$F_{G_{p_1,p_2}} = \sqrt{\frac{ln2}{W_{2,3}^2 \pi}} e^{-\frac{ln2(x - O_{2,3})^2}{W_{2,3}^2}}$$

$$L_{p_1,p_2} = \frac{1}{\pi} \times \frac{W_{2,3}}{(\mathrm{x} - \mathrm{O}_{2,3})^2 + W_{2,3}^2}$$

$$f_b = f_1 \frac{1}{1 + e^{\frac{(x - O_1)ln3}{W_1}}} + f_2 \frac{1}{1 + e^{\frac{(O_1 - x)ln3}{W_1}}}$$

$$f_1 = m_1 \cdot x + YI$$

$$f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)$$

$$f = f_e + f_{p_1} + f_{p_2} + f_b$$

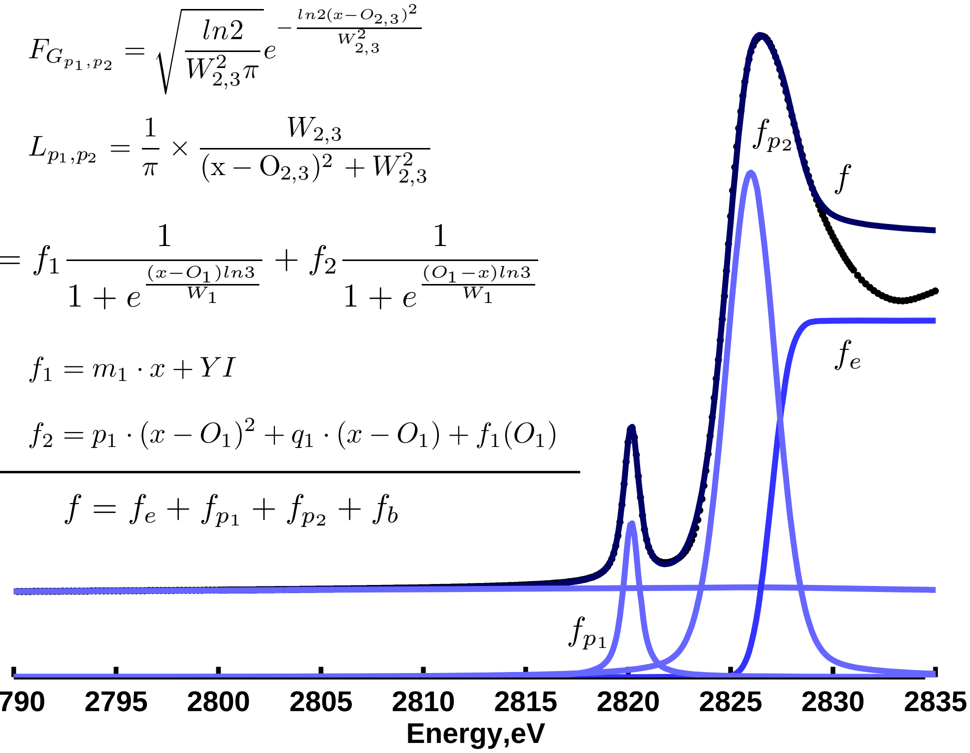
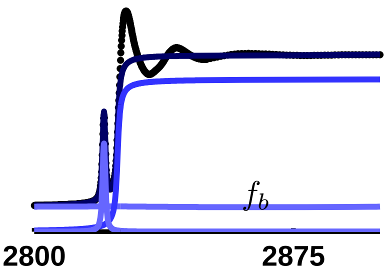


Figure S2. Evaluation function (***f***) for the fitting of the Cl K-edge XAS data sets 1-14 of $(NEt_4)_2CuCl_4$.

$$f_e = I_1(G_1 \cdot C_G + (1 - G_1) \cdot C_L)$$

$$C_G = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1/ln2}\right)\right]$$

$$C_L = \frac{1}{2}\arctan\left(\frac{\mathrm{x} - \mathrm{O}_1}{W_1}\right) + \frac{1}{\pi}$$



$$f_p = I_{2,3} \cdot I_1 * (G_{2,3} \cdot F_G + (1 - G_{2,3}) \cdot L)$$

$$F_G = \sqrt{\frac{ln2}{W_2^2 \pi}} e^{-\frac{ln2(x - O_2)^2}{W_2^2}}$$

$$L = \frac{1}{\pi} \times \frac{W_2}{(\mathrm{x} - \mathrm{O}_2)^2 + W_2^2}$$

$$f_b = f_1 \frac{1}{1 + e^{\frac{(x - O_1)ln3}{W_1}}} + f_2 \frac{1}{1 + e^{\frac{(O_1 - x)ln3}{W_1}}}$$

$$f_1 = m_1 \cdot x + YI$$

$$f_2 = p_1 \cdot (x - O_1)^2 + q_1 \cdot (x - O_1) + f_1(O_1)$$

$$f = f_e + f_m + f_b$$

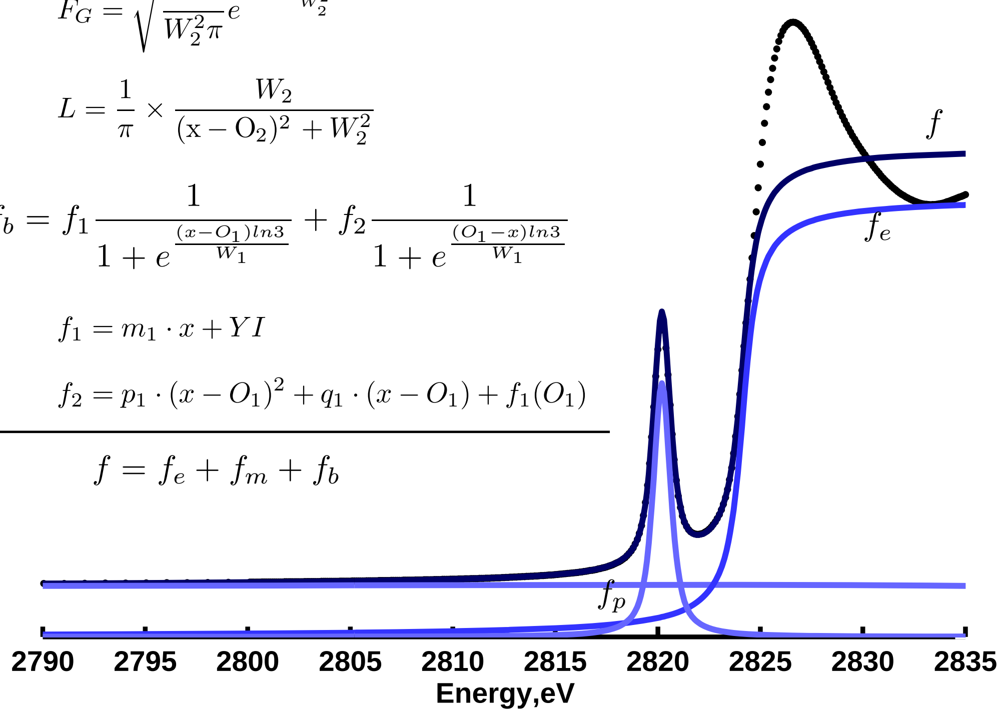


Figure S3. Excluded data (in gray) for the fitting of the Cl K-edge XAS data sets 1-14 of $(NEt_4)_2CuCl_4$.

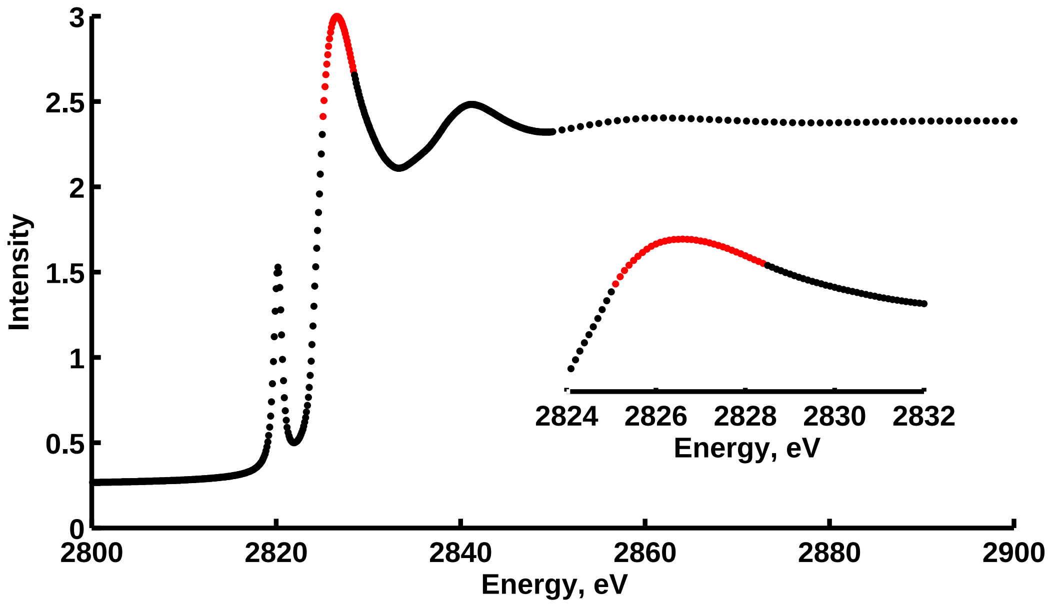


Table S4. Results for the pre-edge peak parameters from additional fit jobs on the Cl K-edge XAS data sets 1 and 3 of $(NEt_4)_2CuCl_4$.

Sample #1 50 % BN	Normalised Intensity		Energy position, eV		Width, (hwhm, eV)		Shape, % Gaussian	
	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
	0.2	1.5	2820	2821	0.1	4	0	1
Fit Job	Avg	Std	Avg	Std	Avg	Std	Avg	Std
1	0.846	0.007	2820.20	<0.01	0.508	0.006	18.8	0.9
2	0.842	0.021	2820.20	<0.01	0.507	0.005	19.0	3.4
3	0.844	0.005	2820.20	<0.01	0.508	0.006	18.8	1.1
4	0.845	0.007	2820.20	<0.01	0.508	0.007	18.9	1.1
Sample #3 50 % BN								
Fit Job	Avg	Std	Avg	Std	Avg	Std	Avg	Std
1	0.914	0.026	2820.20	<0.01	0.535	0.003	20.1	0.3
2	0.914	0.023	2820.20	<0.01	0.535	0.003	20.0	0.2
3	0.915	0.023	2820.20	<0.01	0.535	0.003	20.1	0.4
4	0.919	0.018	2820.20	<0.01	0.535	0.003	20.0	0.4

Figure S5. Comparison between the pre-edge parameters from additional fit jobs on the Cl K-edge XAS data sets 1 and 3 of $(NEt_4)_2CuCl_4$

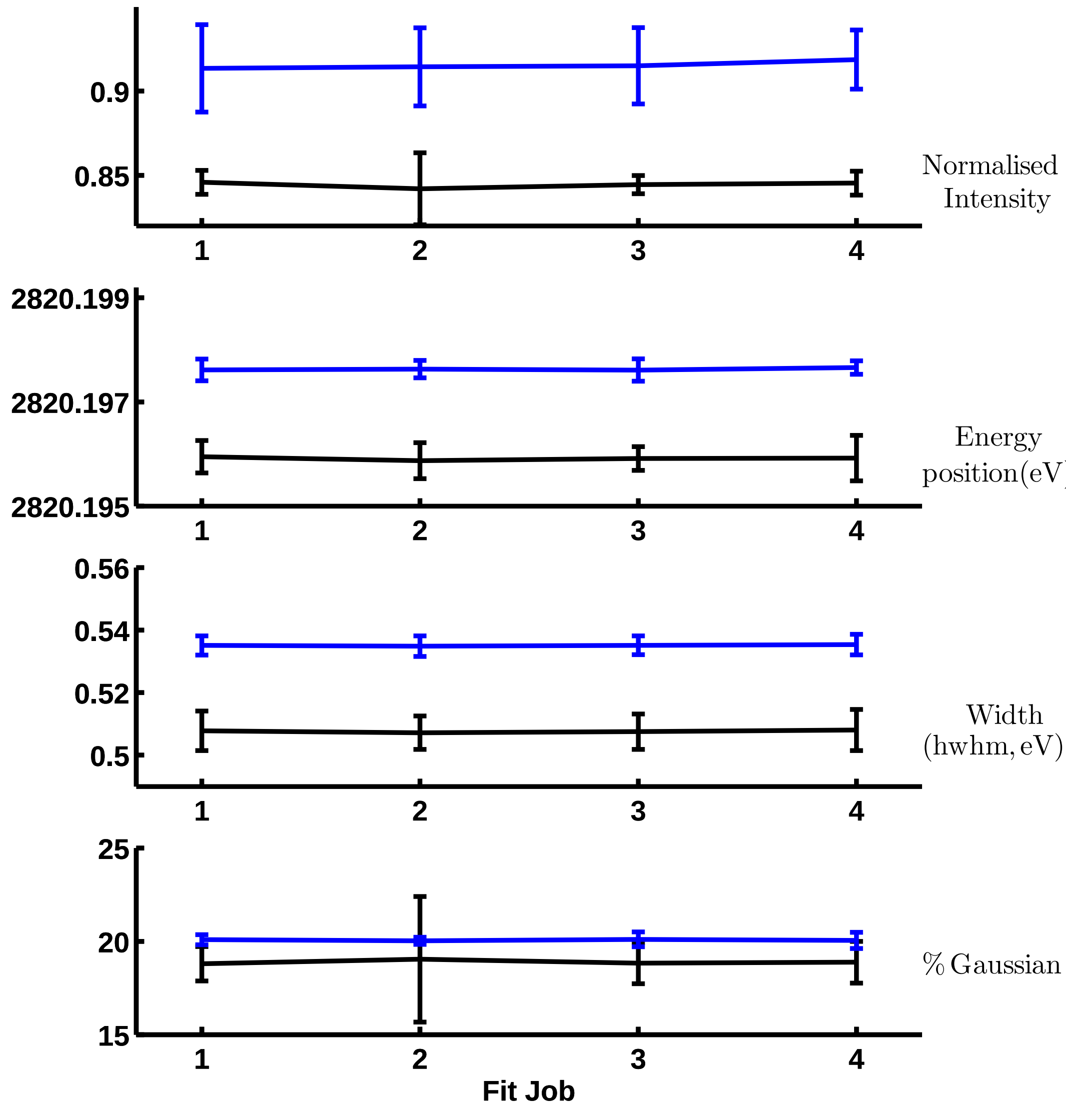


Figure S6. Variability of Background parameters m_1, YI, p_1 and q_1 in the Cl K-edge XAS data sets 1-14 of $(NEt_4)_2CuCl_4$.

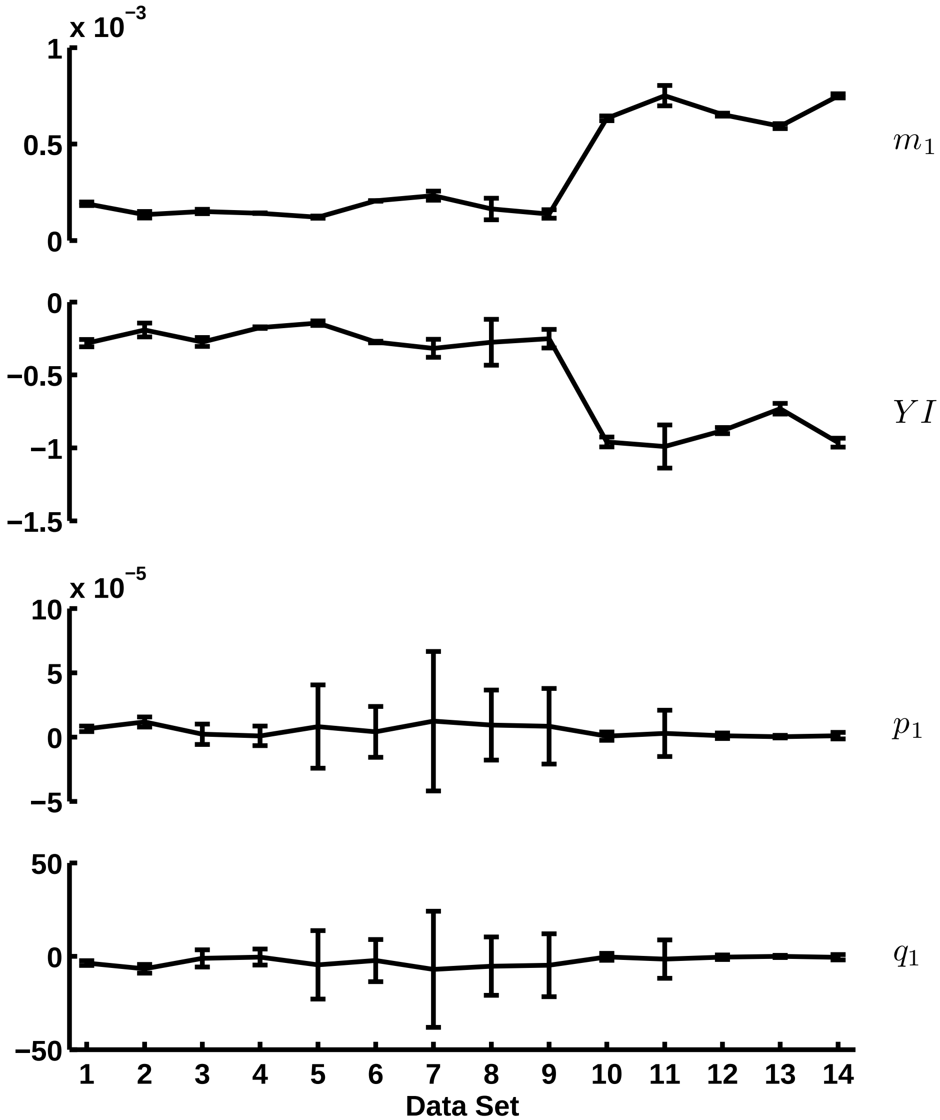
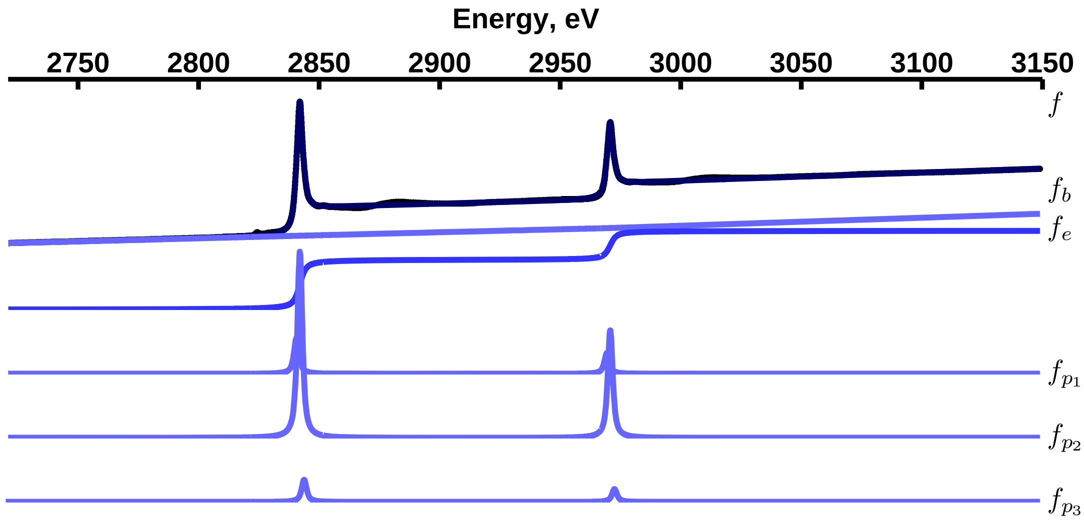


Figure S7. Initial evaluation function for the fitting of the Ru $L_{2,3}$-edges XAS spectrum of compound **1.** The same Branching ratio B_1 is used to correlate the intensity of the two edges, as well as the intensity of equivalent features in the peak functions f_{p1}-f_{p3}.



$$f_b = \frac{f_1}{1+e^{(x-O_1)/W_1}} + \frac{f_2}{\left(1+e^{(O_1-x)/W_1}\right)\left(1+e^{(x-O_2)/W_1}\right)} + \frac{f_3}{1+e^{(O_2-x)/W_1}}$$

$$f_1 = m_1 x + YI,\;\; f_2 = m_2(x-O_1)+f_1(O_1),\;\; f_3 = m_3(x-O_2)+f_2(O_2)$$

$$f_e = B_1 \cdot I_1\Big[G_1 \cdot \frac{1}{2}\Big[1+\mathrm{erf}\Big(\frac{\mathrm{x}-\mathrm{O}_1}{W_1/ln2}\Big)\Big] + (1-G_1)\cdot\Big(\frac{1}{2}\arctan\Big(\frac{\mathrm{x}-\mathrm{O}_1}{W_1}\Big)+\frac{1}{\pi}\Big)\Big]$$

$$+I_1\Big[G_1 \cdot \frac{1}{2}\Big[1+\mathrm{erf}\Big(\frac{\mathrm{x}-\mathrm{O}_2}{W_1/ln2}\Big)\Big] + (1-G_1)\cdot\Big(\frac{1}{2}\arctan\Big(\frac{\mathrm{x}-\mathrm{O}_2}{W_1}\Big)+\frac{1}{\pi}\Big)\Big]$$

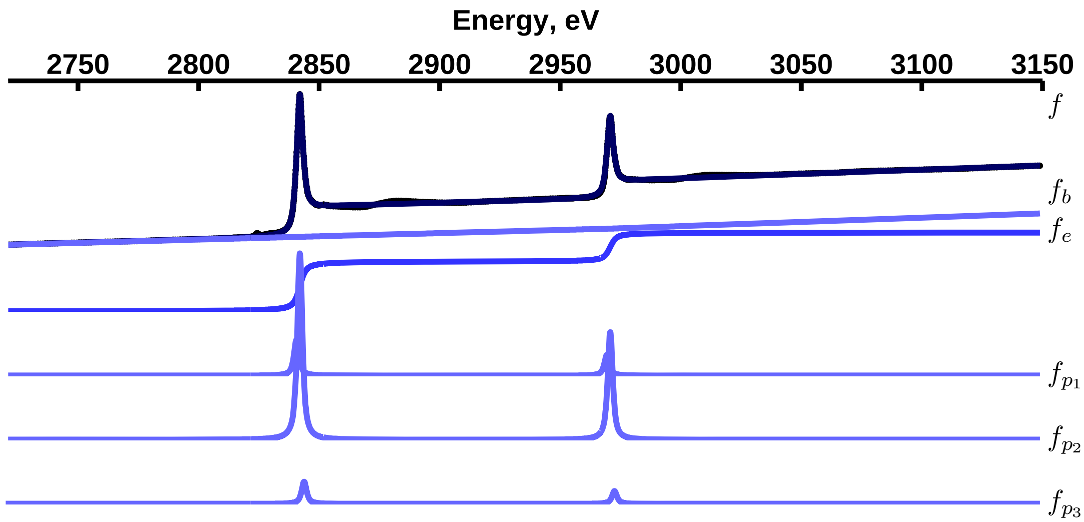
$$f_{p2} = B_1 \cdot I_2 \cdot I_1\Big[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_4)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_4)^2+W_3^2}\Big]$$

$$+I_2 \cdot I_1\Big[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_5)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_5)^2+W_3^2}\Big]$$

$$f_{p_1,p_3} = B_1 \cdot B_{2,3} \cdot I_2 \cdot I_1\Big[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_{6,7}-O_4)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_{6,7}-\mathrm{O}_4)^2+W_3^2}\Big]$$

$$+B_{2,3} \cdot I_2 \cdot I_1\Big[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_{8,9}-O_5)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_{8,9}-\mathrm{O}_5)^2+W_3^2}\Big]$$

Figure S8. Simplified evaluation function used in the fitting of the Ru $L_{2,3}$-edges XAS spectrum of compound **1**. The splitting, due to the 2p spin-orbit coupling, denoted here as W_2 is used to constrain, not only the inflection points of the two edges, but also the position of equivalent peaks in these two edges.



$$f_b = \frac{f_1}{1+e^{(x-O_1)/W_1}} + \frac{f_2}{\left(1+e^{(O_1-x)/W_1}\right)\left(1+e^{(x-O_1-W_2)/W_1}\right)} + \frac{f_3}{1+e^{(O_1+W_2-x)/W_1}}$$

$$f_1 = m_1 x + YI, \;\; f_2 = m_2(x-O_1) + f_1(O_1), \;\; f_3 = m_3(x-O_1-W_2) + f_2(O_1+W_2)$$

$$f_e = B_1 \cdot I_1\left[G_1 \cdot \frac{1}{2}\left[1+\mathrm{erf}\left(\frac{\mathrm{x}-\mathrm{O}_1}{W_1/ln2}\right)\right] + (1-G_1)\cdot\left(\frac{1}{2}\arctan\left(\frac{\mathrm{x}-\mathrm{O}_1}{W_1}\right)+\frac{1}{\pi}\right)\right]$$

$$+I_1\left[G_1 \cdot \frac{1}{2}\left[1+\mathrm{erf}\left(\frac{\mathrm{x}-\mathrm{O}_1-\mathrm{W}_2}{W_1/ln2}\right)\right] + (1-G_1)\cdot\left(\frac{1}{2}\arctan\left(\frac{\mathrm{x}-\mathrm{O}_1-\mathrm{W}_2}{W_1}\right)+\frac{1}{\pi}\right)\right]$$

$$f_{p2} = B_1 \cdot I_2 \cdot I_1\left[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_4)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_4)^2+W_3^2}\right]$$

$$+I_2 \cdot I_1\left[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_4-W_2)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_4-\mathrm{W}_2)^2+W_3^2}\right]$$

$$f_{p_1,p_3} = B_1 \cdot B_{2,3} \cdot I_2 \cdot I_1\left[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_{6,7}-O_4)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_{6,7}-\mathrm{O}_4)^2+W_3^2}\right]$$

$$+B_{2,3} \cdot I_2 \cdot I_1\left[G_2 \cdot \sqrt{\frac{ln2}{W_3^2\pi}}e^{-\frac{ln2(x-O_{6,7}-W_2-O_4)^2}{W_3^2}} + \frac{(1-G_2)}{\pi}\cdot\frac{W_3}{(\mathrm{x}-\mathrm{O}_{6,7}-\mathrm{W}_2-\mathrm{O}_4)^2+W_3^2}\right]$$