Supporting Informations: On the Possible Existence of a Monovalent Coordination for Nitrogen Atoms in $Li_xPO_yN_z$ Solid Electrolyte: Modelling of XPS and Raman Spectra

Émilie Guille, Germain Vallverdu,* Yann Tison, Didier Bégué, and Isabelle Baraille

Université de Pau et des Pays de l'Adour, IPREM - ECP CNRS UMR 5254, Technopole Hélioparc, 2 av. du Président Pierre Angot, 64053 Pau cedex 9, France

E-mail: germain.vallverdu@univ-pau.fr

*To whom correspondence should be addressed

Contents

1 Computed eigenenergies and experimental binding energies

Computed eigenenergies (eV) associated with the periodic structures investigated throughout this study.

System	ϵ_i^{calc} (O1s, O1)	ϵ_i^{calc} (O1s, O2)	ϵ_i^{calc} (N1s, N2)
P_2O_5	-536.76	-538.34	
P_3N_5			-400.87
KH_2PO_4	-538.09		
Mono. $Li_xPO_yN_z$	-536.94		-400.47
Dim. $Li_xPO_yN_z$	-536.73		-402.26
Chain $Li_xPO_yN_z$	-537.36	-539.44	-403.08
M1	-536.56		-401.41
M2	-537.29	-536.61	-402.57
M3	-535.86		-400.96
M4	-536.18		-402.56

Experimental binding energies ($BE_{i,exp}^{ref}$, in eV) associated with the three reference materials

	P2p	O1s (O1)	O1s (O2)	N1s (N2)
P_2O_5	135.6	532.6	534.5	
P_3N_5 [1]	133.0			397.0
KH_2PO_4	133.2	532.4		

2 Structural data

2.1 Li_xPO_y systems

Structural parameters and size of the supercells considered for core-level binding energy computations on both Li_xPO_y and Li_2PO_2N structures.

System	Space group	Parameters (Å)	Distances (Å)	Supercell
γ-Li_3PO_4	Pmnb	$a = 6.173$ $b = 10.610$ $c = 4.990$ $\alpha = \beta = \gamma = 90.0\,^\circ$	P–O1=1.56 Li–O1=1.95–2.05	2×1×2
$Li_4P_2O_7$	P-1	$a = 8.624$ $b = 7.212$ $c = 5.228$ $\alpha = 111.54\,^\circ$ $\beta = 89.99\,^\circ$ $\gamma = 103.07\,^\circ$	P–O1=1.52–1.54 P–O2=1.65 Li–O1=1.93–2.07	2×2×2
$LiPO_3$	P2/n	$a = 13.314$ $b = 5.491$ $c = 16.739$ $\alpha = \gamma = 90.0\,^\circ$ $\beta = 99.0\,^\circ$	P–O1=1.50–1.51 P–O2=1.62–1.64 Li–O1=1.92–2.04	1×2×1

2.2 Original periodic models

Structural parameters and size of the supercells considered for core-level binding energy computations on both Li_xPO_y and Li_2PO_2N structures.

	Cell parameters	P–O1	P–N(i)	Li–O1	Li–N(i)	Supercell
M1 (i=2)	$a = 8.93$ $b = 10.28$ $c = 4.86$ $\alpha = 88.47$ $\beta = 88.93$ $\gamma = 92.39$	1.52–1.56	1.63–1.65	1.78–2.08	2.00	2×1×2
M2 (i=3)	$a = 9.09$ $b = 10.42$ $c = 7.35$ $\alpha = \beta = \gamma = 90.0$	1.54–1.57	1.71–1.75	1.84–2.14	2.04	2×1×2
M4 (i=2,1)	$a = 8.93$ $b = 10.28$ $c = 4.86$ $\alpha = 88.47$ $\beta = 88.93$ $\gamma = 92.39$	1.52–1.57	1.53 1.64–1.65	1.82–2.05	1.77–2.44	2×1×2
M5 (i=2)	$a = 9.54$ $b = 10.93$ $c = 7.71$ $\alpha = \beta = \gamma = 90.0$	1.55–1.58	1.47–1.57	1.98–2.39	1.59–2.04	2×1×2

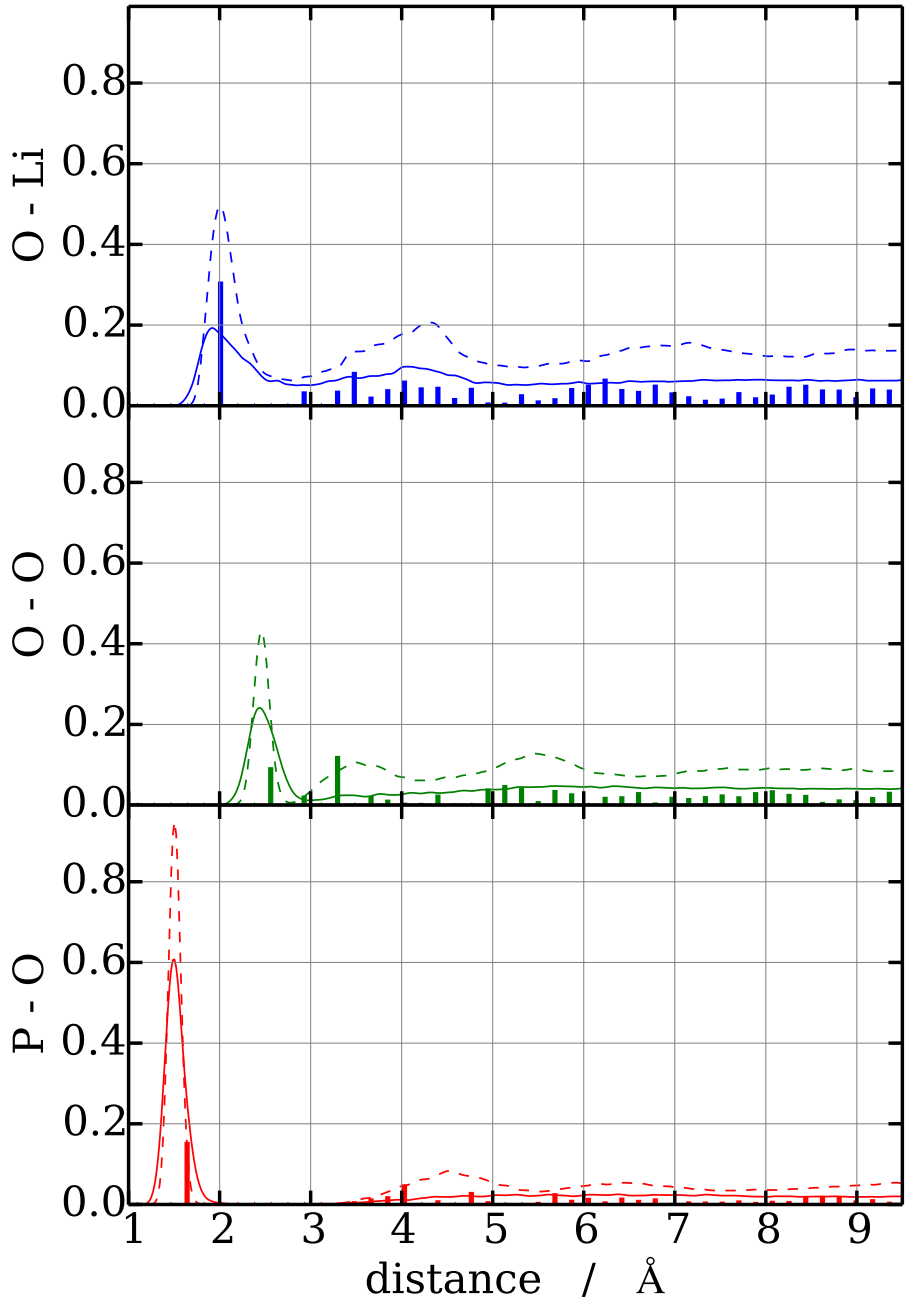
3 Forcefield for MD simulations

Interatomic parameters used in the two-body Buckingham term[2,3]

$i-j$ interaction	A_{ij} (eV)	ρ_{ij} (Å)
Li-Li	206.43	0.0083
Li-O	15900.42	0.16
P-P	10.91	0.001
P-O	900.57	0.225
O-O	3000.43	0.25
Atom i	Z_i	
Li	0.40e	
P	2.00e	
O	-0.80e	

4 Radial distribution functions

Radial distribution functions of the heated structure at 1000K (solid line), the cooled structure at 200K (dashed line) and of the crystal structure (vertical lines) in the case Li_3PO_4.



5 Accuracy of Raman frequencies calculations

Evaluation, on Raman frequencies, of both the DFT (PBE vs hybrid B3LYP) and the basis set effects (double zeta Pople vs Sadlej VTZ). Computations were done on cluster C4.

PBE/6-31G*	PBE/Sadlej VTZ	B3LYP/6-31G*	B3LYP/Sadlej VTZ
1156–1111	1171–1121	1215–1136	1198-1152
980	962	983	966
815–787	792–773	842–794	855–831
686	691	691	692
760–641	669–626	658–605	674-618

Evaluation, on Raman ferquencies, of the functional (PBE vs hybrid B3LYP), the basis set effects (double zeta Pople vs Dunning VTZ) and anharmonic corrections (values in parenthesis). Computations were done on cluster C3. (s) strong, (m) medium, (w) weak, (vw) very weak.

PBE 6-31G*	PBE cc-pVTZ	B3LYP 6-31G*	B3LYP cc-pVTZ	B3LYP (aug)-cc-pVTZ	Intensity
1082 (-19)	1082	1116	1110	1113	(w)
1040 (-30)	1046	1088	1094	1096	(s)
1015 (-21)	1013	1049	1057	1057	(m)
895 (-15)	897	904	909	916	(vw)
859 (-19)	858	883	886	888	(w)
763 (-19)	775	761	752	751	(vw)
682 (-13)	682	685	680	682	(w)
666 (-8)	659	642	639	639	(vw)
523 (-9)	518	542	537	542	(w)

6 Simulated Raman spectra

Considering Ci aggregates, the raman spectra were weighted using :

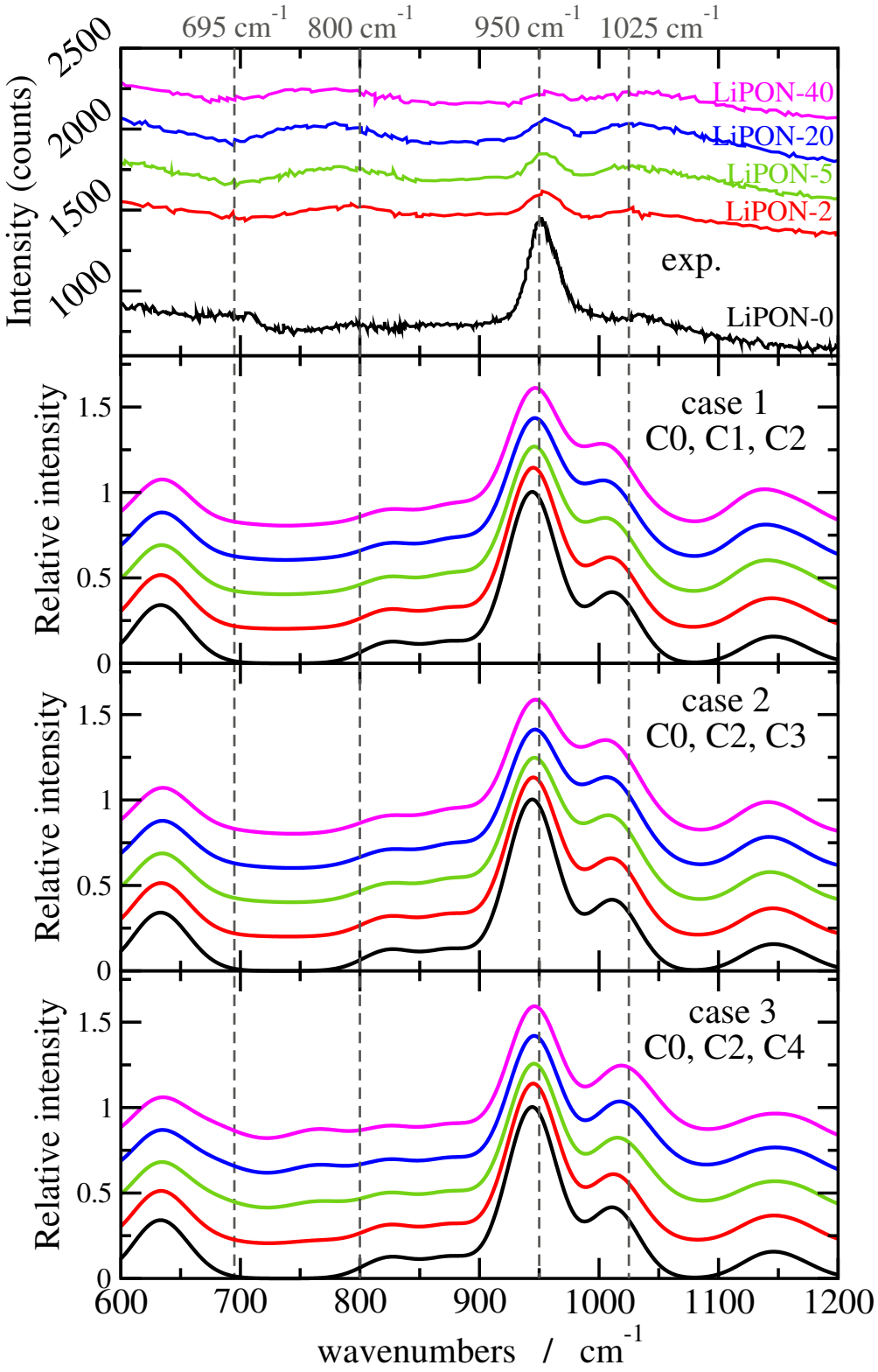
$$S(\sigma) = \sum_i \alpha_i S_{C_i}(\sigma)$$

Where α_i are given in the following table and come from the work of Fleutot et al.[4] and $S_{C_i}(\sigma)$ are the computed raman spectra.

Weighting applied to simulated raman spectra. Case 1 : i=1, j=2, Case 2 i=1, j=3 and Case 3 i=4, j=2.

Experimental material	Chemical composition	Simulation
LiPON-0	$Li_{4.4}PO_{4.3}$	C0 (100%)
LiPON-2	$Li_{4.0}PO_{3.9}N_{0.4}$	C0 (89.7%), Ci (4.6%), Cj (5.7%)
LiPON-5	$Li_{3.7}PO_{3.4}N_{0.7}$	C0 (78.6%), Ci (12.0%), Cj (9.4%)
LiPON-20	$Li_{3.4}PO_{3.1}N_{0.9}$	C0 (74.2%), Ci (15.5%), Cj (10.3%)
LiPON-40	$Li_{3.2}PO_{3.0}N_{1.0}$	C0 (71.0%), Ci (18.0%), Cj (11.0%)

The following figures present all simulated spectra



References

(1) Vepřek, S.; Iqbal, Z.; Brunner, J.; Schärli, M. *Philosophical Magazine Part B* **1981**, *43*, 527–547.

(2) Prasada Rao, R.; Seshasayee, M. *Solid State Communications* **2004**, *131*, 537–542.

(3) Prasada Rao, R.; Tho, T. D.; Adams, S. *Journal of Power Sources* **2009**, *189*, 385–390.

(4) Fleutot, B.; Pecquenard, B.; Martinez, H.; Letellier, M.; Levasseur, A. *Solid State Ionics* **2011**, *186*, 29–36.