-Supplementary data-

Étude structurale des analogues du bleu de Prusse par spectroscopie infra-rouge

Application of the infra-red spectroscopy to the structural study of Prussian blue analogues

Julien Lejeune[a,*], Jean-Blaise Brubach[b], Pascale Roy[a,b], Anne Bleuzen[a,*]

[a] *Institut de Chimie Moléculaire et des Matériaux d'Orsay,UMR CNRS 8182, Université Paris-Sud, 15 rue Georges Clémenceau, F-91405 Orsay Cedex, France*

[b] *Synchrotron SOLEIL, l'Orme des merisiers Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France*

-Supplementary data-

A1. Evolution of the different contributions to the ν{O-H} bands as a function of the chemical composition of A_xCoFe PBAs

The IR spectrum of PBAs exhibits very sharp bands in the 3550-3700 cm^{-1} spectral range, associated with water molecules that are not involved in a hydrogen-bonded network. The number of these sharp bands may vary depending on the nature of the PBA (Fig. A1).

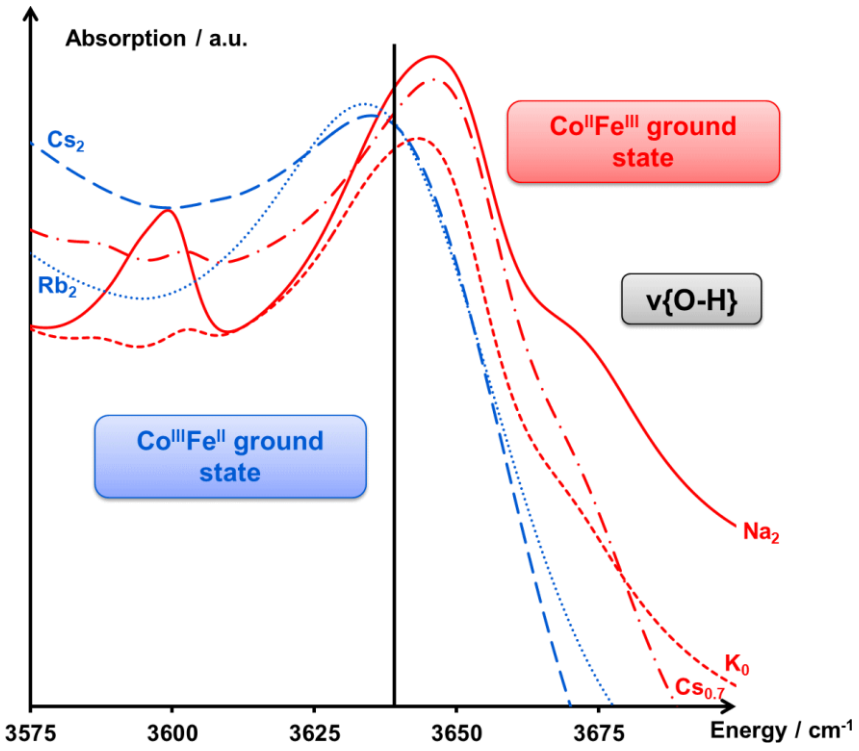

Fig. A1. IR spectrum of several A_xCoFe PBAs in the spectral range associated with the ν{O-H} vibration band of water molecules bound to the cobalt cations at the $Fe(CN)_6$ vacancies, at T = 300 K. Spectra associated with A_xCoFe PBAs exhibiting a $Co^{II}Fe^{III}$ (resp. $Co^{III}Fe^{II}$) ground state at T = 300 K are plotted in red (resp. blue). Legend: K_0CoFe (---), $Cs_{0.7}CoFe$ (—·—), Na_2CoFe (—), Rb_2CoFe (···), Cs_2CoFe (———).

The position in term of energy of the main band, associated with the ν{O-H} vibration of water molecules bound to the cobalt cations at the $Fe(CN)_6$ vacancies, mostly depends on the electronic state of the system (and, therefore, of the oxidation state of the cobalt cations): in the

-Supplementary data-

$Co^{II}Fe^{III}$ electronic state, the ν{O-H} vibration band associated with water molecules bound to the Co^{II} cations is located above 3638 cm^{-1}; in the $Co^{III}Fe^{II}$ electronic state, the ν{O-H} vibration band associated with water molecules bound to the Co^{III} cations is located below 3638 cm^{-1}. The nature and the amount of alkali cations inserted in the structure may modulate the position in terms of energy of this band.