QUE SAIT-ON DE L'ENVIRONNEMENT DU FER DANS LES VERRES SILICATÉS ?

Gérald LELONG, V. Vercamer, A. Juhin, G. Calas, L. Galoisy, C. Brouder, MA Arrio

Institut de Minéralogie, Physique des Matériaux et Cosmochimie, Paris, France

LE FER DANS LES MINÉRAUX ET GEMMES

Almandin (grenat)

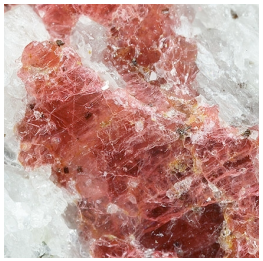
Andradite (grenat)

Orthose

Péridot

Hypersthene

Diopside



Gillespite

LE FER DANS LES MINÉRAUX ET GEMMES

Almandin (grenat)
$Fe^{2+}_3Al_2(SiO_4)_3$

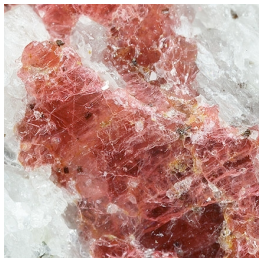
Andradite (grenat)
$Ca_3Fe^{3+}_2(SiO_4)_3$

Orthose
Fe^{3+}:$KAlSi_3O_8$

Péridot
$(Mg,Fe^{2+})_2SiO_4$

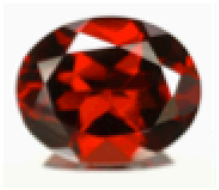
Hypersthene
$(Fe^{2+},Mg)SiO_3$

Diopside
$Ca(Mg,Fe^{2+})Si_2O_6$



Gillespite
$BaFe^{2+}Si_4O_{10}$

RELATION STRUCTURE / COULEUR



almandine garnet
$Fe^{2+}_3Al_2(SiO_4)_3$

andradite garnet
$Ca_3Fe^{3+}_2(SiO_4)_3$

orthoclase
Fe^{3+}:$KAlSi_3O_8$

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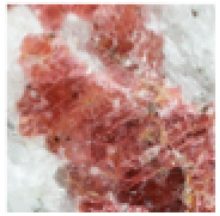

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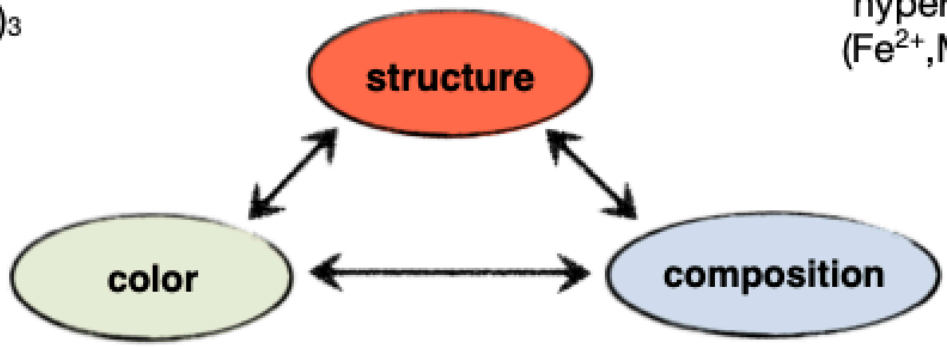
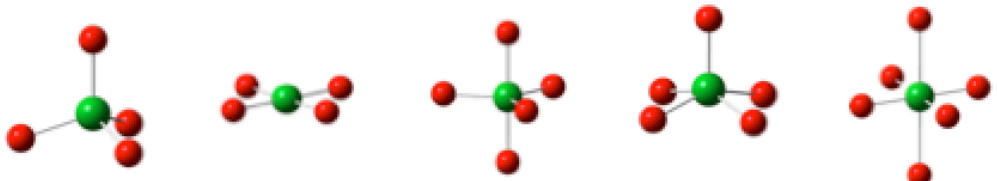




Variety of Fe environments

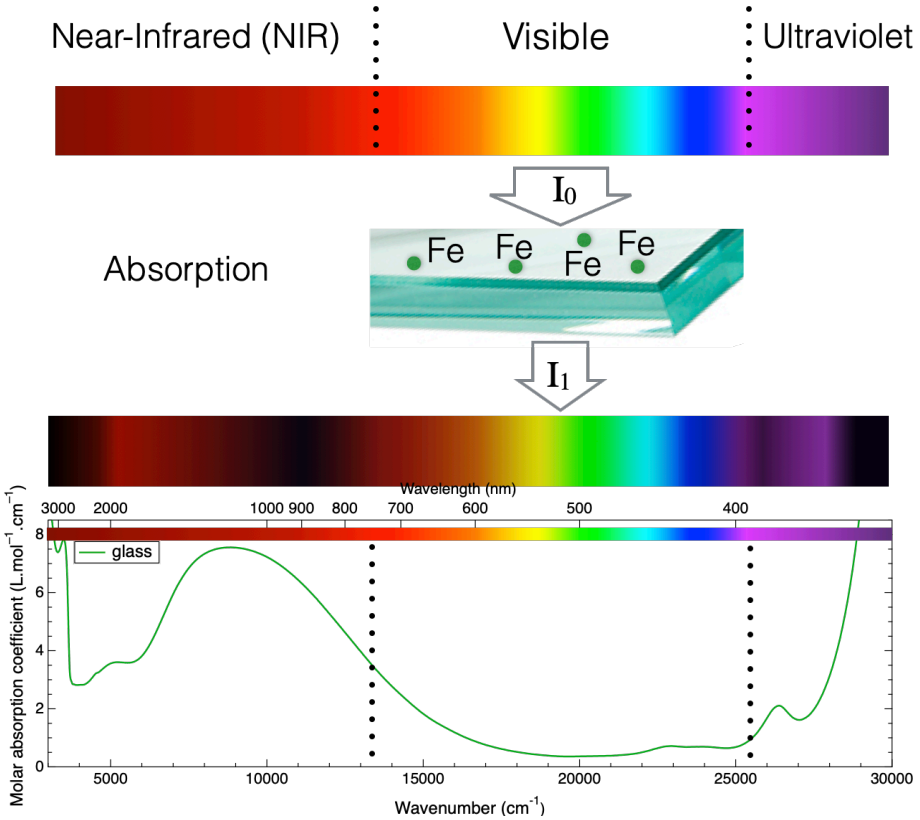
LE FER DANS LES VERRES SODO-CALCIQUES

0.5wt.% de Fe_2O_3

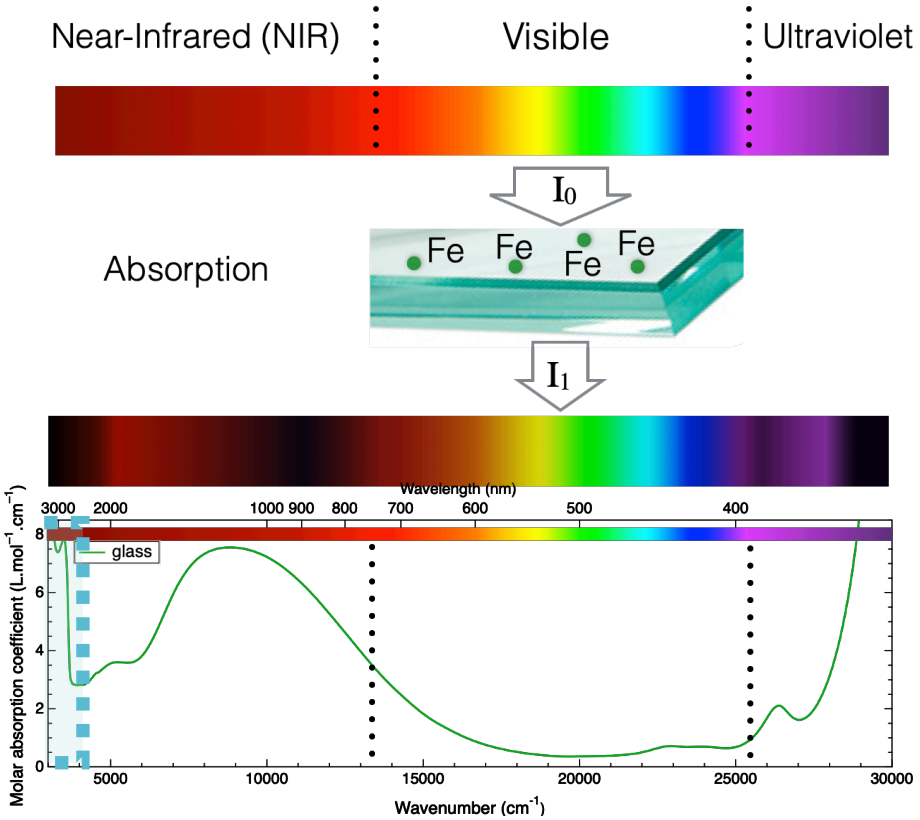
Fe^{3+} $Fe^{2+} + Fe^{3+}$ Fe^{2+}

Conditions réductrices →

LE FER DANS LES VERRES SODO-CALCIQUES

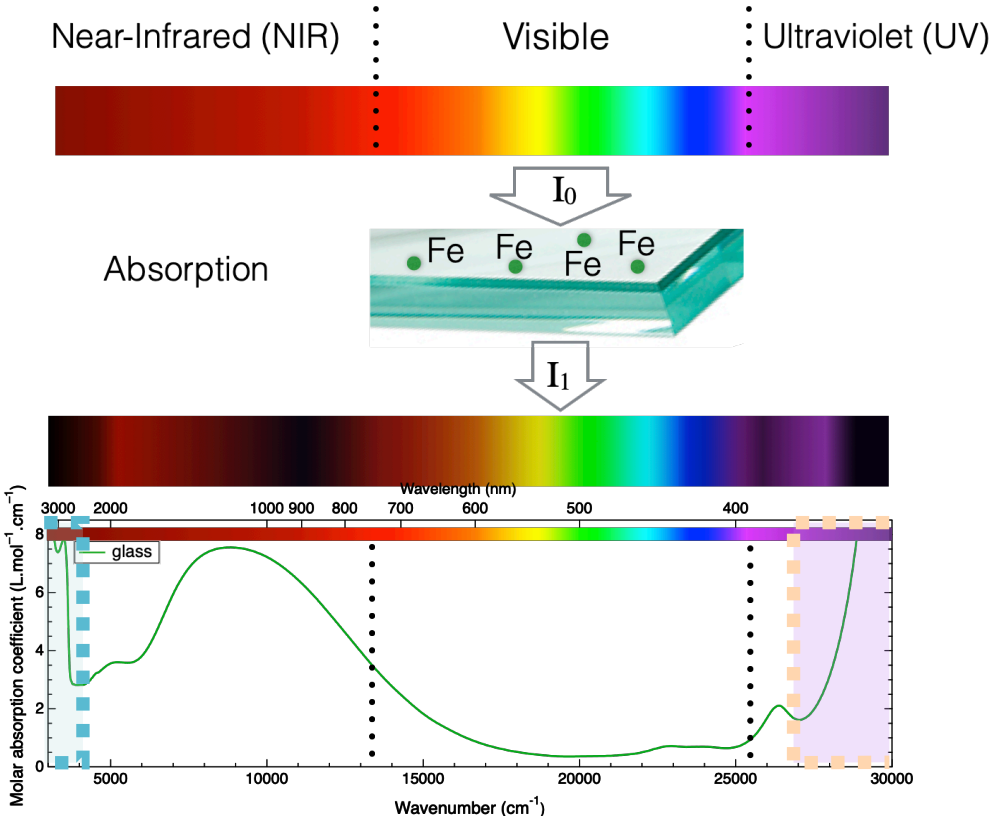


LE FER DANS LES VERRES SODO-CALCIQUES



Front IR
Bandes Si-O & O-H

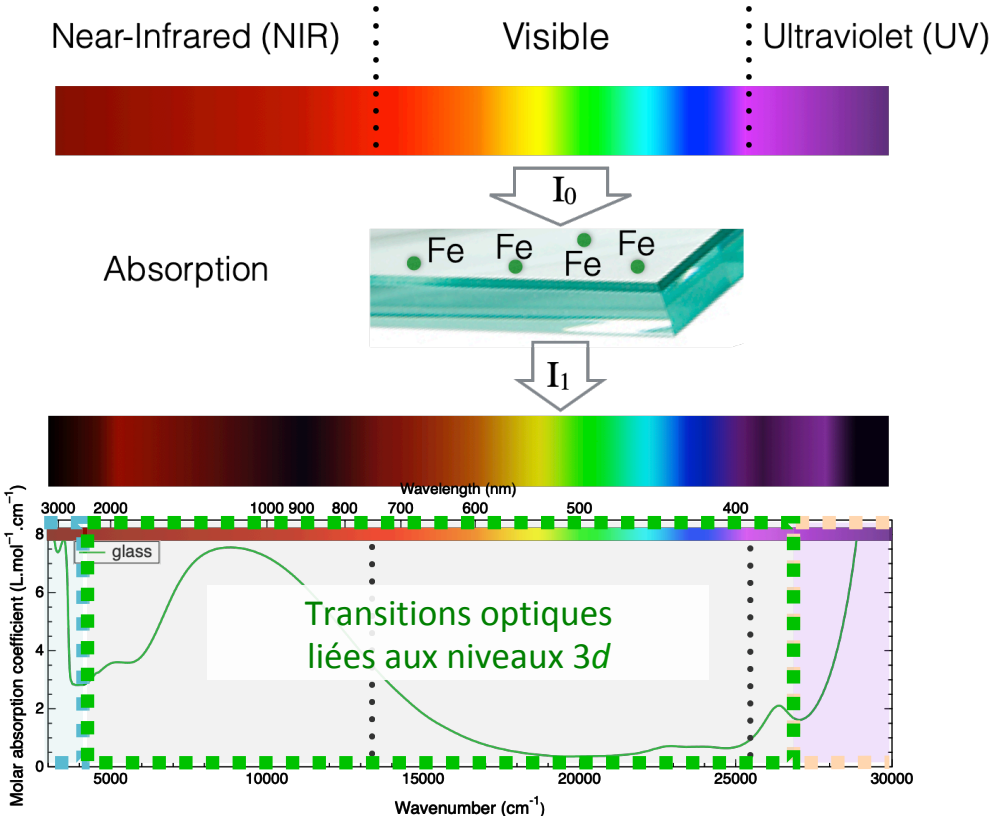
LE FER DANS LES VERRES SODO-CALCIQUES



Front IR
Bandes Si-O & O-H

Front UV
Transfert de charge
Fe→O

LE FER DANS LES VERRES SODO-CALCIQUES



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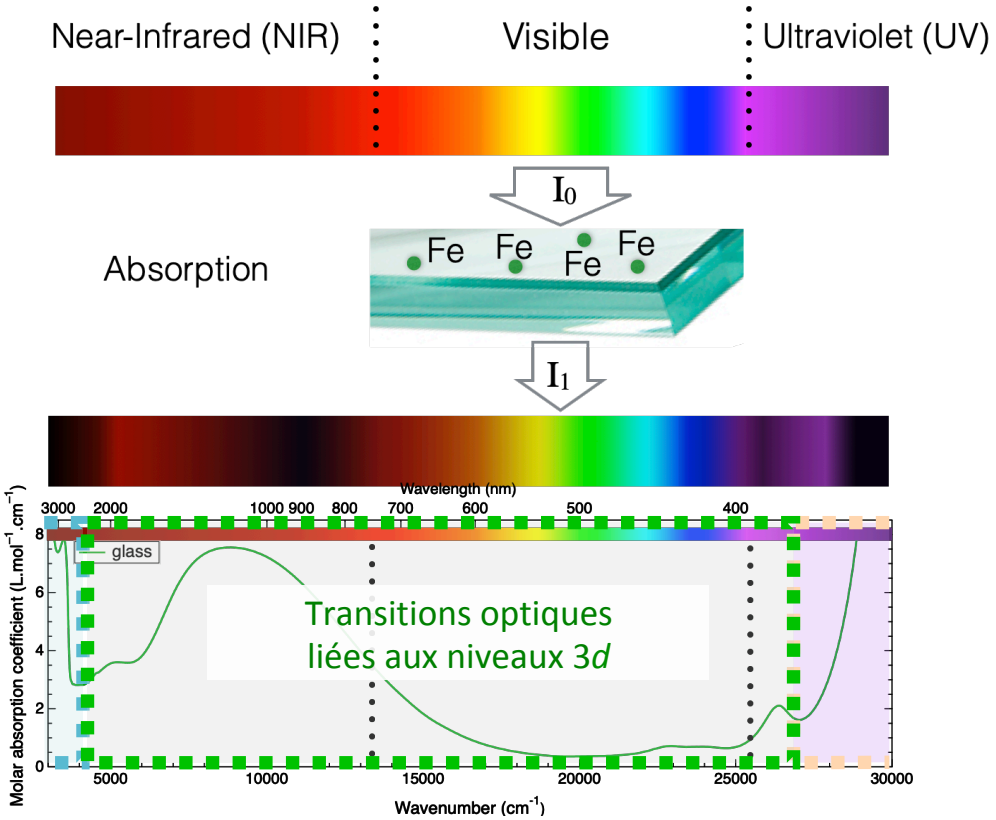
LE FER DANS LES VERRES SODO-CALCIQUES



Front IR
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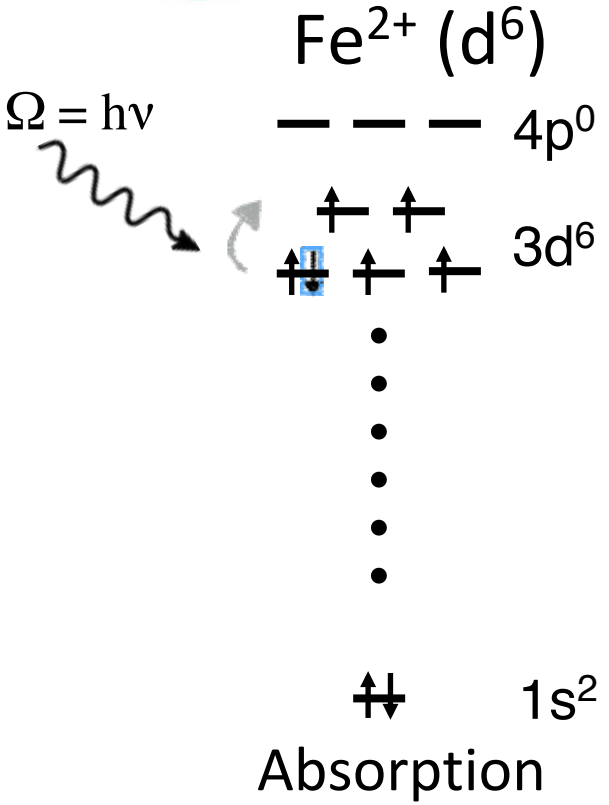
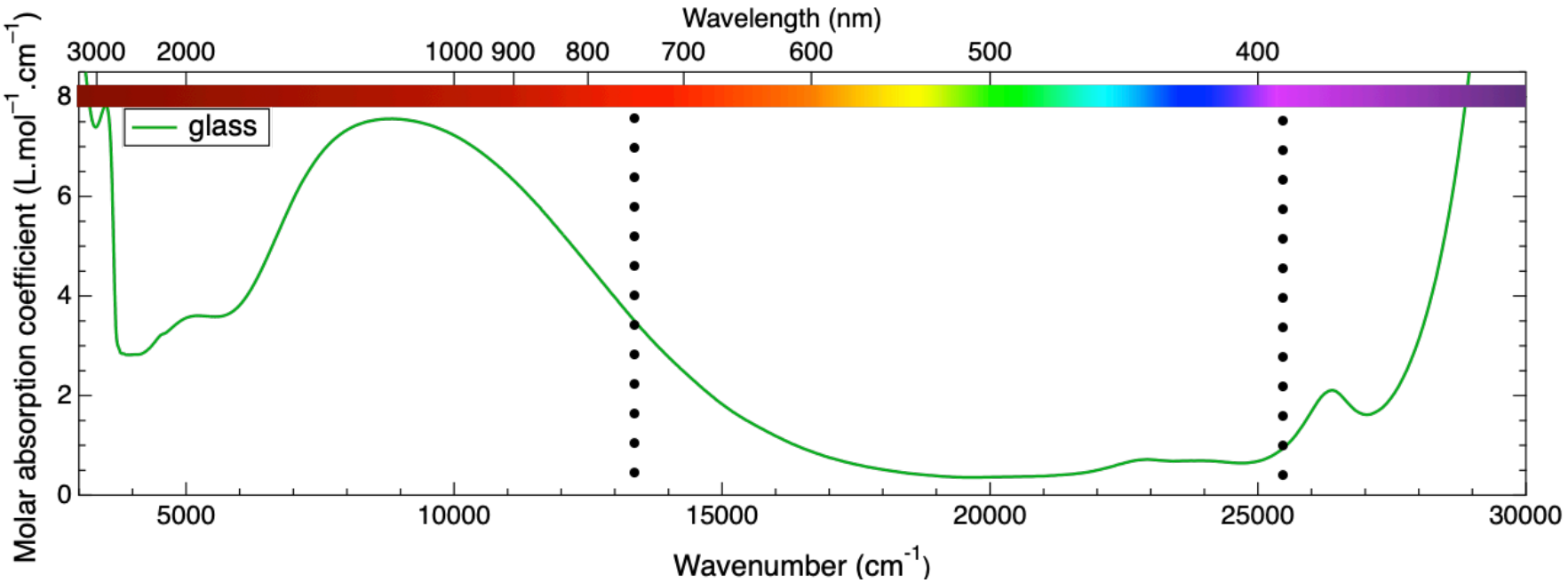
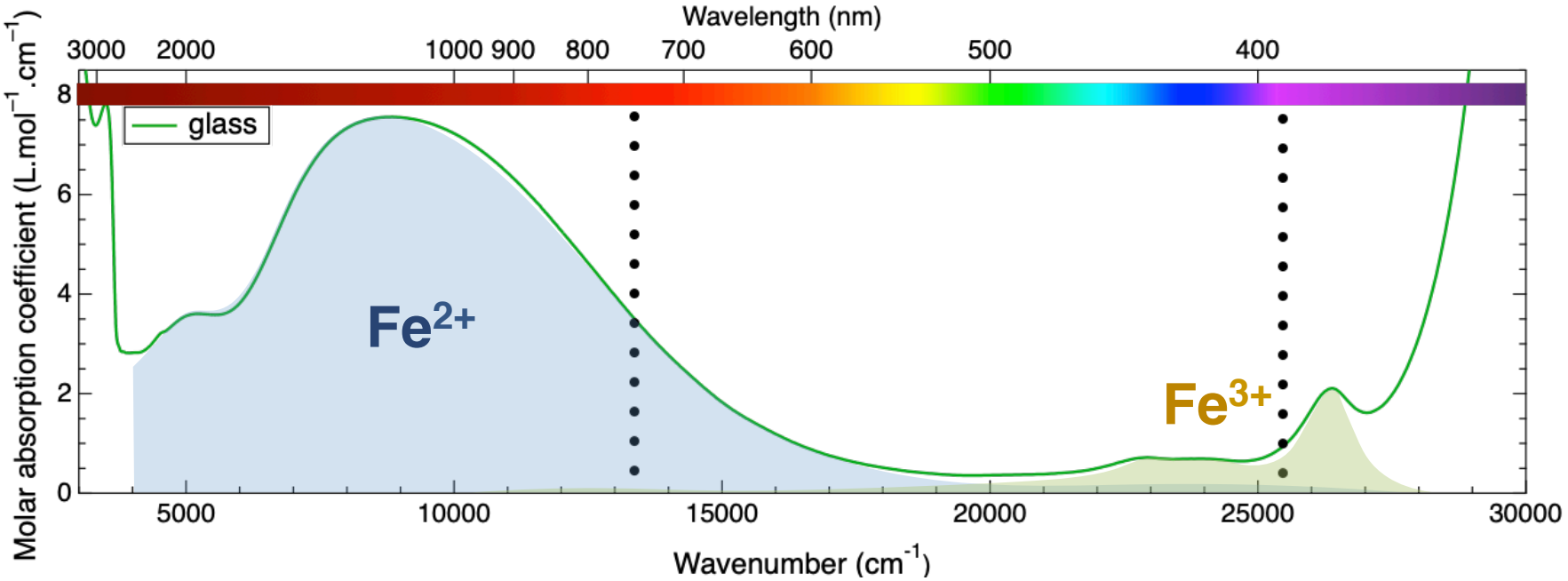


Sonde les niveaux 3d

SPECTROSCOPIE D'ABSORPTION UV-VIS



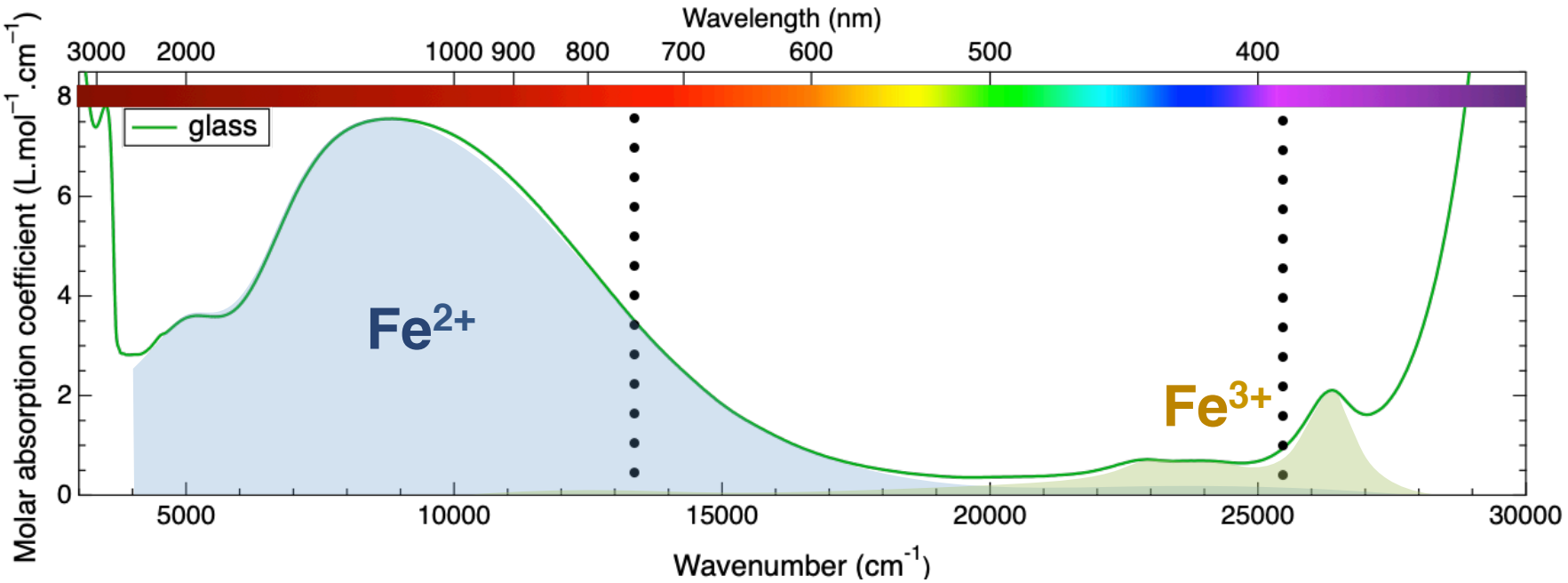
SPECTROSCOPIE D'ABSORPTION UV-VIS



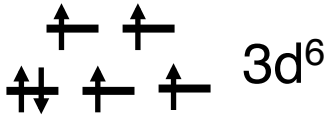
Coefficient d'absorption du Fe dans un verre à vitre:

Rôle majeur des ions Fe^{2+} alors qu'ils ne représentent que 25% du fer total !

SPECTROSCOPIE D'ABSORPTION UV-VIS

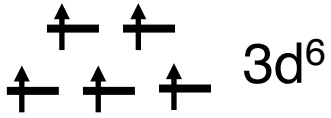


Fe^{2+} (d^6)



Autorisé de spin

Fe^{3+} (d^5)



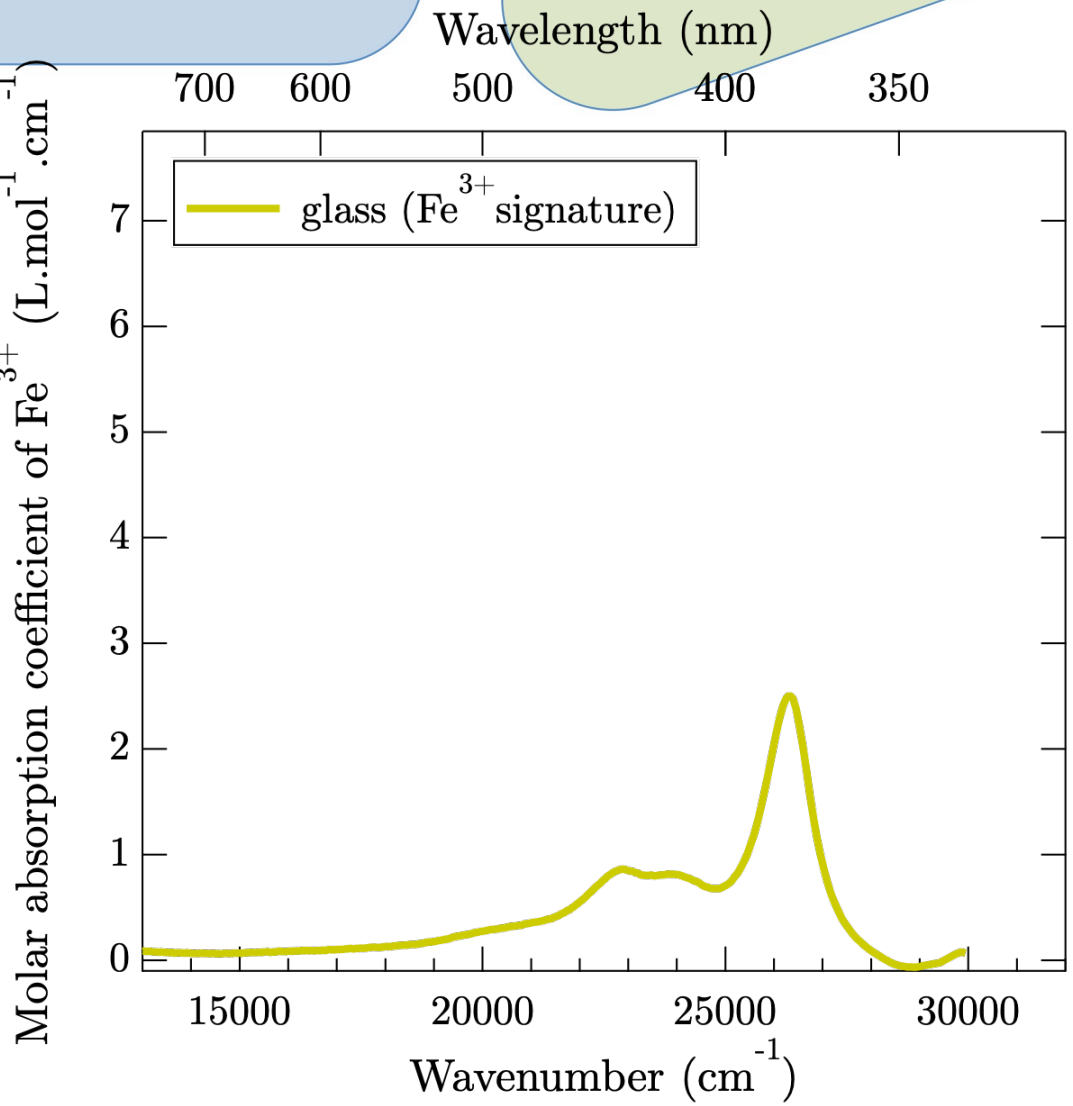
Interdite de spin

Fe^{3+} verre vs minéral

Fe^{3+} dans un sodo-calcique
$16Na_2O–10CaO–74SiO_2$

Oxidized

5%



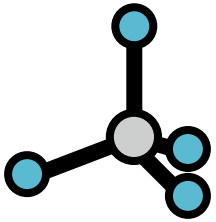
Fe^{3+} verre vs minéral

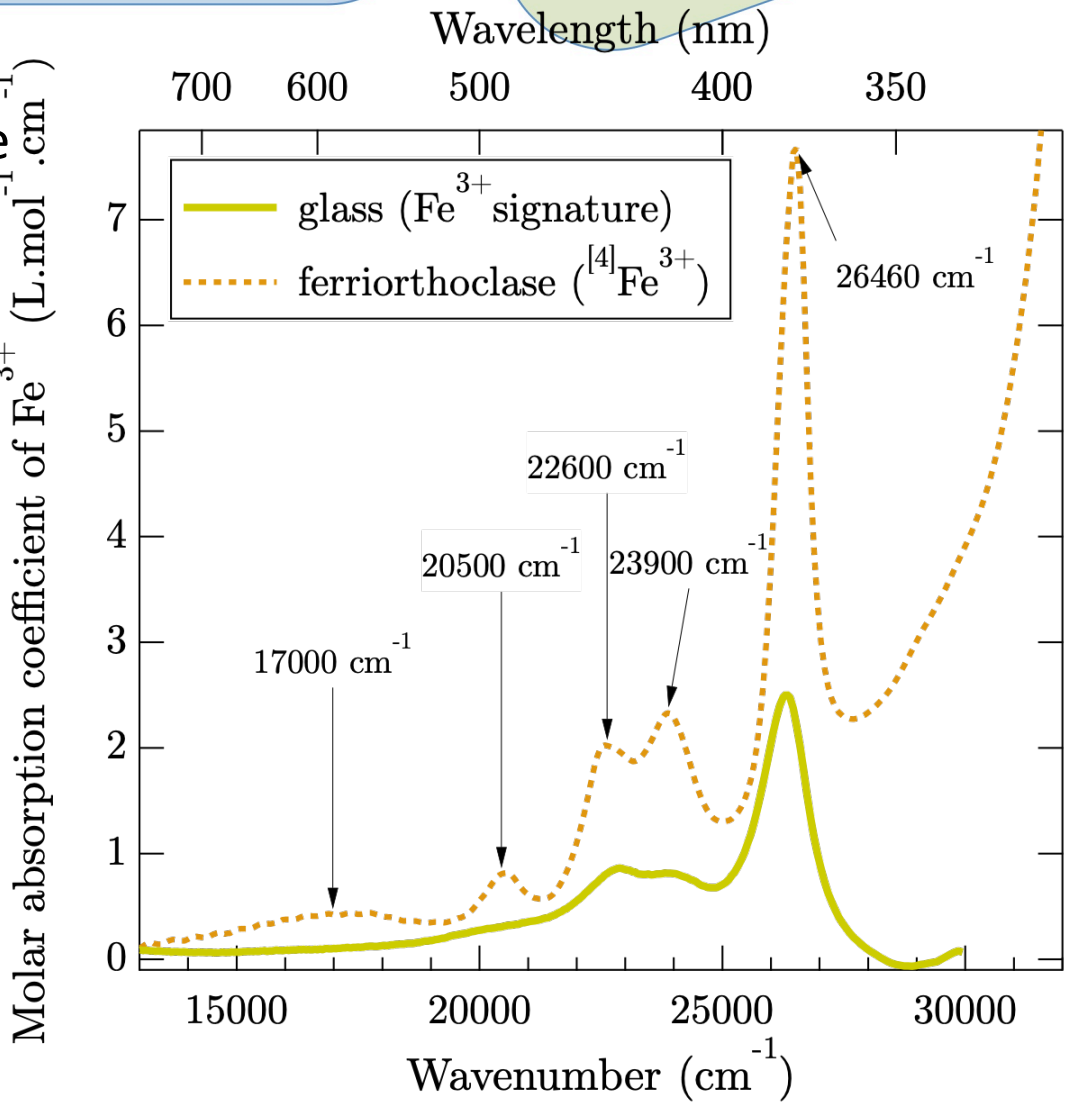
Fe^{3+} dans un sodo-calcique
$16Na_2O–10CaO–74SiO_2$

Oxidized

5%

ferriorthoclase
$^{[4]}Fe^{3+}$ dans $KAlSi_3O_8$





Fe^{3+} verre vs minéral

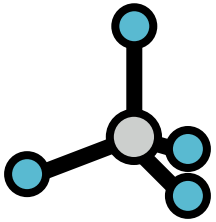
Signaux additionnels dans le verre

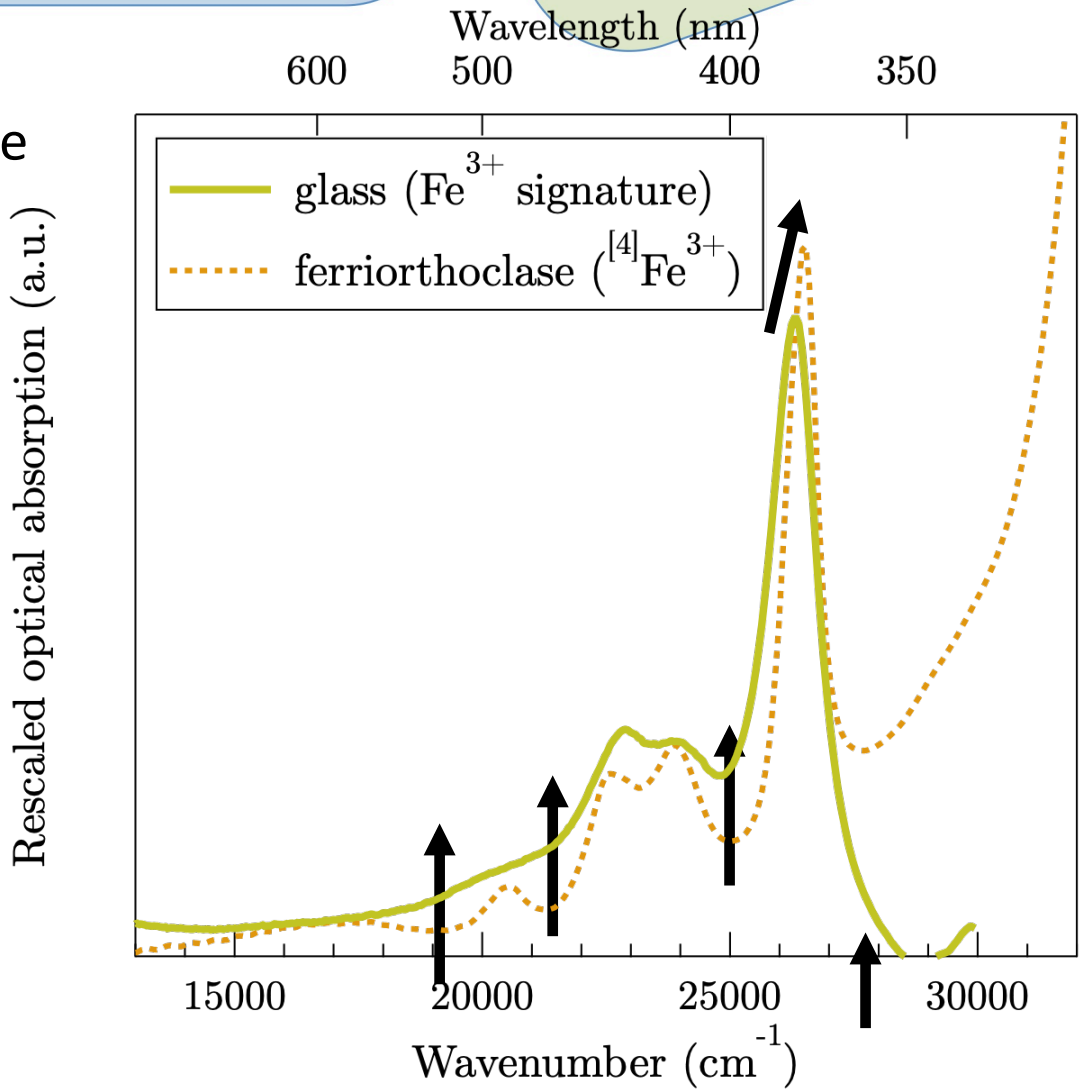
Fe^{3+} dans un sodo-calcique
$16Na_2O–10CaO–74SiO_2$

Oxidized

5%

ferriorthoclase
$^{[4]}Fe^{3+}$ dans $KAlSi_3O_8$





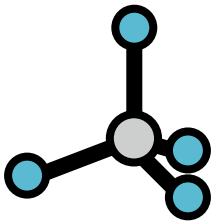
Comparaison avec la yoderite $^{[5]}Fe^{3+}$

Présence de $^{[5]}Fe^{3+}$

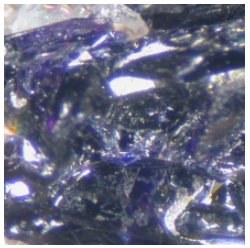
Fe^{3+} dans un sodo-calcique
$16Na_2O–10CaO–74SiO_2$

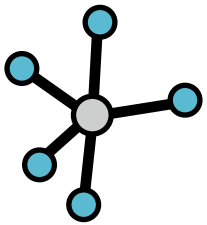
Oxidized

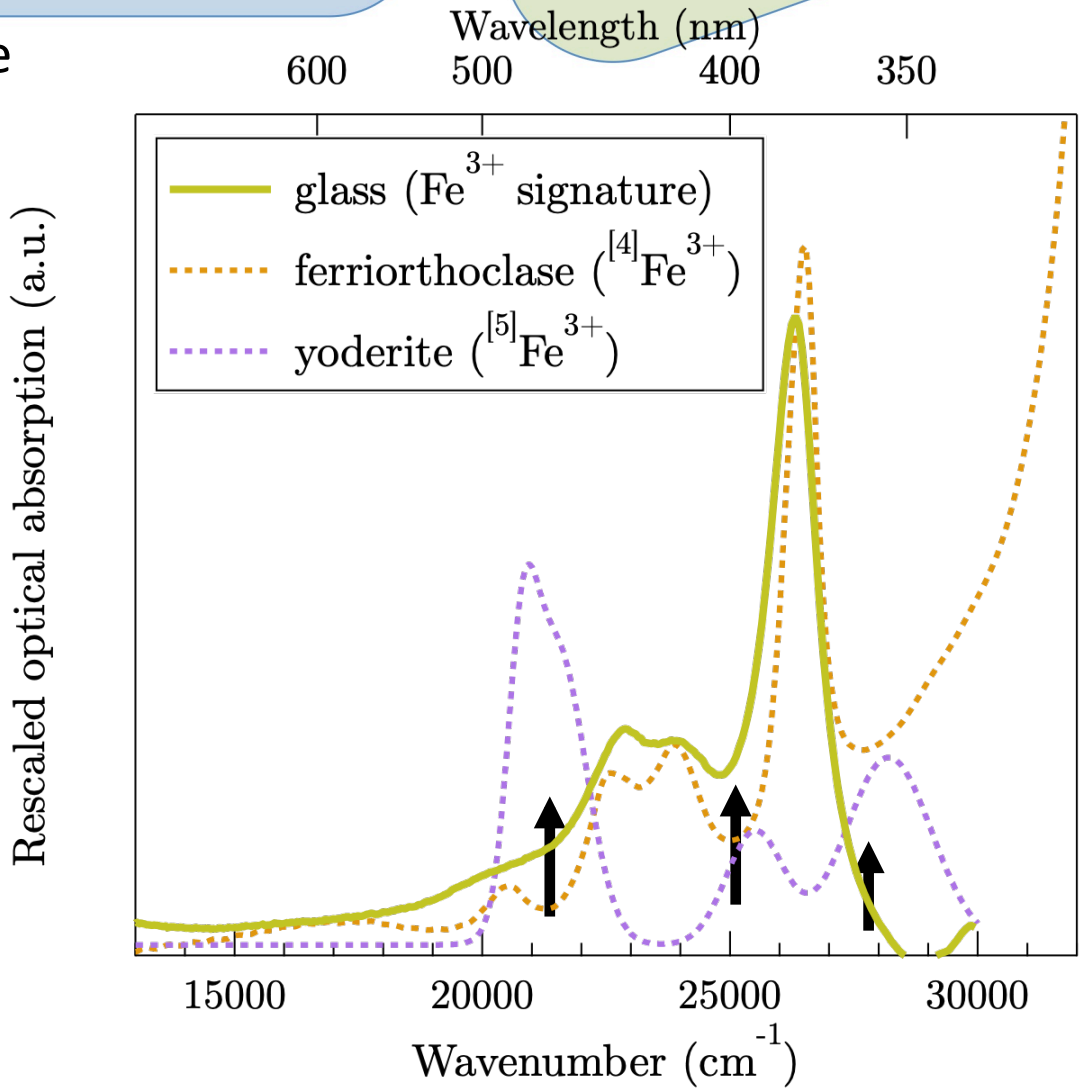
ferriorthoclase
$^{[4]}Fe^{3+}$ dans $KAlSi_3O_8$



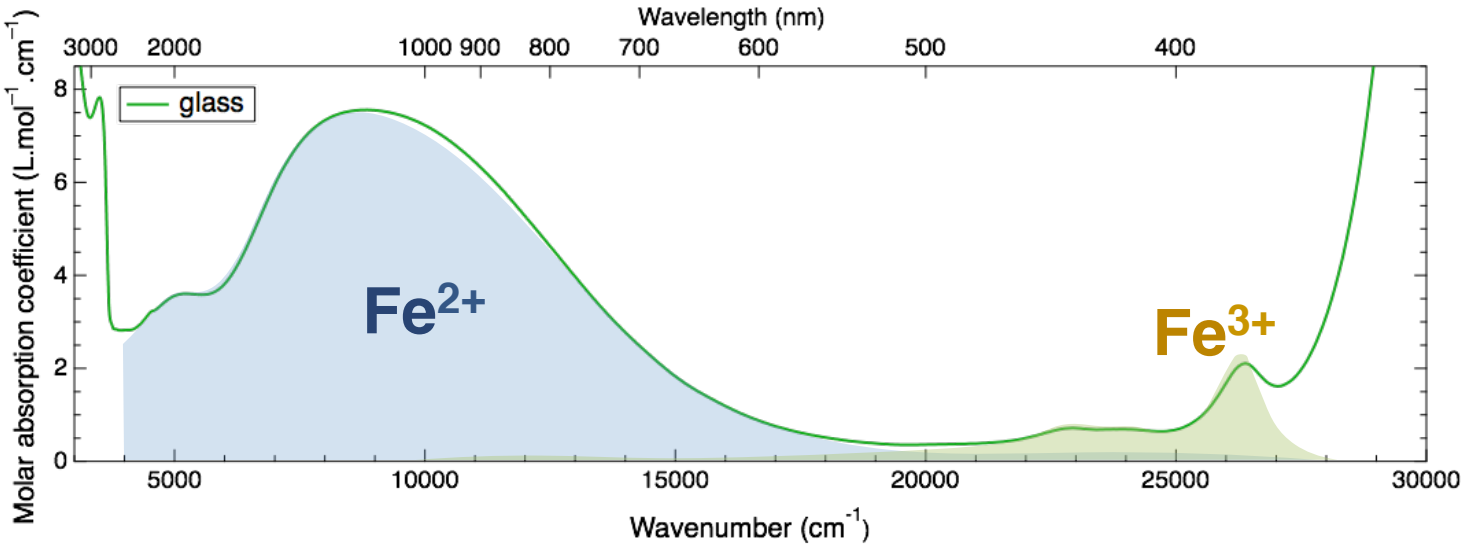
yoderite
$^{[5]}Fe^{3+}$



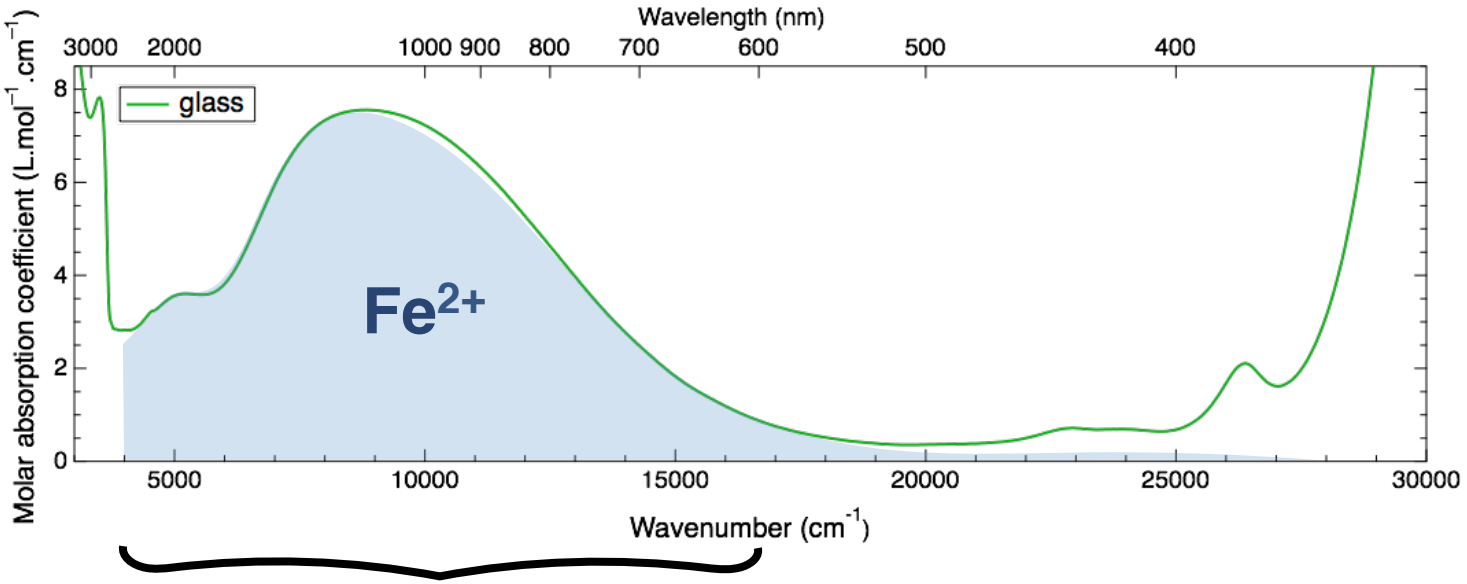




SPECTROSCOPIE D'ABSORPTION OPTIQUE



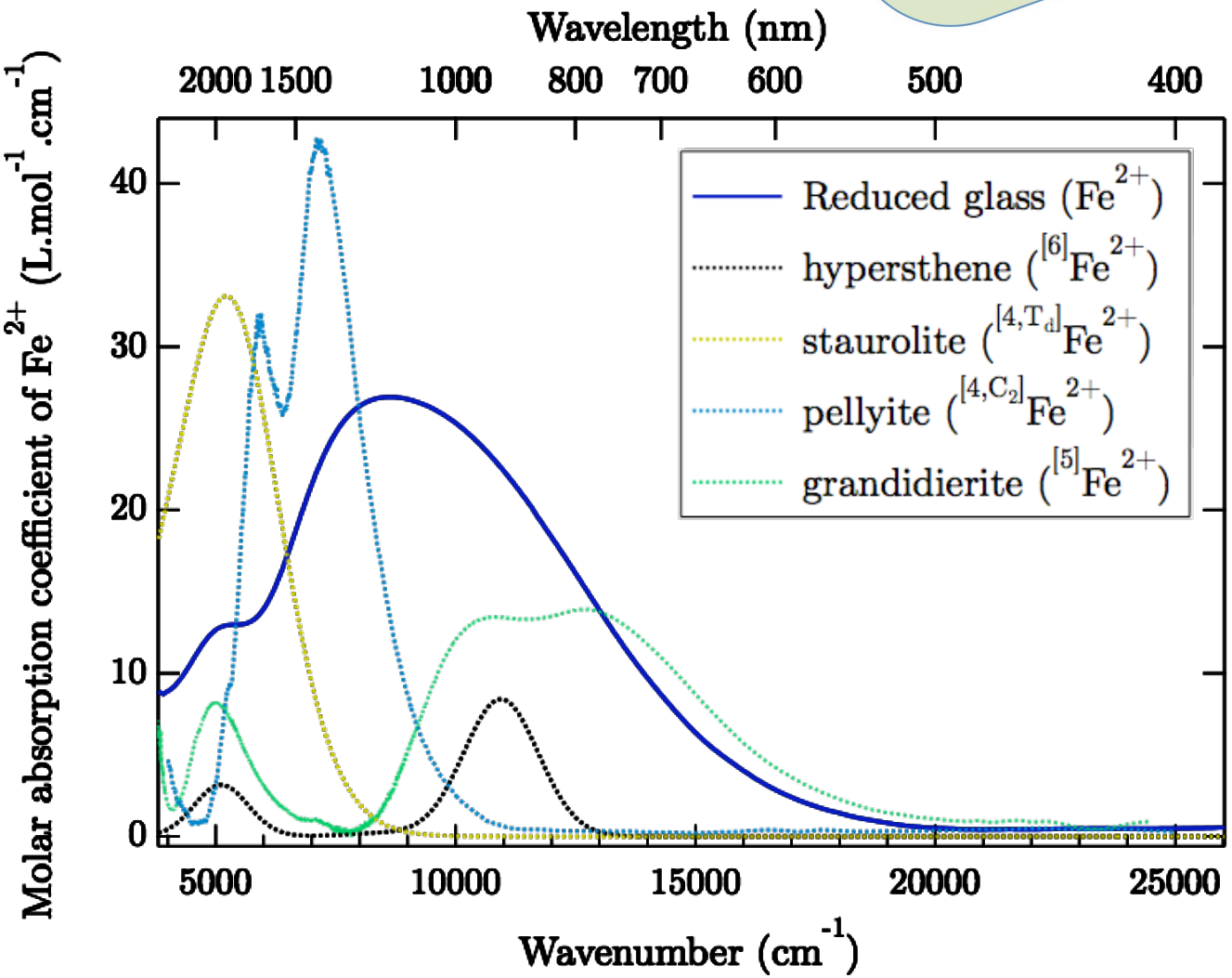
SPECTROSCOPIE D'ABSORPTION OPTIQUE



Bande asymétrique

POURQUOI ?

MINERAUX COMME REFERENCES



LIMITES DU « FINGERPRINT »

Minerals give a good overview of the spectroscopic trends, but there are some major differences to keep in mind:

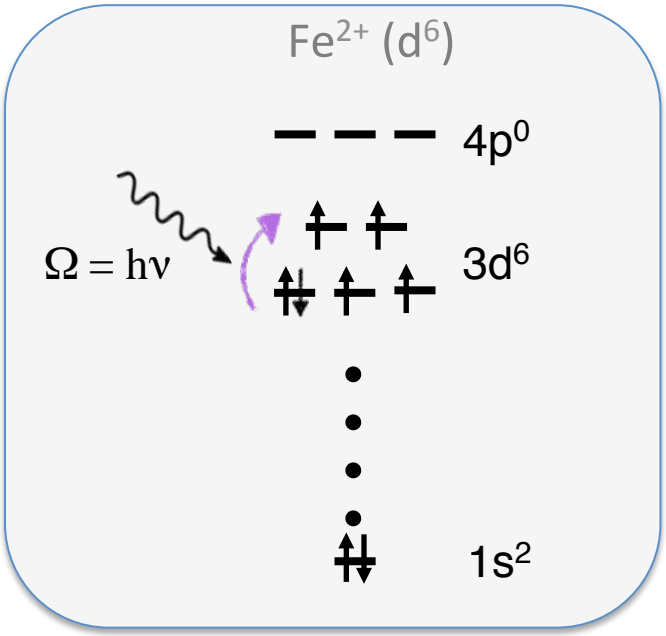
- iron sites are distributed in glasses :
  - Coexistence of several coordination number,
  - Site distorsions (bond length, angles…)
  - Crystal field

- some symetries do not exist in minerals…
- heterovalence of Fe (Fe^{2+} & Fe^{3+} simultaneously)

Optical absorption spectra calculations
→ Access intermediate geometries that do not exist in minerals

ORIGINES DES TRANSITIONS OPTIQUES

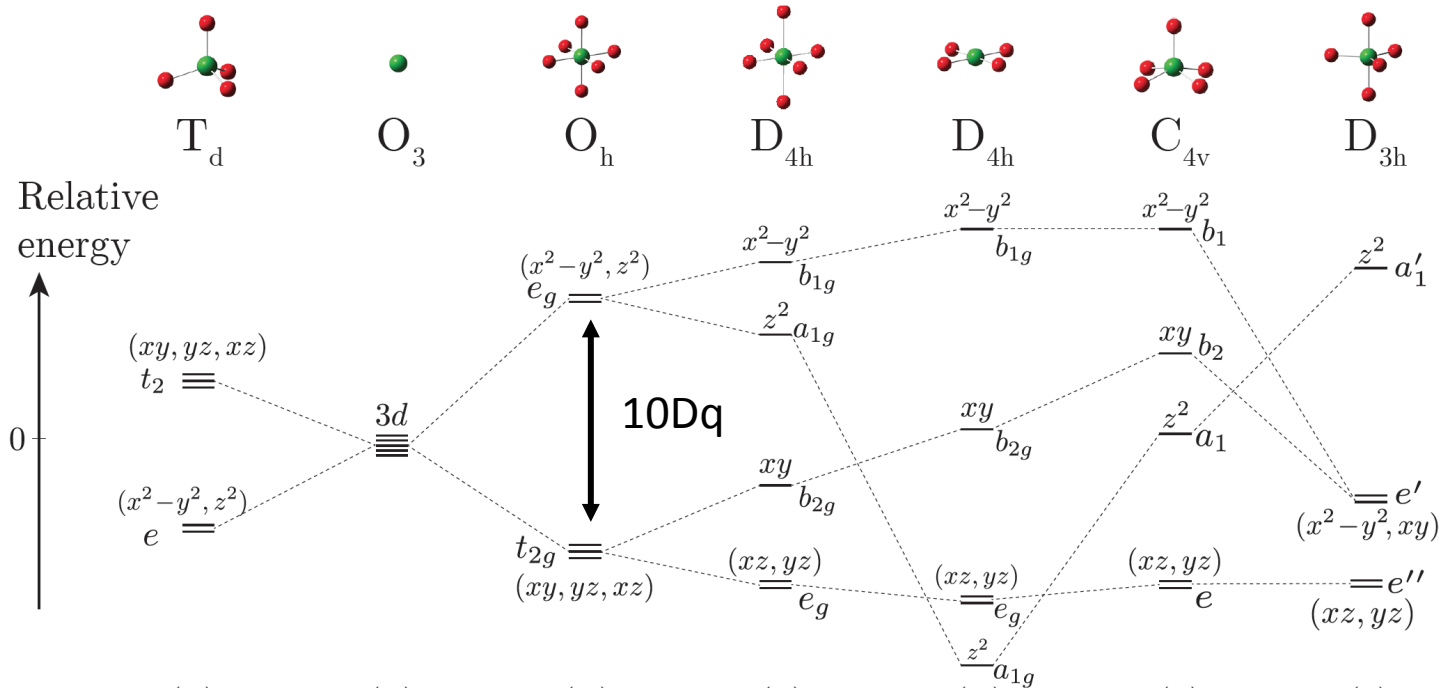
→ Origine des bandes d'absorption: **transitions entre niveaux du fer**



ORIGINES DES TRANSITIONS OPTIQUES

→ Origine des bandes d'absorption: **transitions entre niveaux du fer**

→ L'éclatement des niveaux 3d est liée à la symétrie locale imposée par les ligands



LIGAND FIELD MULTIPLETS APPROACH

$$\hat{H}_{ion} = \hat{H}_{kin} + \hat{H}_{e^-/N} + \hat{H}_{e^-/e^-} + \hat{H}_{SO} + \hat{H}_{LF}$$

Kinetic energy
(free ion calculation)

Electron-nucleus interaction
(free ion calculation)

Electron-electron interaction
(free ion calculation,
might be reduced due to covalency)

Spin-orbit coupling
(on every open-shell,
free ion calculation)

Ligand field

(strongly material dependent,
parameterized to fit experiments,
no straightforward calculation methods)

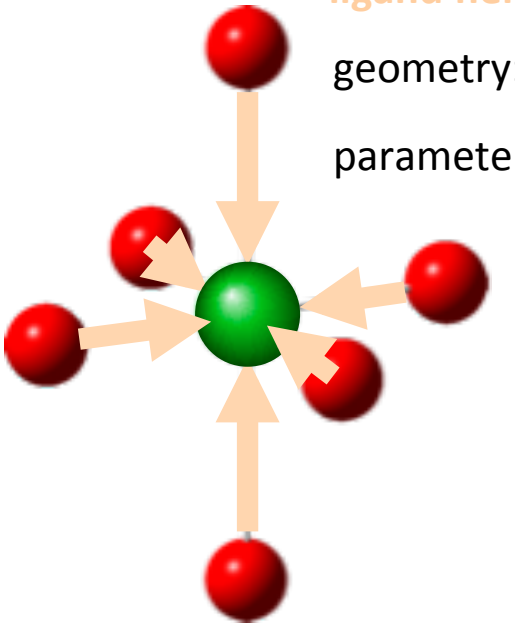
LIGAND FIELD MULTIPLETS APPROACH

$$\hat{H}_{ion} = \hat{H}_{kin} + \hat{H}_{e^-/N} + \hat{H}_{e^-/e^-} + \hat{H}_{SO} + \hat{H}_{LF}$$

Ligand field represents the local geometry

Mono-atomic model
➞ no explicit Fe–O distances and angles

Problem:
***d-d* transitions are forbidden**
⇒ no optical spectra



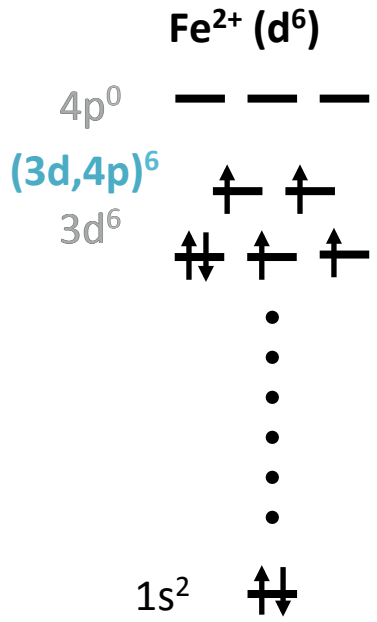
LIGAND FIELD MULTIPLETS APPROACH

$$\hat{H}_{ion} = \hat{H}_{kin} + \hat{H}_{e^-/N} + \hat{H}_{e^-/e^-} + \hat{H}_{SO} + \hat{H}_{LF} + \hat{H}_{hybrid}$$

In the case of non-centrosymmetric geometry (e.g. T_d, C_{4v} or D_{3h}) 3*d* and 4*p* can mix (V_{pd} hybridization parameter)

With hybridization, you give a 4p character to the 3d electrons, which enables the d-d transitions:

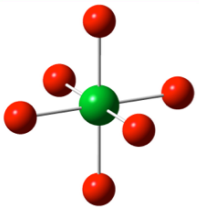
(*3d,4p*)^6 → (*3d,4p*)^6 (Electric dipole)

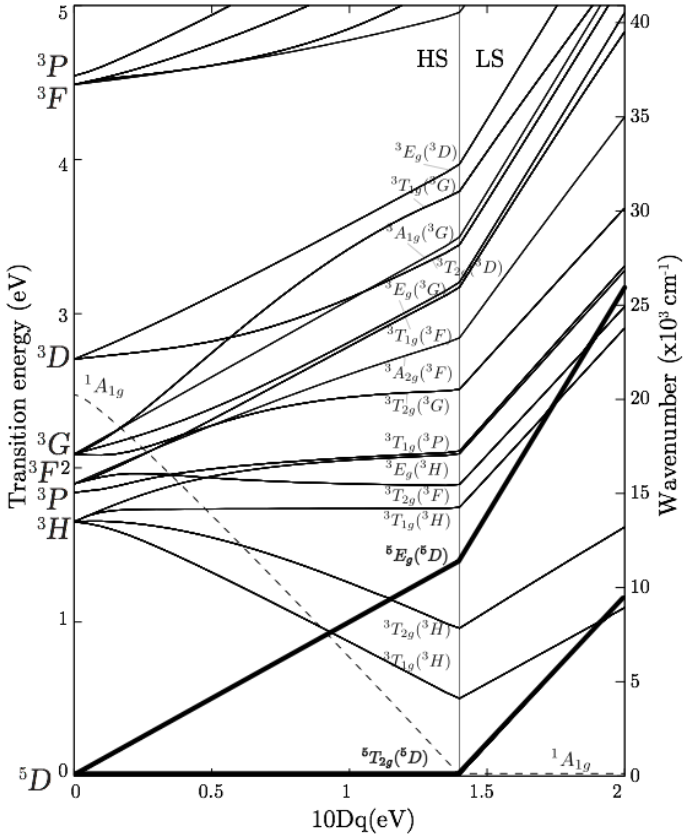


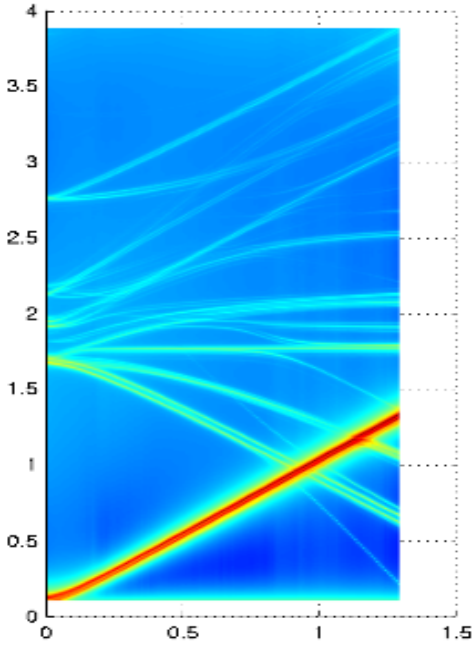
Here implemented with `Quanty`
(M. W. Haverkort and co-workers)

All calculations with one model

TANABE-SUGANO OF Fe^{2+} IN O_h

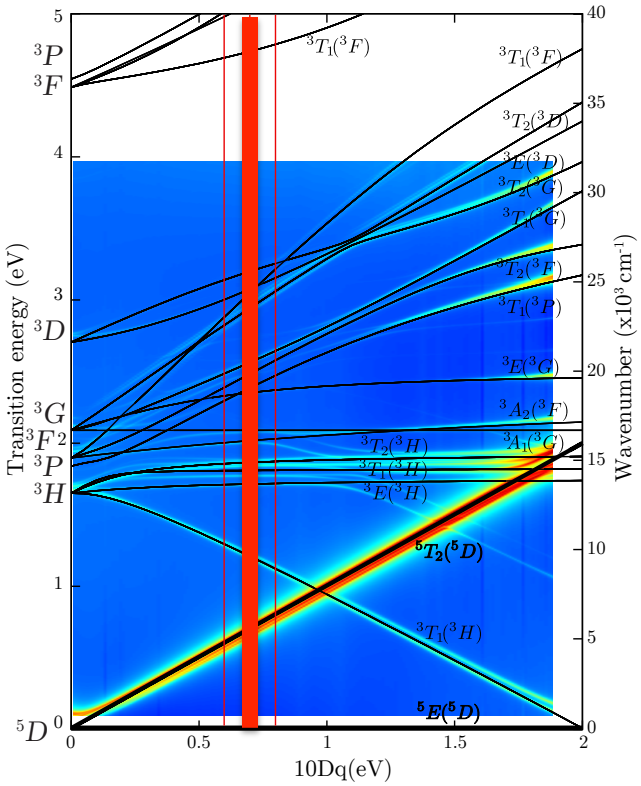




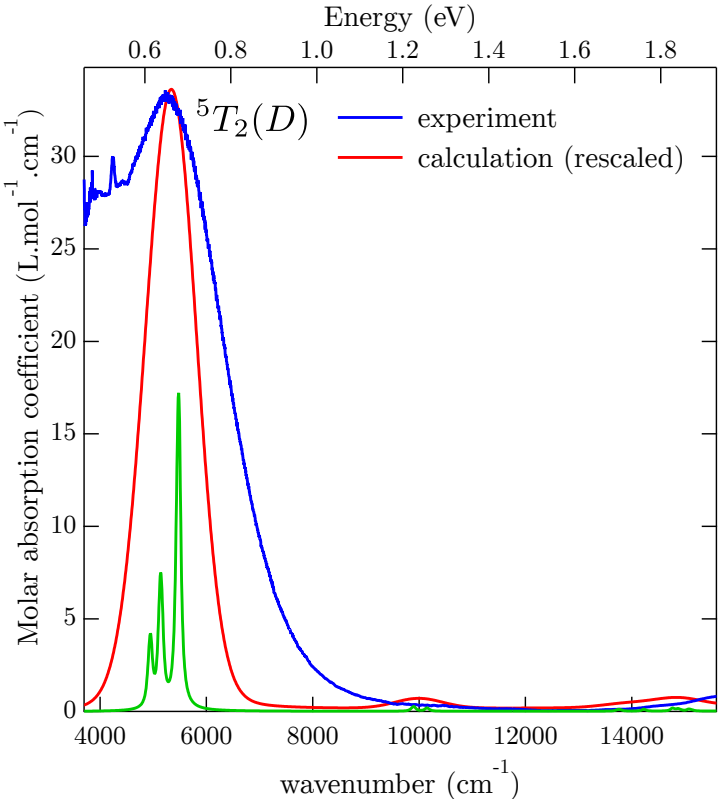


each 10Dq corresponds to a calculated optical spectra

TANABE-SUGANO OF Fe^{2+} IN O_h



Comparaison with staurolite

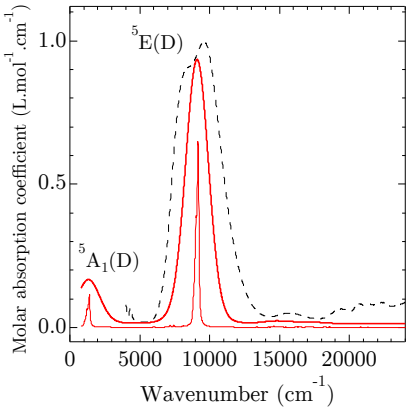


Vercamer et al. Physical Review B 94 245115 (2016)

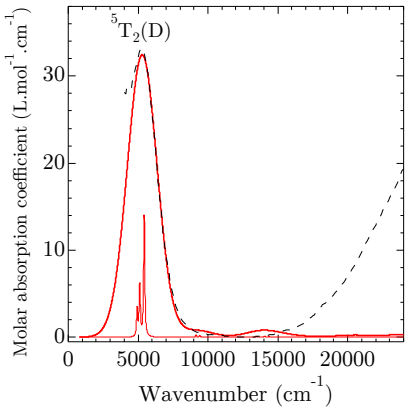
EXP. VS CALC. FOR Fe^{2+} IN MINERALS

optical abs.

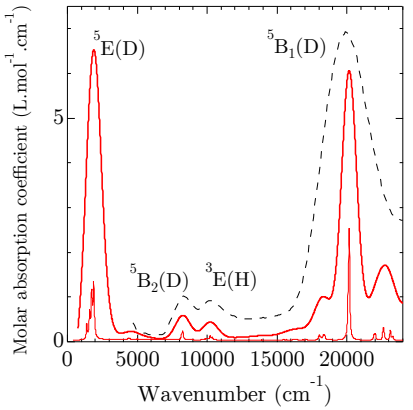
[6,Oh]Fe^{2+}



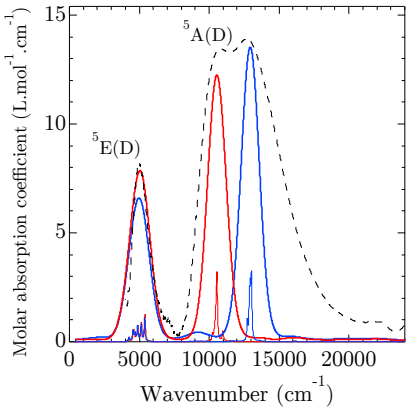
[4,Td]Fe^{2+}



[4,D4h]Fe^{2+}



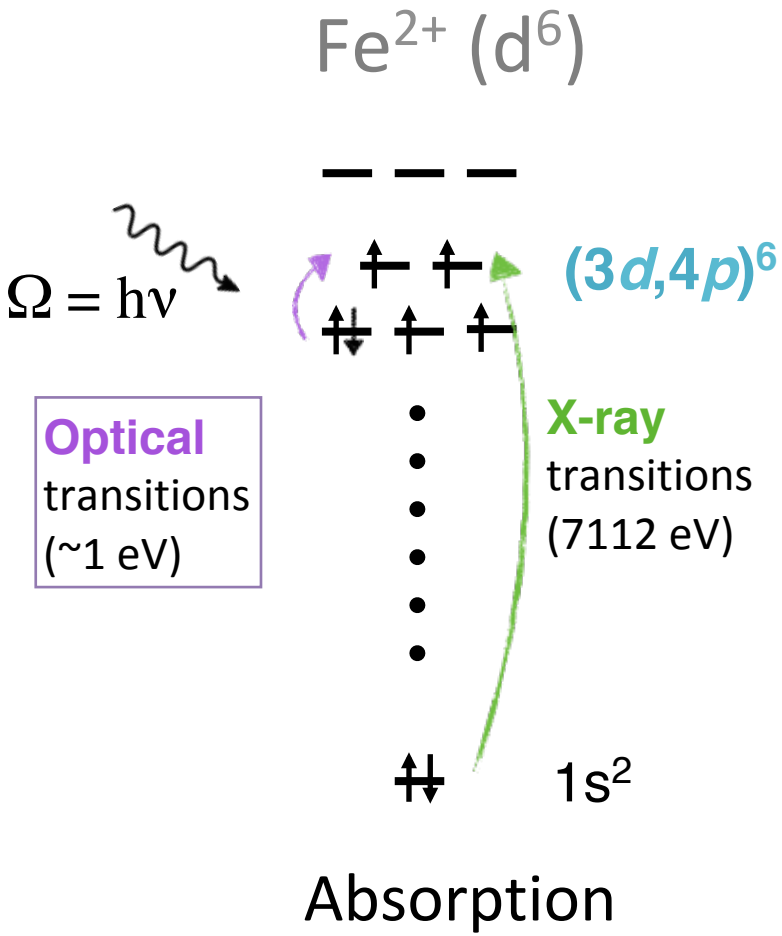
[5,D3h]Fe^{2+}

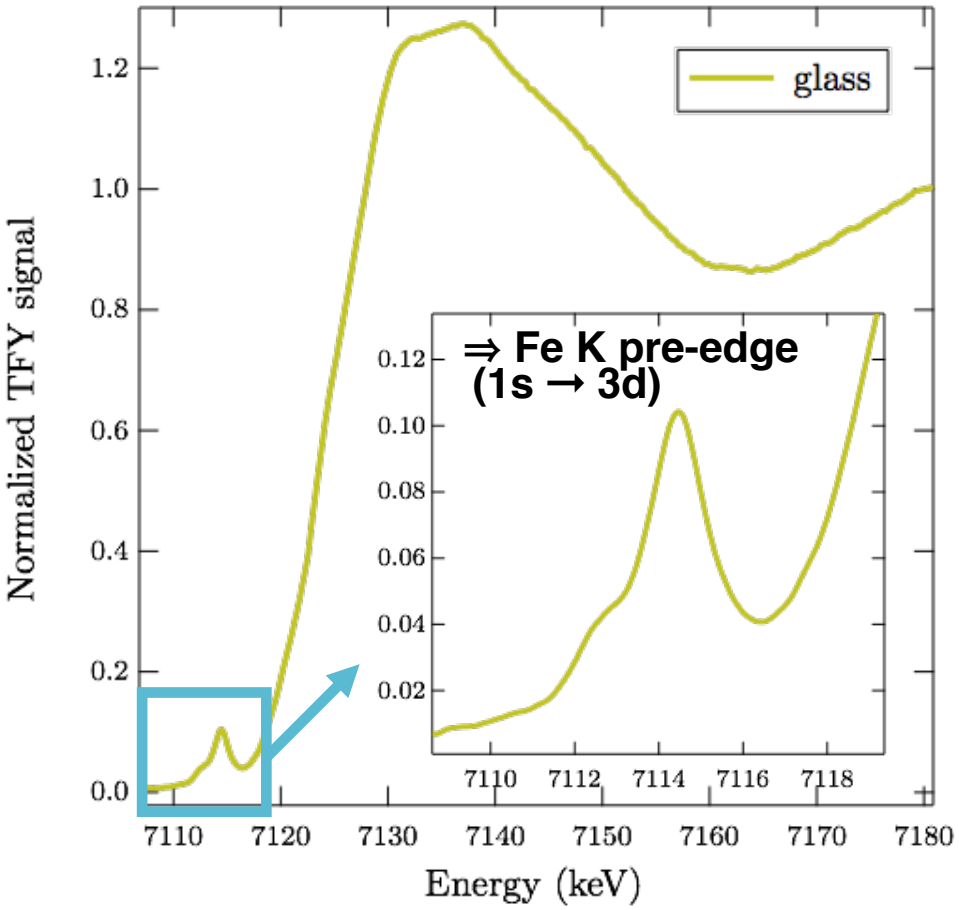


⇒ Multiplet calculations allow to reproduce the optical absorption spectra of Fe^{2+} in a wide variety of site symmetries

Vercamer et al. Physical Review B 94 245115 (2016)

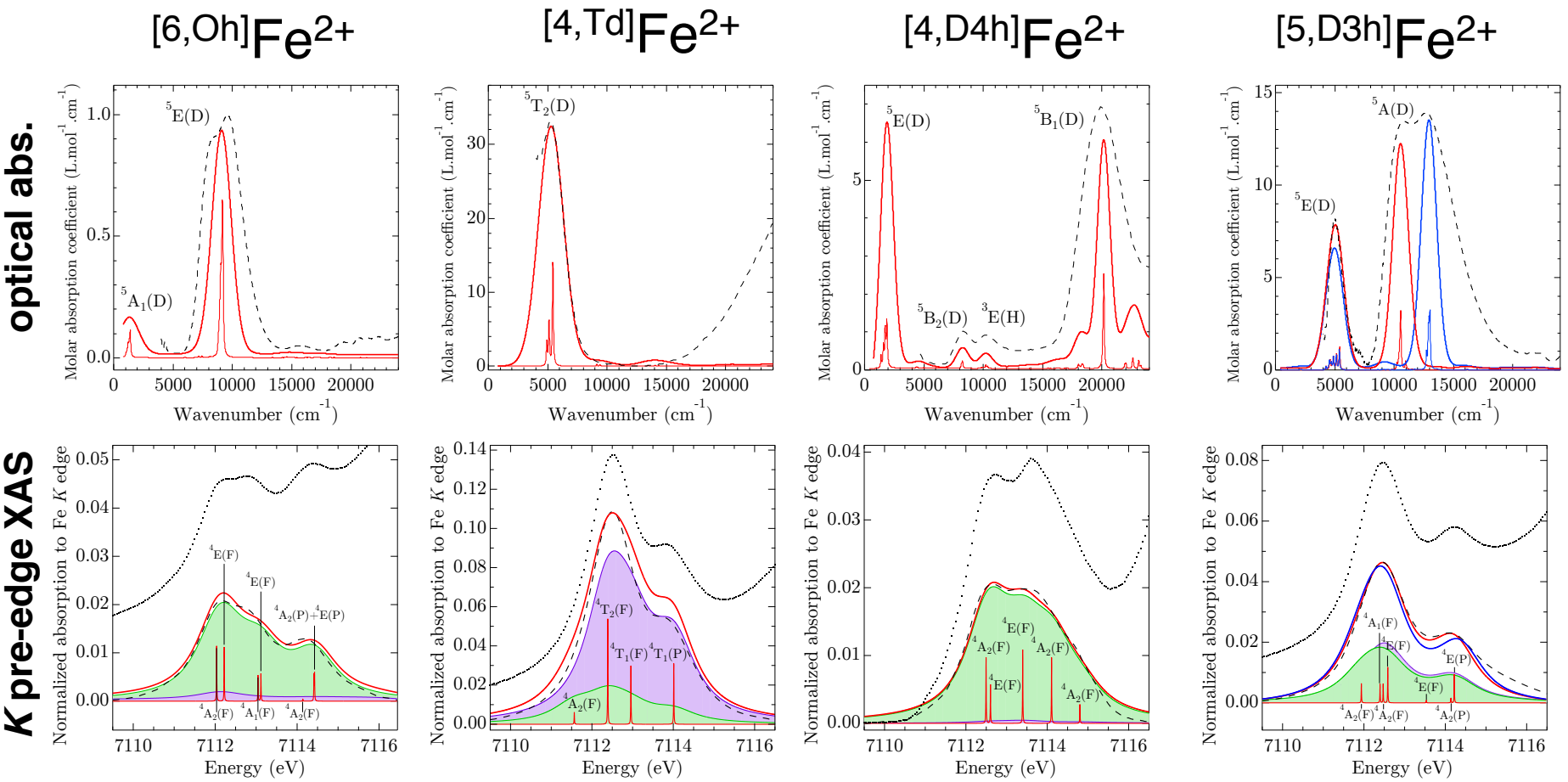
How to probe the 3d levels of Fe ?





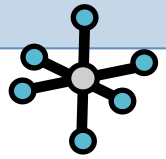
XAS measured @ ID26 (ESRF)

EXP. VS CALC. FOR Fe^{2+} IN MINERALS

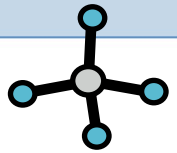


Vercamer et al. Physical Review B 94 245115 (2016)

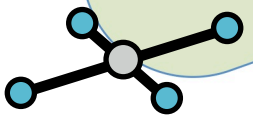
EXP. VS CALC. FOR Fe^{2+} IN MINERALS



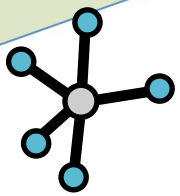
[6,Oh]Fe^{2+}



[4,Td]Fe^{2+}

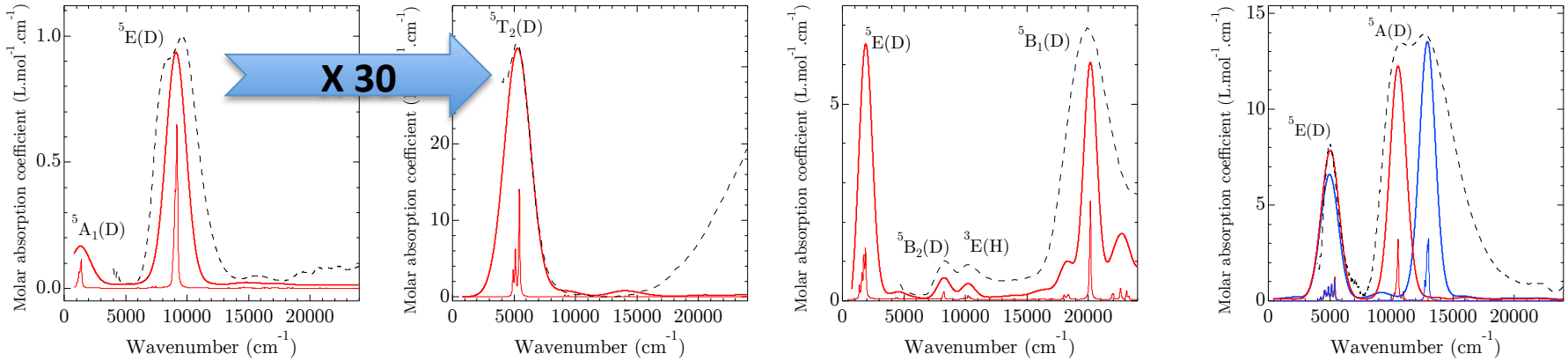


[4,D4h]Fe^{2+}

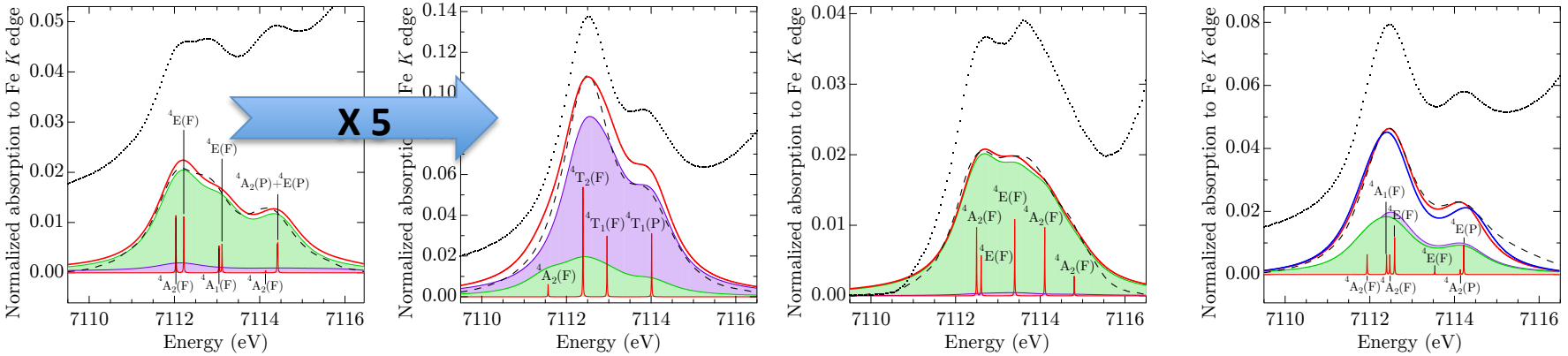


[5,D3h]Fe^{2+}

optical abs.

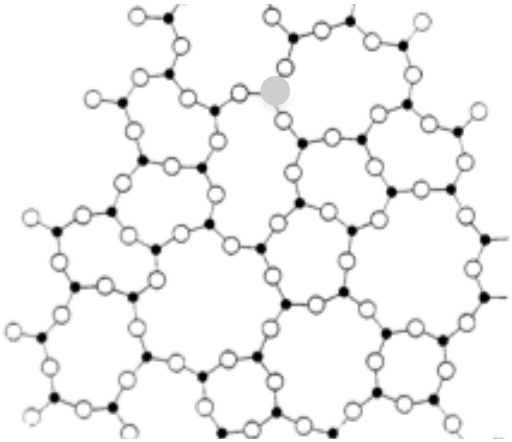


***K* pre-edge XAS**

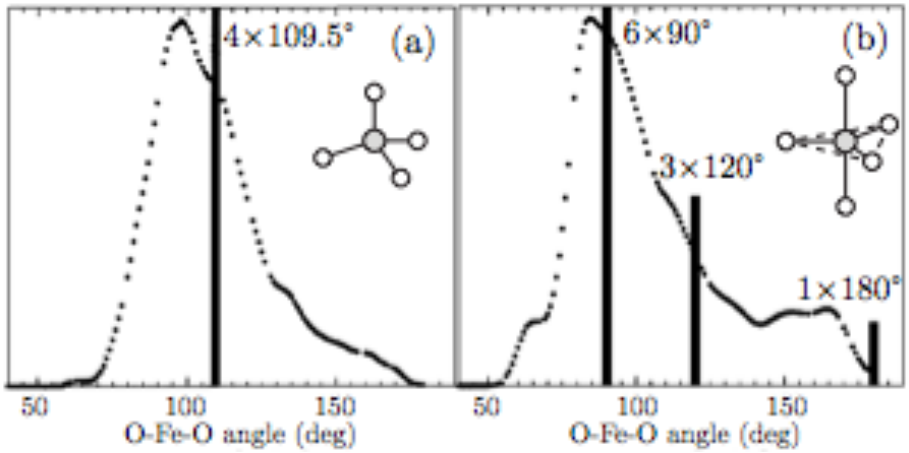


Good correlation experiment/calculation

Fe environment in glasses ?



MD calculations of $CaO\text{-}FeO\text{-}2SiO_2$ glass



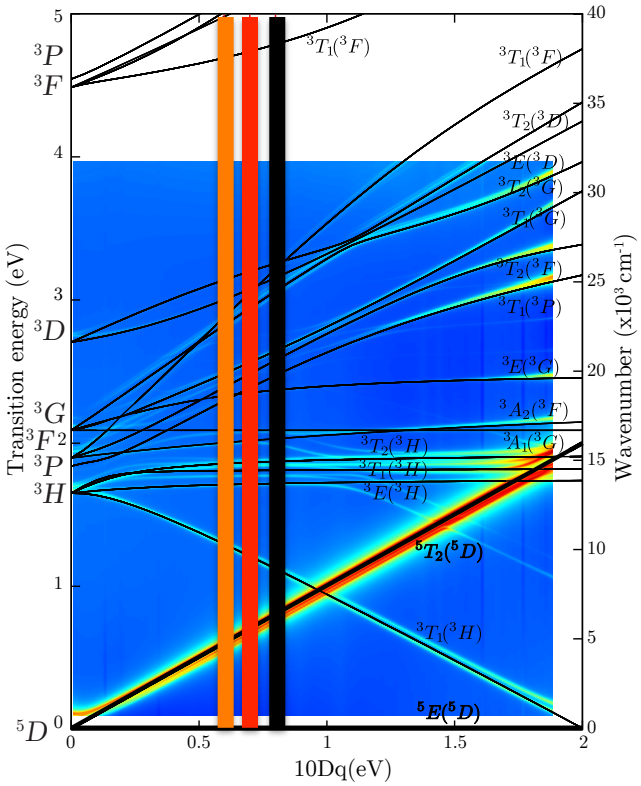
from Rossano *et al.* 2000

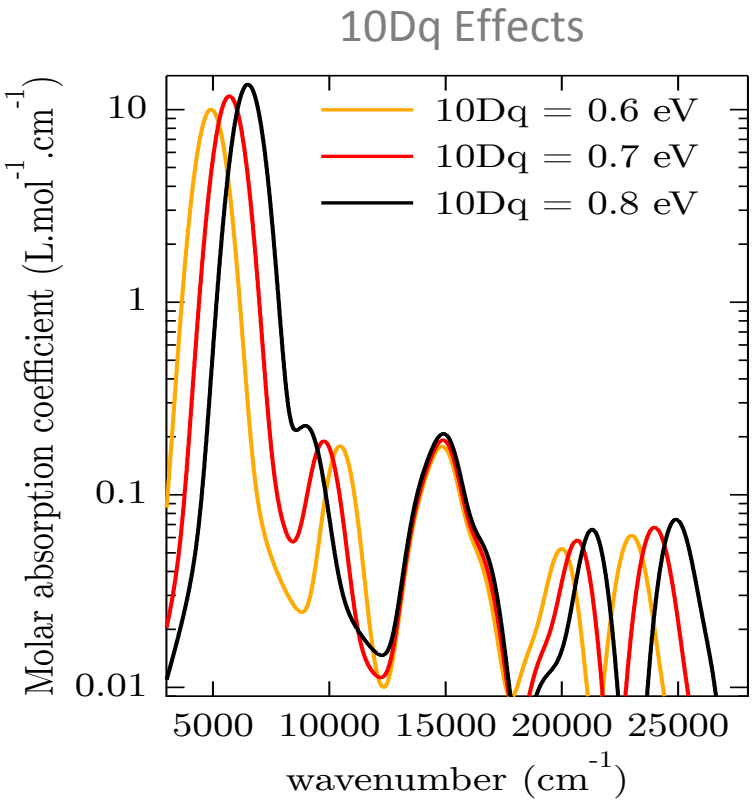
⇒ Distribution of Fe environment in glasses

⇒ By distributing the crystal field parameters around the values of crystalline samples

Fe environment in glasses ?

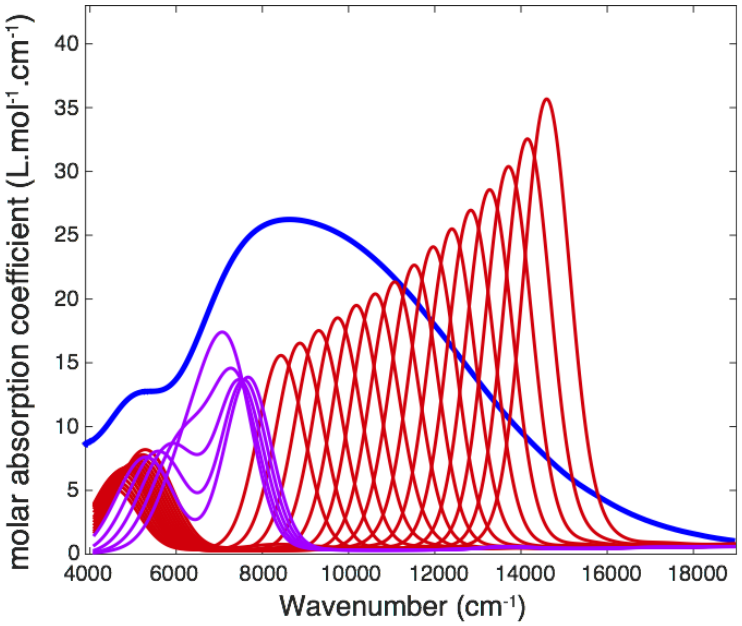
Thanks to multiplet calculations, we can probe the effects of parameters 10Dq and β

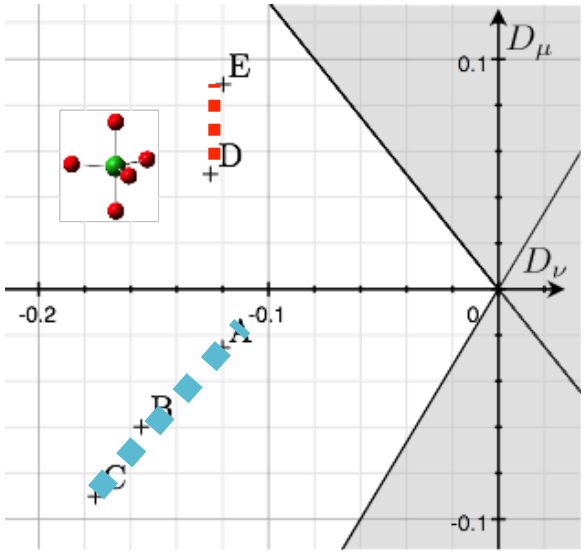




APPLICATION TO GLASSES…

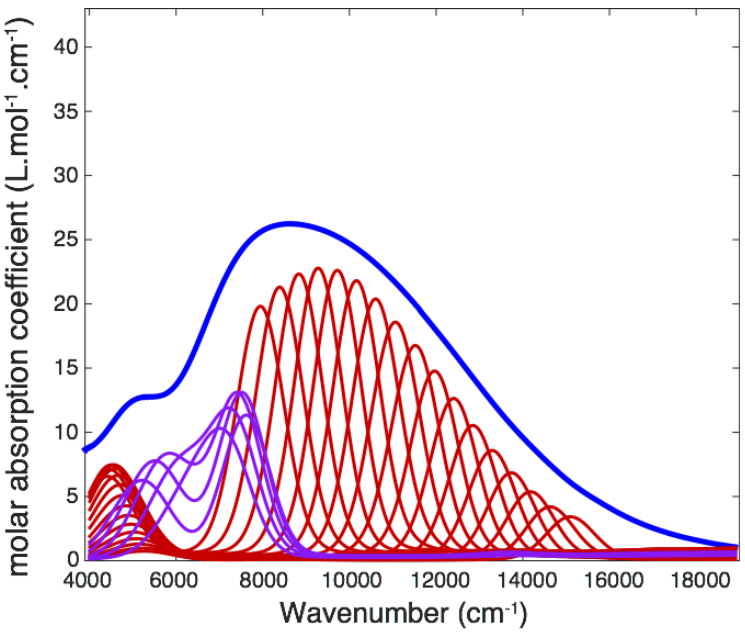
Example with 25 optical spectra calculated with a D3h symmetry
Uniform proportion of each site

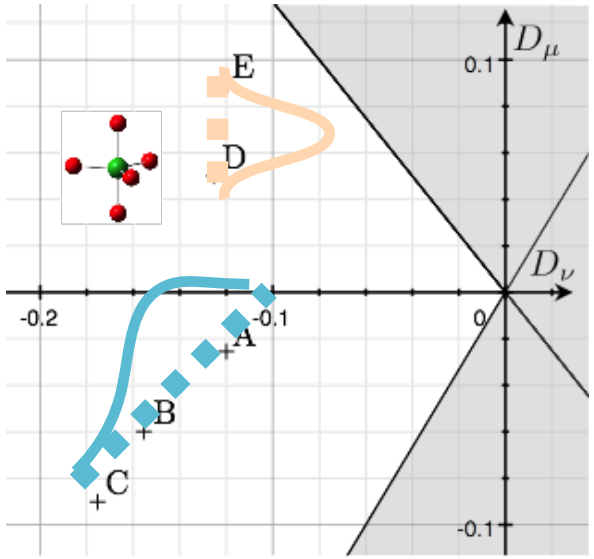




APPLICATION TO GLASSES…

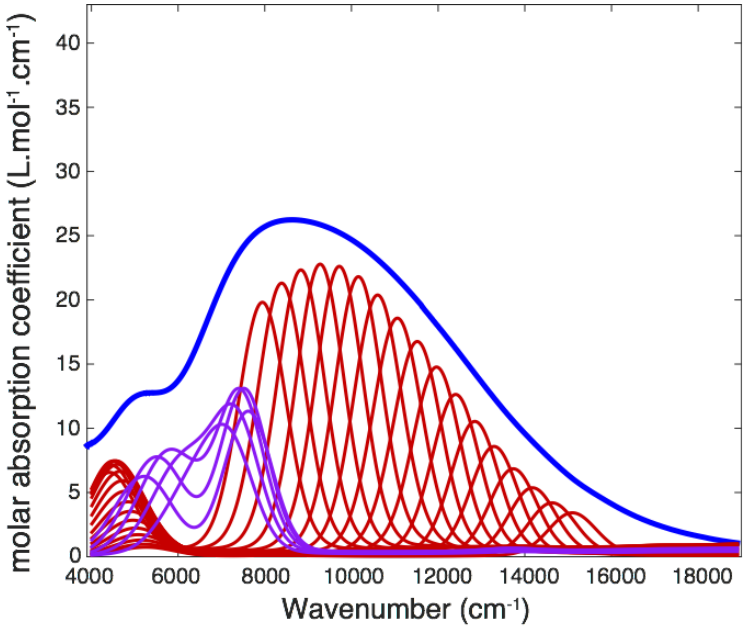
Example with 25 optical spectra calculated with a D3h symmetry
Distributed proportion of each site

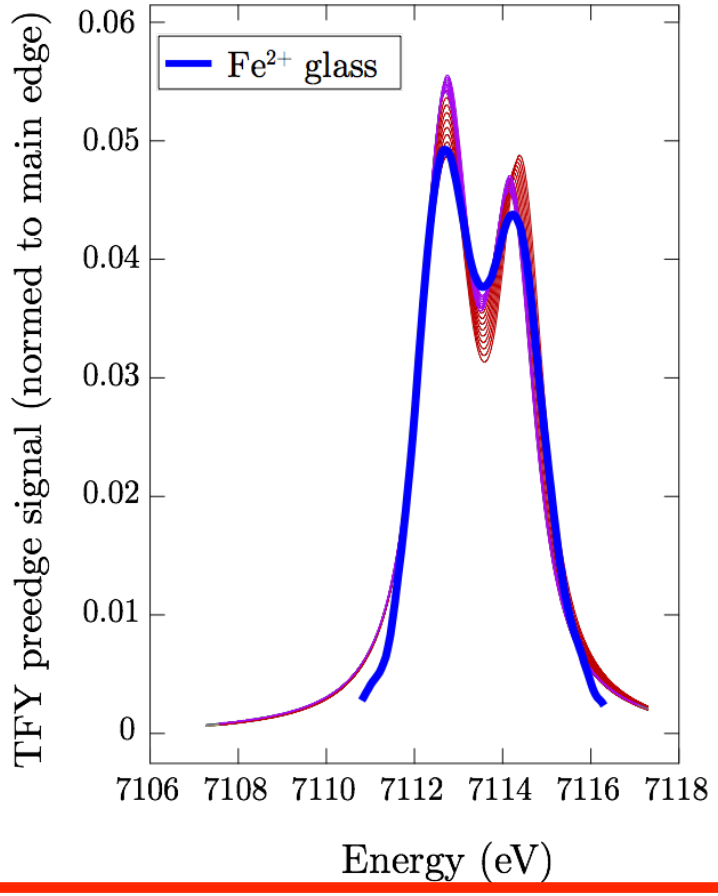




APPLICATION TO GLASSES…

Example with 25 optical spectra
Distributed proportion of each site





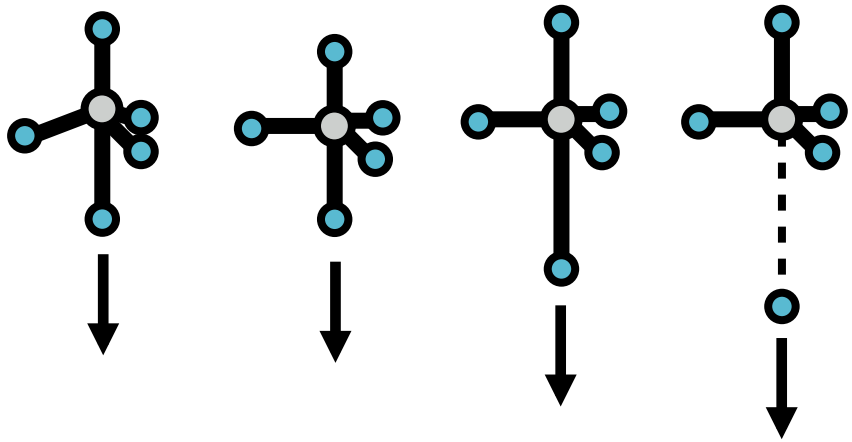
⇒ XAS Fe K pre-edge is less sensitive than OAS for slight distribution of Fe^{2+} sites

A GENERAL COMMENT…

Fe^{2+} optical signature in glass can be understood with a limited distribution of ligand field parameters in C_{3v} geometry

→ preferential C_{3v} sites have been found

→ several kind of **5-fold** sites from pure 5-fold to 4+1 ?

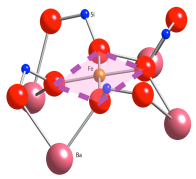


? Can we still talk about coordination number if the structure is composed of a distribution of sites?

CONCLUSIONS

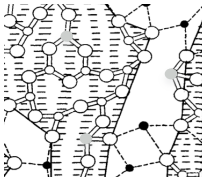
Fingerprint analysis of glasses

Fingerprint brings useful but limited information on structure and spectroscopy of iron in glasses



Multiplet calculations on crystals

Multiplet calculations are fast and adapted to the multi-spectroscopic approach to extract tendencies



Application: calculation of Fe^{2+} in glass

5-fold Fe^{2+} have to be considered for optical interpretation.
Site distribution to reproduce glass amorphous nature.
Optical absorption → sensitive to slight geometry variations

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