

# EXAFS characterization of the structure and stoichiometry of lanthanide-carbonate complexes in solution

M. L. Schlegel<sup>1</sup>, V. Philippini<sup>2</sup>, B. Siboulet<sup>3</sup>, P. Vitorge<sup>1</sup>, Th. Vercouter<sup>1</sup>

(1) CEA, DEN, Department of Physical Chemistry, CEN saclay, F 91 191 Gif sur Yvette, France (2) University of Nice, LRSAE, F-06108 Nice, France

(3) CEA, DEN, Department of Radiochemistry and processes; CEN Marcoule, F 30207 Bagnols-sur-Cèze, France

contact: Michel Schlegel (michel.schlegel@cea.fr)



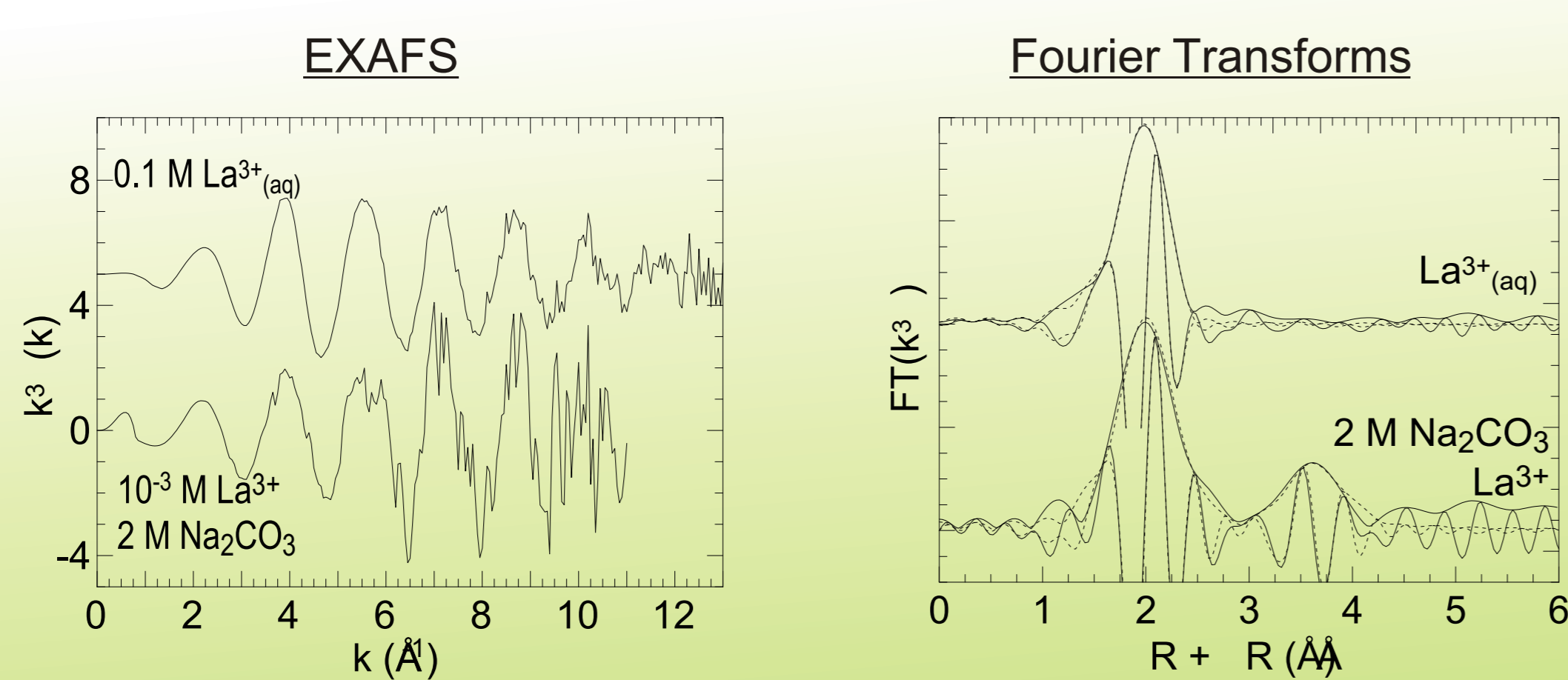
## Introduction

Trivalent actinides (An) and lanthanides (Ln) are present in high level nuclear waste. Migration of these elements in natural systems is controlled in part by complexation with solutions ligands such as (bi)carbonate, a ubiquitous complexant in clay rocks. Thus, correct prediction of Ln (and An) fate in the environment hinges on an accurate description of the molecular structure and stoichiometry of solution complexes between Ln and carbonate.

## Materials and Methods

- Solutions of 0.001 M La, Nd, Eu and Lu carbonate freshly prepared by mixing 2 M Na<sub>2</sub>CO<sub>3</sub> and an aliquot of Ln stock solutions were filtered and loaded in polycarbonate cells fitted with Mylar windows. aqueous references (0.1 M in acidified water) were also prepared and loaded in cells.
- L3-edge EXAFS spectra were recorded in fluorescence detection mode on XAS and INE beamlines (ANKA, Karlsruhe).
- K-edge EXAFS spectra were recorded in transmission mode on BM 29 beamline (ESRF, Grenoble)
- EXAFS data were reduced, and analyzed using standard procedures. Multiple scattering (MS) analyses were performed using FEFF8.

## Lanthanum (K-edge)

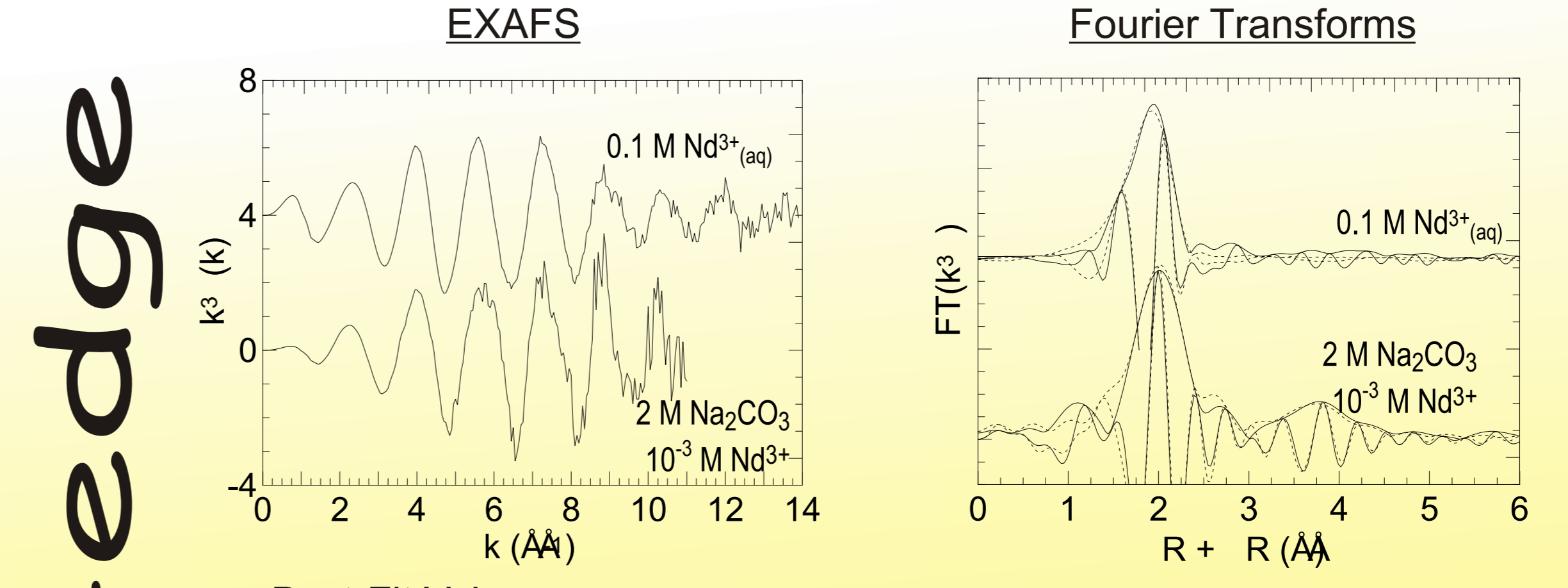


### Best-Fit Values

Samples	FT range (Å)	Fit range (Å)	La-O <sub>1</sub> shell		La-O <sub>2</sub> shell		La-C shell		La-O <sub>dist</sub> shell		E <sub>0</sub> (eV)	R <sub>p</sub>			
			R <sub>La-O1</sub> (Å)	N <sub>O1</sub> (A)	R <sub>La-O2</sub> (Å)	N <sub>O2</sub> (A)	R <sub>La-C</sub> (Å)	N <sub>C</sub> (A)	R <sub>La-Odist</sub> (Å)	N <sub>Odist</sub> (A)					
La <sup>3+</sup> (aq)	2.5-12	1.2-2.4	2.536	0.6	2.664	3	0.06				9.8	1.1x10 <sup>-4</sup>			
La <sup>3+</sup> in 2 M Na <sub>2</sub> CO <sub>3</sub>	2.5-11	1.35-4.15	2.55	8(2)	0.07			2.96	4.7(7)	0.07	4.25	4.7(7)	0.07	10	0.016

No increase in d(La-O) for the first shell from aqueous to carbonated ion d(La-C) and d(La-O<sub>dist</sub>) consistent with bidentate complexation

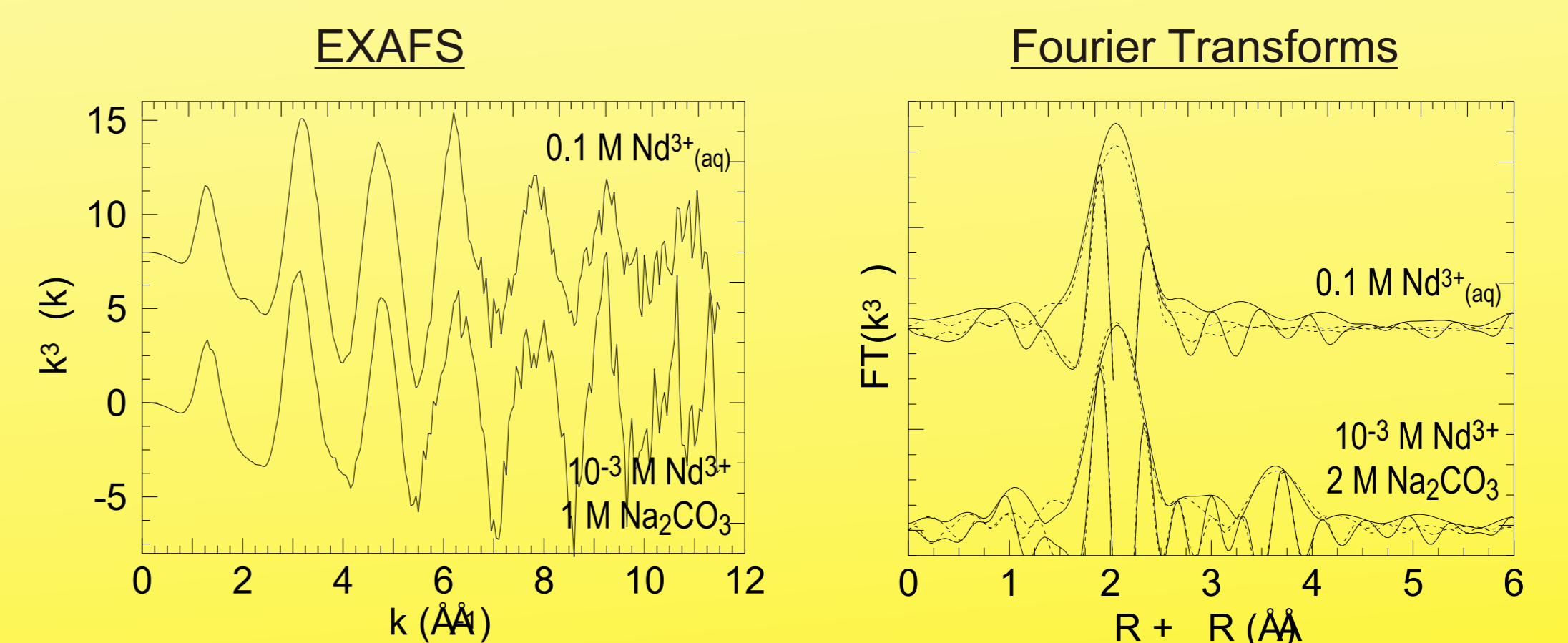
## Neodymium (K-edge and L3-edge)



### Best-Fit Values

Samples	FT range (Å)	Fit range (Å)	Nd-O <sub>1</sub> shell		Nd-O <sub>2</sub> shell		Nd-C shell		Nd-O <sub>dist</sub> shell		E <sub>0</sub> (eV)	R <sub>p</sub>			
			R <sub>Nd-O1</sub> (Å)	N <sub>O1</sub> (A)	R <sub>Nd-O2</sub> (Å)	N <sub>O2</sub> (A)	R <sub>Nd-C</sub> (Å)	N <sub>C</sub> (A)	R <sub>Nd-Odist</sub> (Å)	N <sub>Odist</sub> (A)					
Nd <sup>3+</sup> (aq)	2.8-14.2	1.3-2.35	2.46	6	0.08	2.52	3	0.08				3.6	0.025		
Nd <sup>3+</sup> in 2 M Na <sub>2</sub> CO <sub>3</sub>	3.0-10.5	1.45-4.2	2.56	8.4	0.07			2.91	3.7	0.07	4.31	3.7	0.07	6.9	0.006

L3-edge K-edge

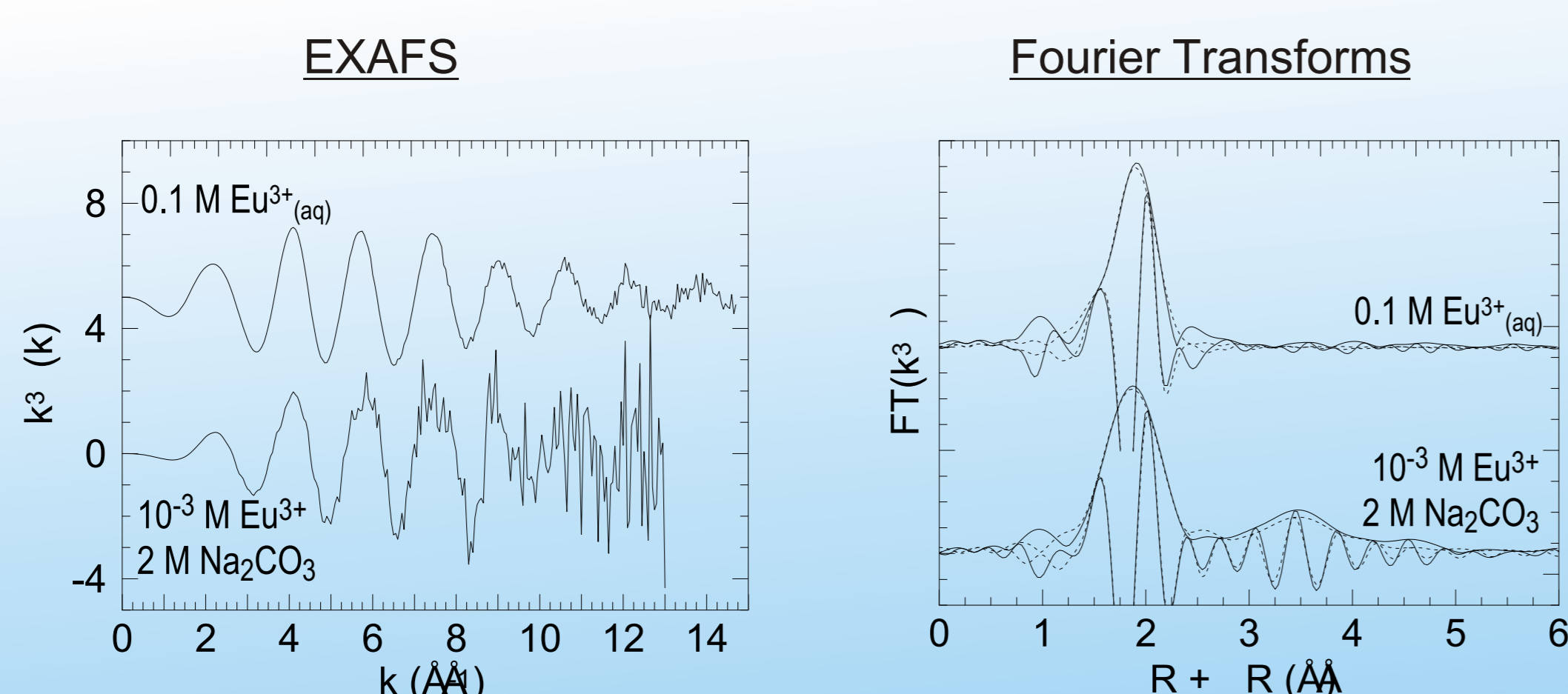


### Best-Fit Values

Samples	FT range (Å)	Fit range (Å)	Nd-O <sub>1</sub> shell		Nd-O <sub>2</sub> shell		Nd-C shell		Nd-O <sub>dist</sub> shell		E <sub>0</sub> (eV)	R <sub>p</sub>			
			R <sub>Nd-O1</sub> (Å)	N <sub>O1</sub> (A)	R <sub>Nd-O2</sub> (Å)	N <sub>O2</sub> (A)	R <sub>Nd-C</sub> (Å)	N <sub>C</sub> (A)	R <sub>Nd-Odist</sub> (Å)	N <sub>Odist</sub> (A)					
Nd <sup>3+</sup> (aq)	2.55-10.5	1.2-2.55	2.46(4)	6	0.05	2.61	3	0.05				8.0	0.006		
Nd <sup>3+</sup> in 2 M Na <sub>2</sub> CO <sub>3</sub>	2.5-11	1.35-4.15	2.50	8.2	0.06			2.86	3.3	0.06	4.17	3.3	0.06	13.7	0.019

Fits at K- and L3-edges support the same structural model but are not consistent Very long interatomic distances for the carbonated Nd<sup>3+</sup> at the K-edge: decreased accuracy due to the limited spectral range?

## Europium (K-edge)

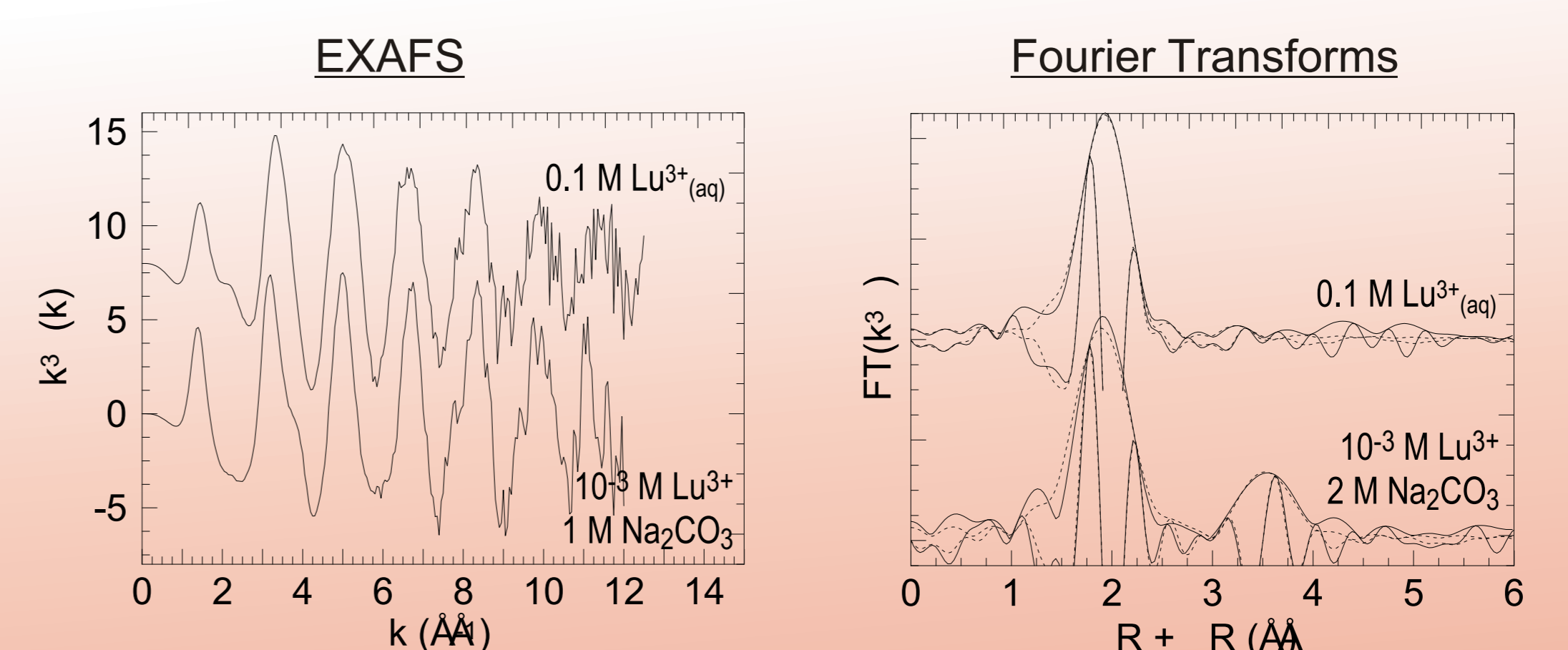


### Best-Fit Values

Samples	FT range (Å)	Fit range (Å)	Eu-O <sub>1</sub> shell		Eu-O <sub>2</sub> shell		Eu-C shell		Eu-O <sub>dist</sub> shell		E <sub>0</sub> (eV)	R <sub>p</sub>			
			R <sub>Eu-O1</sub> (Å)	N <sub>O1</sub> (A)	R <sub>Eu-O2</sub> (Å)	N <sub>O2</sub> (A)	R <sub>Eu-C</sub> (Å)	N <sub>C</sub> (A)	R <sub>Eu-Odist</sub> (Å)	N <sub>Odist</sub> (A)					
Eu <sup>3+</sup> (aq)	2.7-14.3	1.2-2.3	2.40	8.2	0.06	2.52	4.1	0.06				10.3	0.002		
Eu <sup>3+</sup> in 2 M Na <sub>2</sub> CO <sub>3</sub>	2.5-10	1.2-4	2.45	9.2	0.08			2.77	4	0.07	4.11	4	0.07	13.9	0.009

No increase in d(Eu-O) for the first shell from aqueous to carbonated ion d(La-C) and d(Eu-O<sub>dist</sub>) consistent with bidentate complexation

## Lutetium (L3-edge)



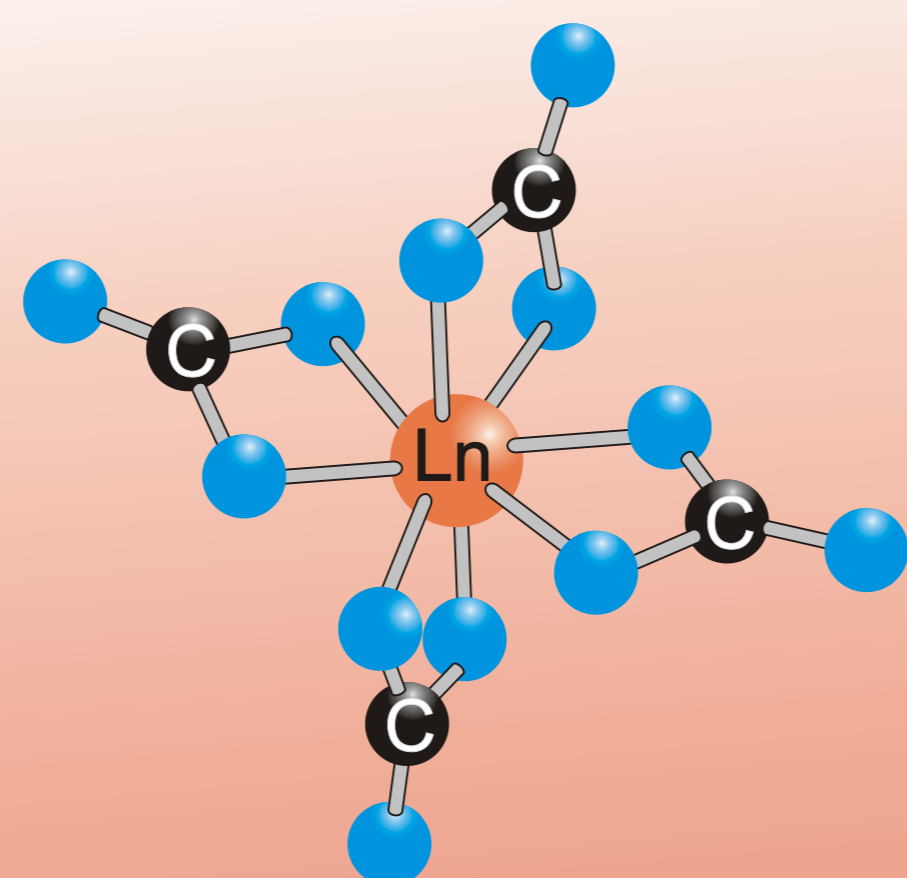
### Best-Fit Values

Samples	FT range (Å)	Fit range (Å)	Lu-O <sub>1</sub> shell		Lu-C shell		Lu-O <sub>dist</sub> shell		E <sub>0</sub> (eV)	R <sub>p</sub>			
			R <sub>Lu-O1</sub> (Å)	N <sub>O1</sub> (A)	R <sub>Lu-C</sub> (Å)	N <sub>C</sub> (A)	R <sub>Lu-Odist</sub> (Å)	N <sub>Odist</sub> (A)					
Lu <sup>3+</sup> (aq)	2.5-12	1.2-2.4	2.32	8.2	0.08						-1.6	0.003	
Lu <sup>3+</sup> in 2 M Na <sub>2</sub> CO <sub>3</sub>	2.8-10.4	1.34-4	2.31	7.4	0.08	2.76	3.6	0.08	4.00	3.6	0.08	-5.8	0.008

No increase in d(Lu-O) for the first shell from aqueous to carbonated ion d(Lu-C) and d(Lu-O<sub>dist</sub>) consistent with bidentate complexation

## Conclusions

Contraction in d(Ln-O) distance for the first shell follows the expected order: d(La-O) > d(Nd-O) > d(Eu-O) > d(Lu-O). For all probed systems, a correct fit is obtained assuming 3 to 4 carbonate groups forming bidentate complexes with Ln. Strong contribution from O<sub>dist</sub> due to MS focusing effects. No evidence for monodentate complex (marginal importance?).



Model of Ln(CO<sub>3</sub>)<sub>4</sub><sup>2-</sup> complex

**Acknowledgements.** Supports from DDIN/HAVL/CHSOL, from ANKA-INE (B. Brendebach), XAS (S. Mangold) and from ESRF-BM29 (M. Vaccari) are acknowledged. ESRF and ANKA are thanked for provision of beamtime.