

# An original empirical method for simulating $V$ $L_{2,3}$ edges: the example of $KVPO_4$ and $KVOPO_4$ cathode materials

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## Supplementary information

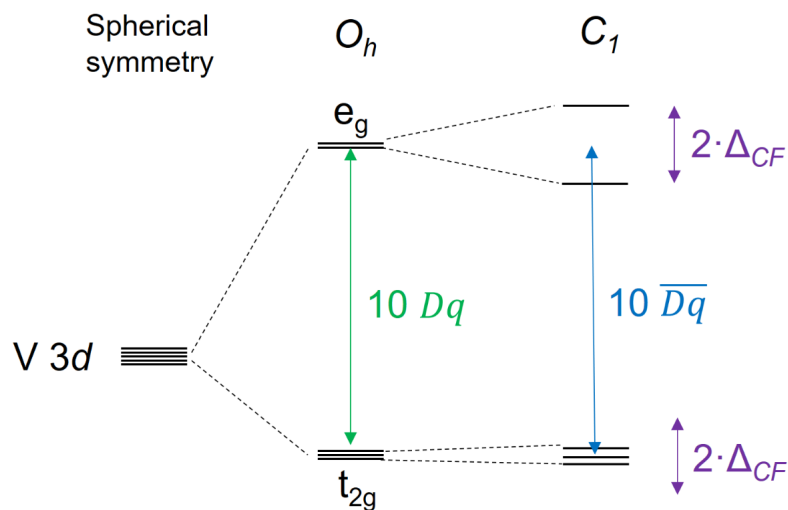


Figure S 1: Orbital splitting in  $O_h$  and  $C_1$  symmetries and corresponding crystal field parameters.

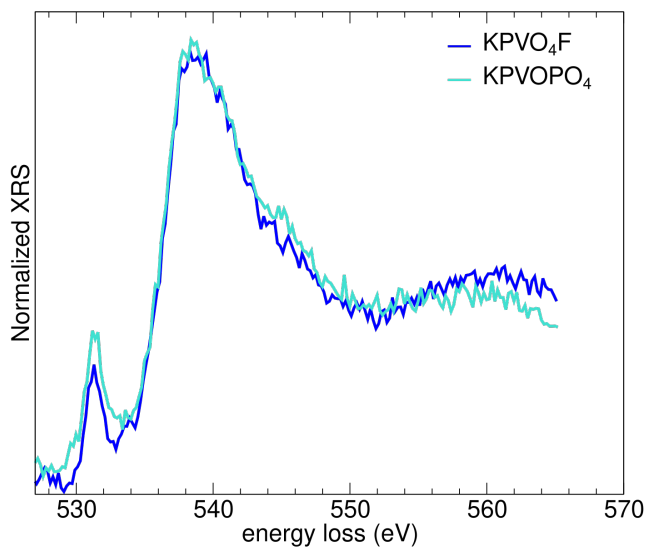


Figure S 2: Normalized Oxygen  $K$ -edge of  $KVOPO_4$  and  $KVPO_4F$ .

Figure S2 shows the normalized O  $K$ -edge of  $KVOPO_4$  and  $KVPO_4F$ . It is worth noticing that, irrespective of the different chemical composition of the samples, the O  $K$  edges spectra are quite similar. This evidences that the possible electronic modification induced by

the presence of fluoride ligands are negligible in the whole structure. On the other hand one has to consider that oxygen is bonded to different cations in the structure. So the XRS spectrum averages all the different K-, V- and P-oxygen environments in the structure. Accordingly, the occurring electronic modifications are spread out resulting in negligible electronic modifications. Moreover, most of the signal (80%) comes from oxygen atoms belonging to phosphate group in  $\text{KVOPO}_4$  (100% for  $\text{KVPO}_4\text{F}$ ).

As already described, the crystal structure of  $\text{KVPO}_4\text{F}$  is made up of undulating chains of  $\text{VO}_4\text{F}_2$  octahedra with an alternating *cis* or *trans* arrangement of  $\text{F}^-$ , the latter ion being corner shared. The chains are linked together by  $\text{PO}_4$  groups. The structure of the  $\text{KVOPO}_4$  is quite similar and also characterized by the alternating  $\text{V}(1)\text{O}_6$  and  $\text{V}(2)\text{O}_6$  sites with four oxygen atoms belonging to phosphate groups and two bridging the chains. In order to simplify the calculation and to overcome the presence of the  $\text{K}^+$  cations, whose positions is not perfectly defined due to site splitting,<sup>1,2</sup> we have focused the simulation on the main representative units block necessary to build up the whole structure. This corresponds to the chain formed by corner-sharing  $\text{VO}_4\text{X}_2$  ( $\text{X} = \text{O}, \text{F}$ ) octahedra connected together with two phosphate groups (see Figure S3 ). These block units have been obtained from the VASP relaxed structures reported above. The same CIF files have been used to calculate the V  $L_{2,3}$ -edges. To take the structural environment into account, the XRS spectrum of this molecular-like structure has to be calculated in a constant potential which also accounts for the presence of positive charges. In the calculations, a value of *dilatorb* equal to 0.1 has been set. Even though a quite simplified structural model is used, the existence of structurally different oxygens is evident and has to be considered. Hence, the final oxygen XRS signal corresponds to the average over all these contributions. However, a more realistic structure has to be considered to fully reproduce the XRS features which in this approach are underestimated. The results are reported for both  $\text{KVOPO}_4$  and  $\text{KVPO}_4\text{F}$  structures in Figure S3 and Figure S4 respectively. The role of the V=O vanadyl bond is evident by the

appearance of the pre-edge peak. Interestingly, even though a very simple structural model extracted from the VASP relaxed full structure has been considered, the agreement between the calculated and the experimental O *K*-edge is quite satisfactory (see Figures above). This allows somehow to validate the structure obtained by the DFT calculation and used in the multiplet calculations also from the oxygen point of view.

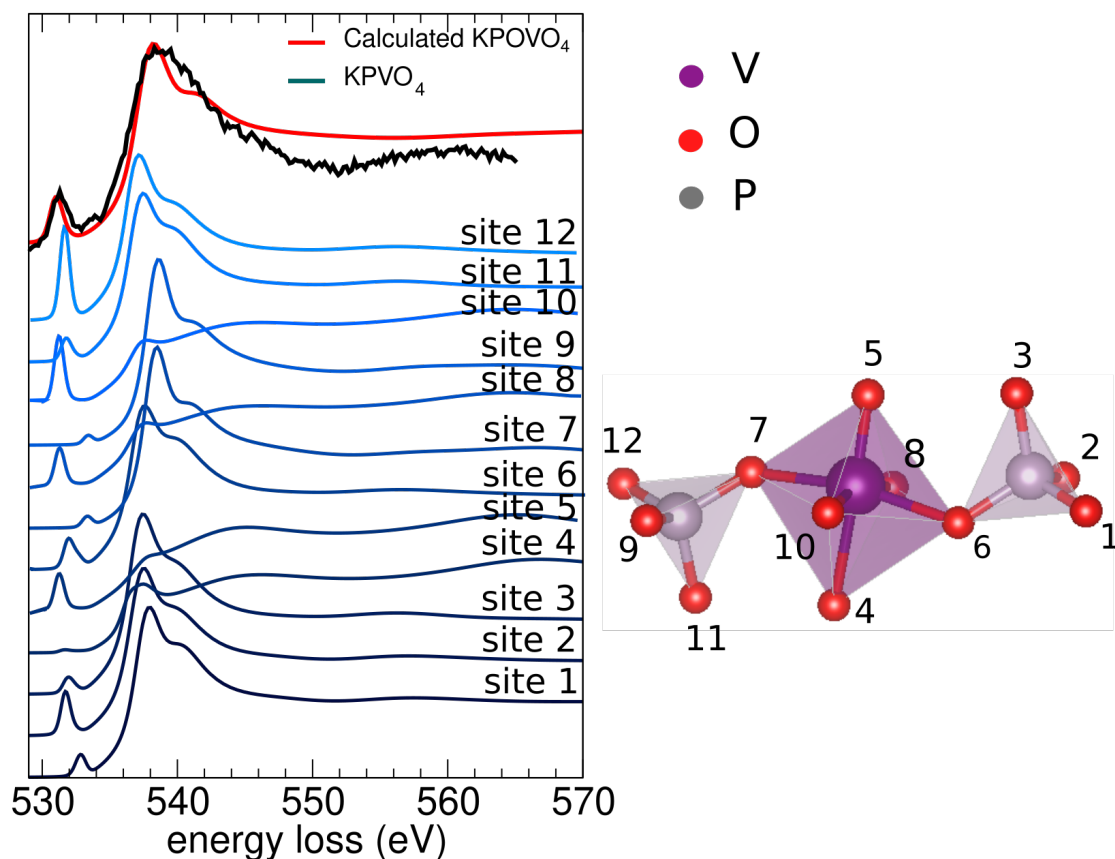


Figure S 3: Simulations of different oxygen sites of the pure KVOPO<sub>4</sub> material. The different sites used in the calculation are shown in the aside structure.

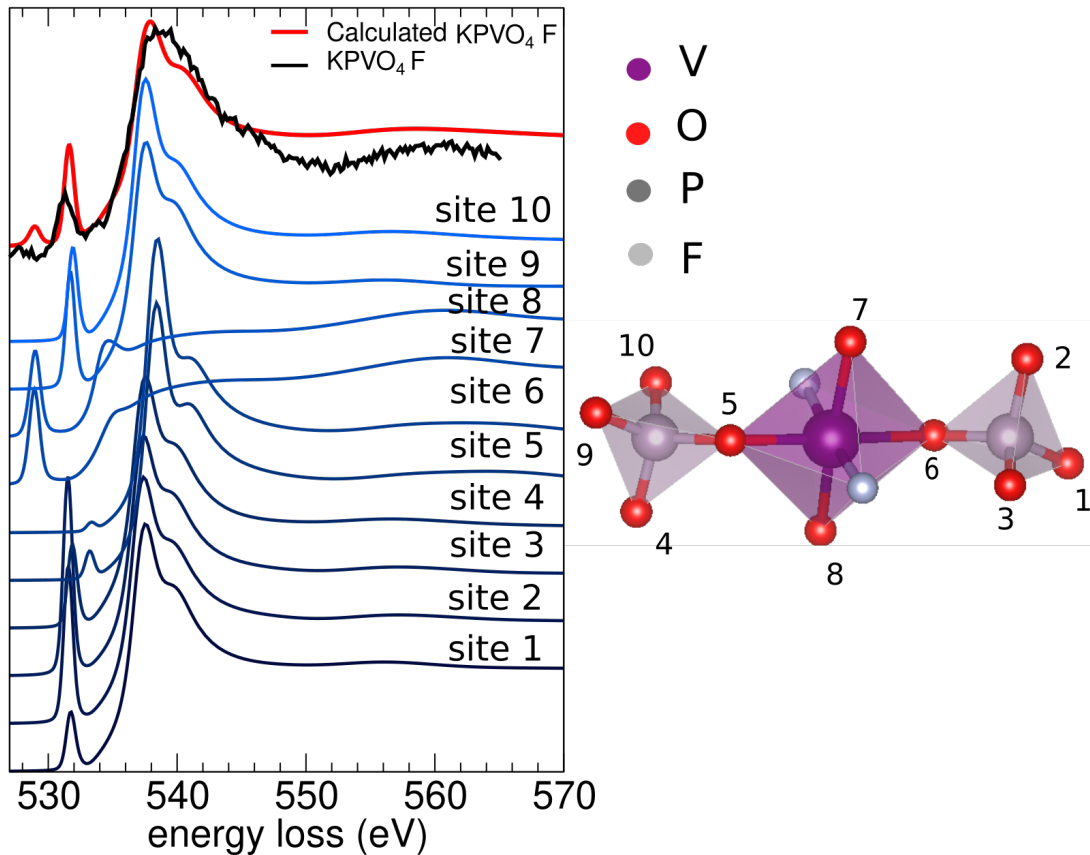


Figure S 4: Simulations of different oxygen sites of the KVPO<sub>4</sub>F. The different sites used in the calculation are shown in the aside structure.

## An example of input file for Hilbert++

```

## this string describes the studied transition
transition = "2p3d"

## optionally, the crystal field and hybridisation parameters, can be obtained
## by the following two files, if they are given.
## They are obtained by postprocessing the output of quantum espresso
## and wannier90 codes.
## The first is the Hamiltonian in the basis of wannierised function.
## The second one is the density matrix, given on the same basis.

```

```

wannier_hr_file    = "input_cis_hr.txt"
wannier_dens_file  = "input_cis_dens.txt"

## The central atom
atom = "V"

## The atomic parameters ( Slater integrals, spin-orbit, estimation of
## the transition energies) are obtained by the Amarcord code, written
## in the nineties by Mirone during stages at LULI and LURE laboratories
## and recently wrapped in the pycord package. The estimation of these parameters
## is done on the basis of parameter atom ( here "V") and the following modifications
## to the corresponding nominal atomic occupancies,
## which are described in the following two lines.

occs_base_pycord = {"3d":2}
occs_exci_pycord = {"2p":5, "3d":3}

## The development of the Hilber space ( active configurations) is done on the
## basis of the occupation number (here 2) and the max_hoppedA parameter below.
## With the below described parameters (max_hoppedA=1) the initial statespace
## is formed of all the configurations with two electrons in the 3D shell, plus
## the configurations with 3 electrons in the 3d shell and an hole in the ligands.
## The excited space is formed of all the configuration with one hole in 2p and
## 3 electrons in 3d plus all the configuration with an hole in 2p, 4 electrons
## in 3d and one hole in the ligands
occupancy = 2

## The position of the neighboring atoms can be given here. It is used
## when empirical parameters are used
bonds = [
    [ 1.98667, -0.29783,  0.45094],
    [ 0.34608,  1.18553, -1.21541],

```

```
[-2.00837, 0.13868, -0.27903],  
[-0.36025, -1.43011, 1.43726],  
[ 0.00514, 1.31441, 1.50051],  
[ 0.09588, -1.56636, -1.21801]  
]
```

*## The two parameters below are the transferable parameters for empirical crystal field*

*## Here they are set to zero because the Wannier Hamiltonian is used. Unit is eV.*

```
vc_d0 = 0.0
```

```
vc_d1 = 0.0
```

*## The two parameters below are the transferable parameters for empirical hopping term*

*## Here they are set to zero because the Wannier Hamiltonian is used. Unit is eV.*

```
vhopA_d0=0.0
```

```
vhopA_d1=0.0
```

*## This parameters is the maximum number of electrons that can hop on the central atom*

```
max_hoppedA=1
```

*## This parameter tunes, by a rigid shift of all the one particle energies of the*

*## neighbouring atoms 2p orbitals, relatively to the energy at which, when the hopping*

*## strenght is vanishing, the ground state has an extra electron fall*

*## in the 3d shell from the neighbouring 2p orbitals*

```
relative_E_hopperA=0.0
```

*## this is, ins Angstrom\*\*-1 units, the exchange wave vectro.*

```
q_exp = 0.1
```

*## A powder is considered*

```
average_is_spherical = True
```

*## The Slater integrals reduction*

```
slater_reduction = 0.8
```

```
## The spectra is iteratively refined till a resolution of 0.45 eV is obtained
e_step_target = 0.45
```

## References

- (1) Fedotov, S. S.; Khasanova, N. R.; Samarin, A. S.; Drozhzhin, O. A.; Batuk, D.; Karakulina, O. M.; Hadermann, J.; Abakumov, A. M.; Antipov, E. V.  $\text{AVPO}_4\text{F}$  (A = Li, K): A 4 V cathode material for high-power rechargeable batteries. *Chemistry of Materials* **2016**, *28*, 411–415.
- (2) Benhamada, L.; Grandin, A.; Borel, M. M.; Leclaire, A.; Raveau, B.  $\text{KVPO}_5$ , an intersecting tunnel structure closely related to the hexagonal tungsten bronze. *Acta Crystallographica Section C Crystal Structure Communications* **1991**, *47*, 1138–1141.



# TOC Graphic

