The University of Sydney

Phosphate adsorption on goethite: *in-situ* ATR-FTIR spectroscopy, batch adsorption study, surface complexation modelling and density functional theory calculations

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Soil phosphorus

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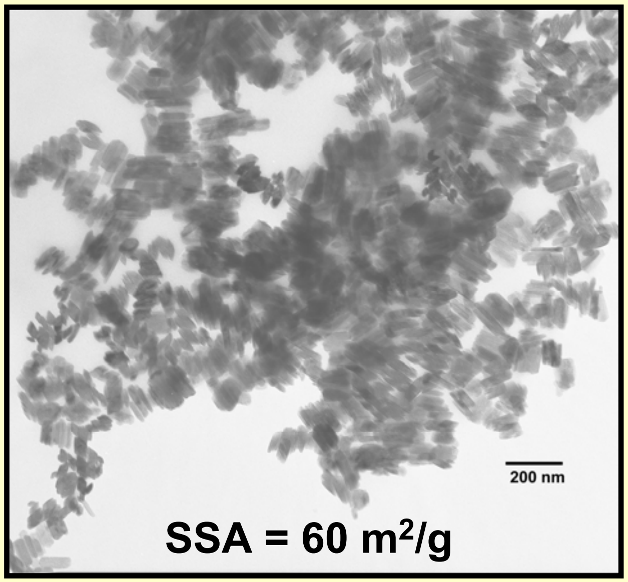
Goethite synthesis and batch adsorption experiments



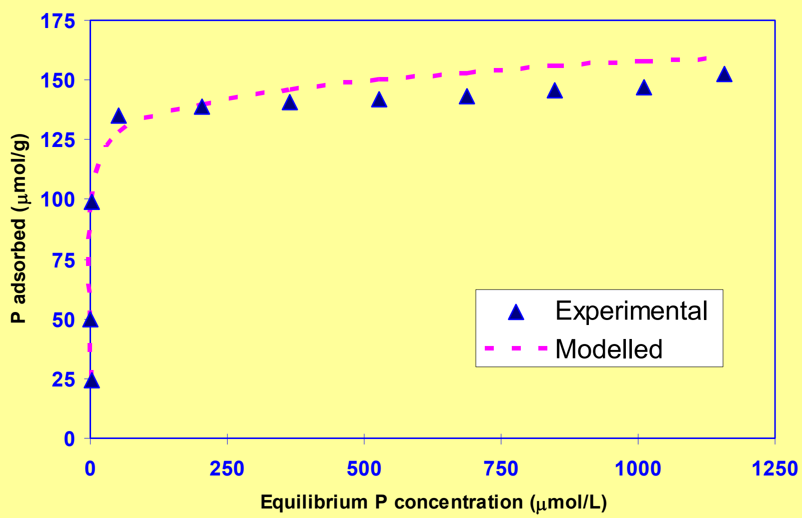
- Goethite synthesized by $Fe(NO_3)_3$ hydrolysis with NaOH (OH/Fe = 2) at room temp. for 50 h.

- Adsorption isotherm at 23±2°C using 0.4 g L^{-1} suspension in 0.01 M NaCl containing 0-2 ml of 10 mM NaH_2PO_4 and equilibrium pH 4.

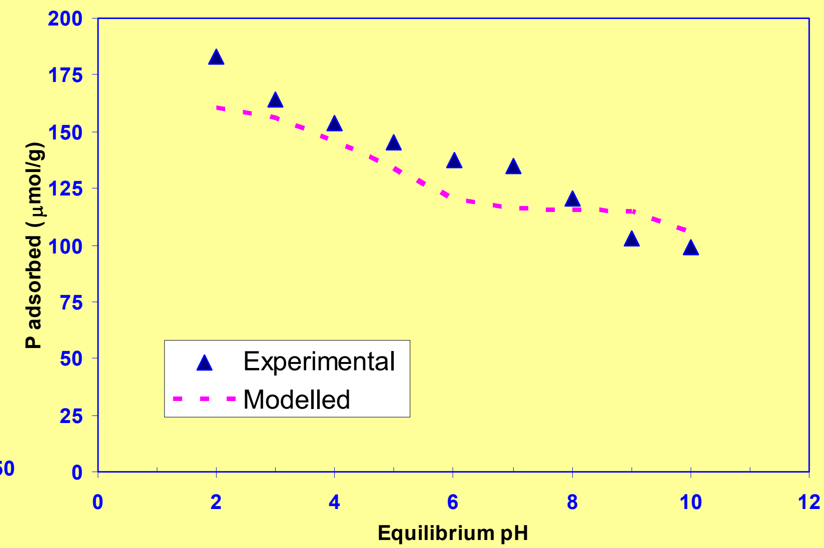
- Adsorption envelope at pH 3-10.

Surface complexation modelling: CCM monodentate species

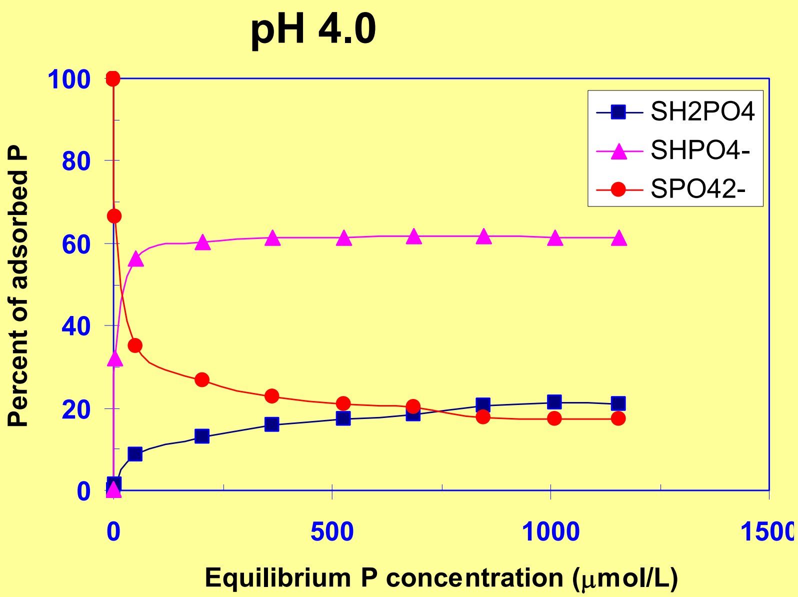
pH 4.0

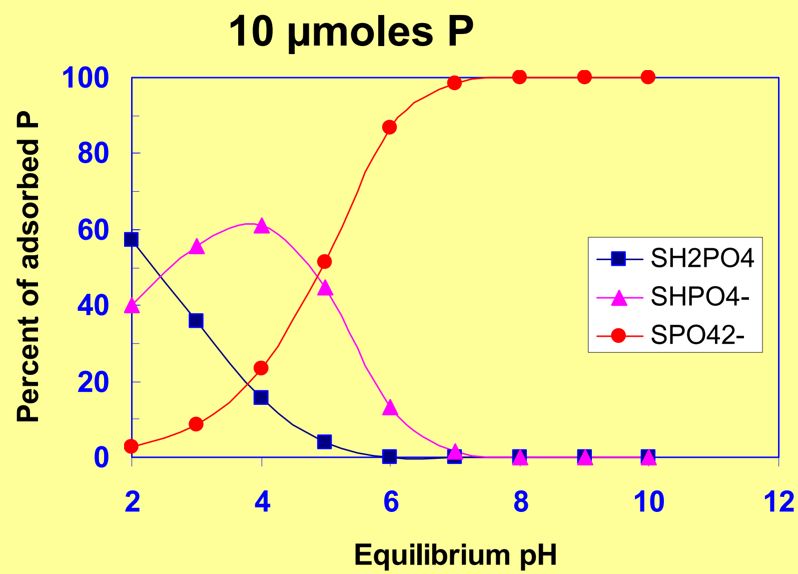


10 μmoles P



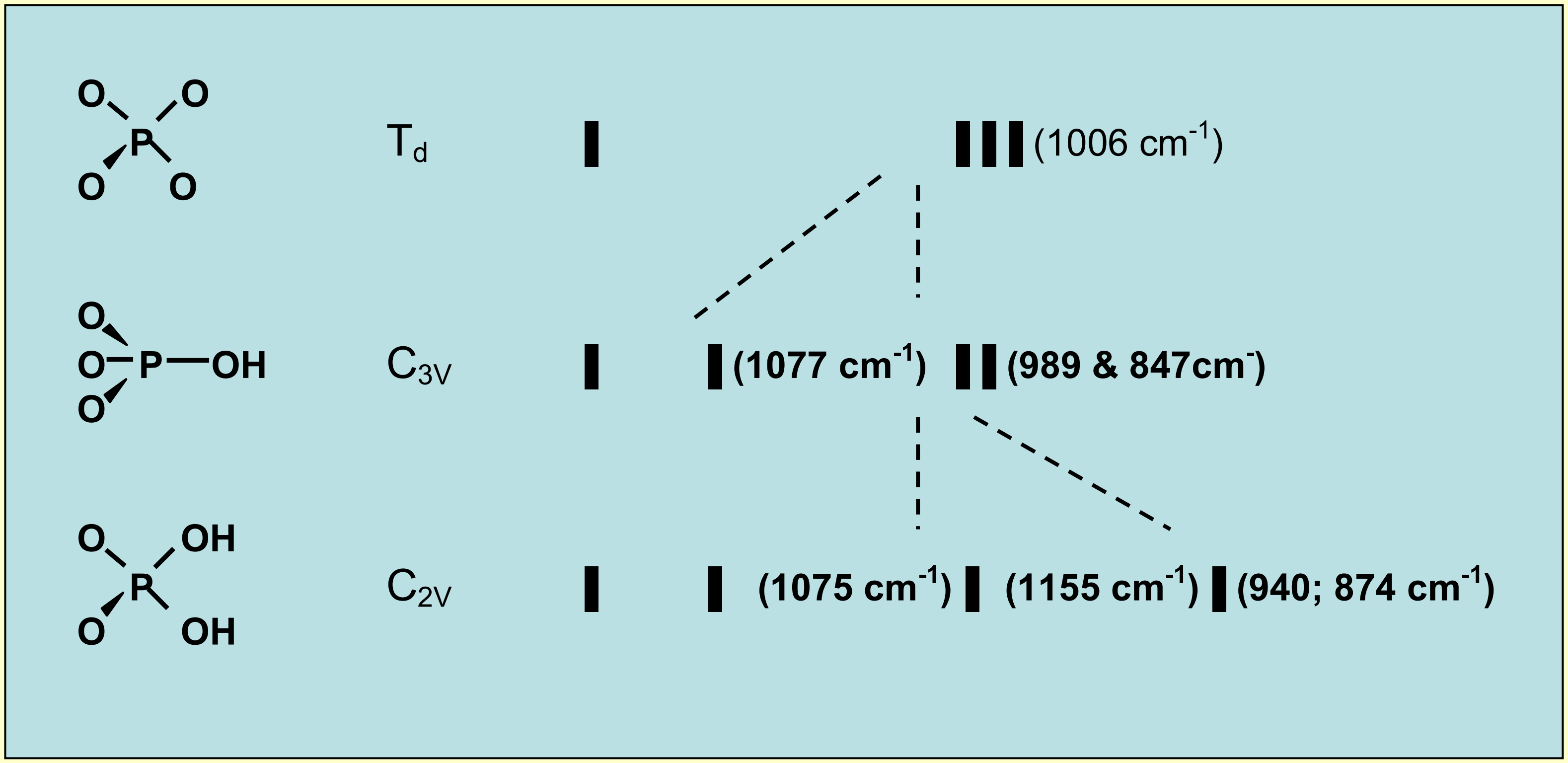
Constant Capacitance Model showed the formation of three monodentate species





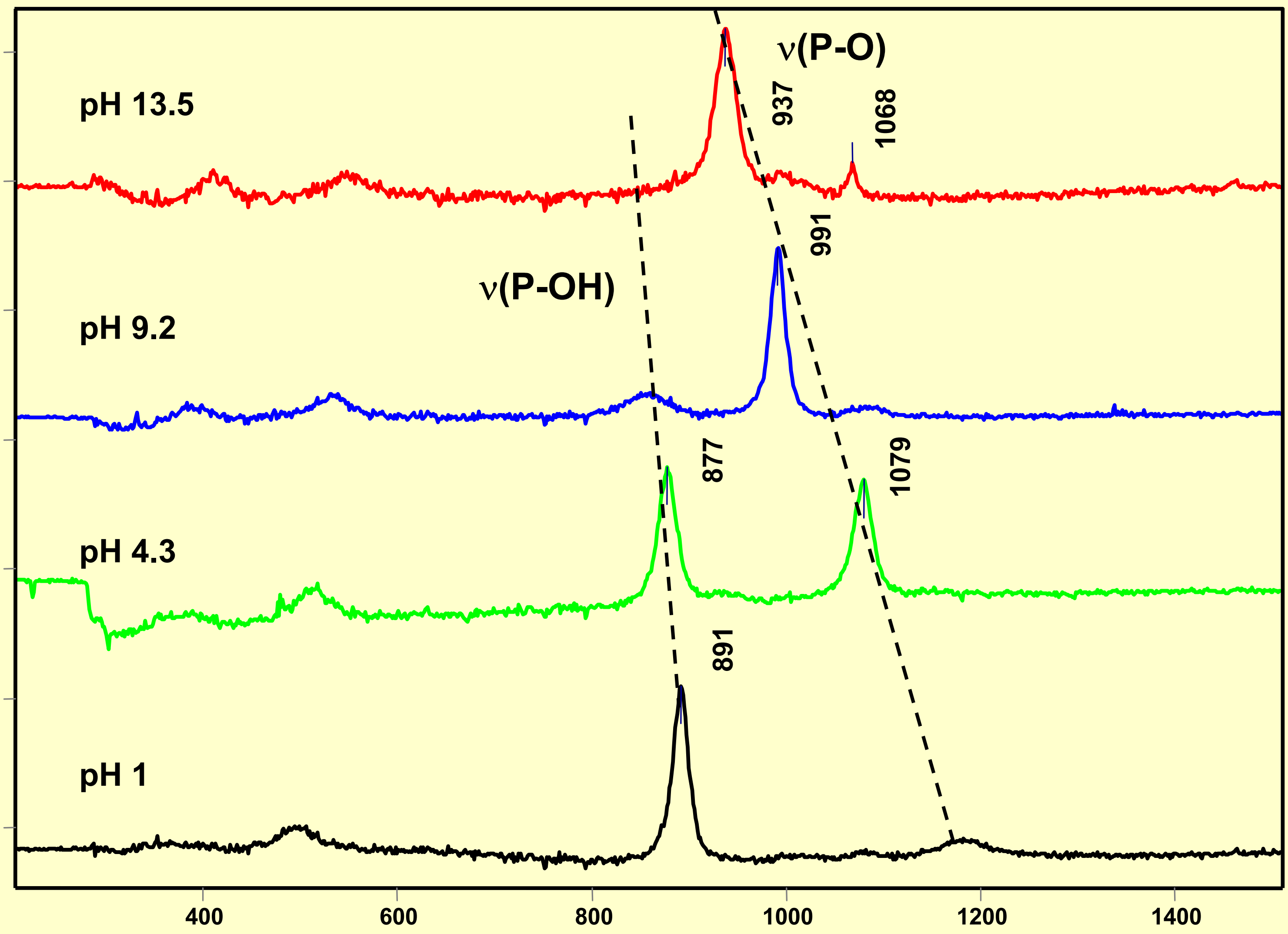
FTIR bands of orthophosphate species

- **Molecular symmetry of orthophosphate species is lowered on protonation**

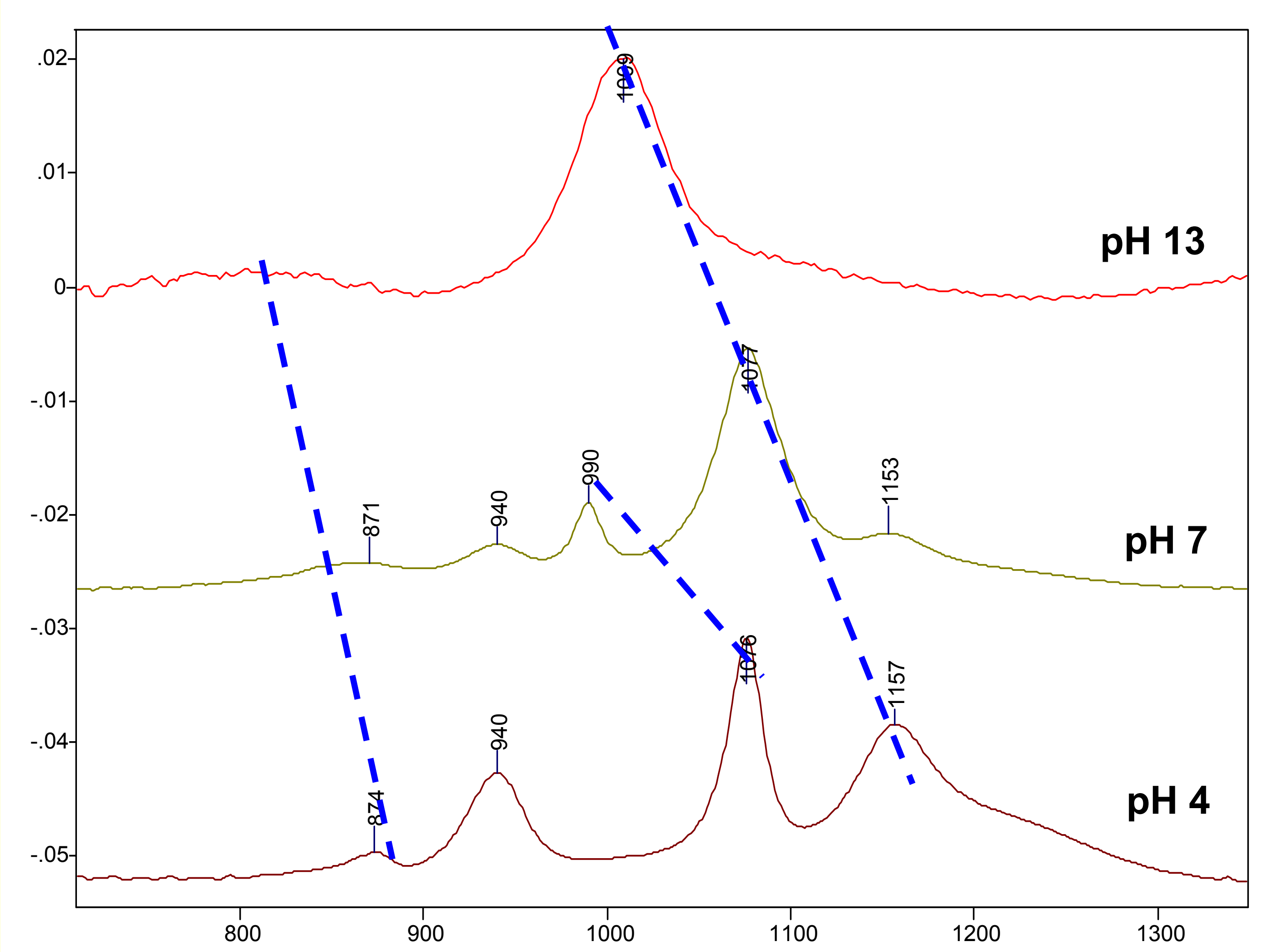


H_3PO_4: C_{3v} symmetry and three stretching modes at 1174, 1006 and 890 cm^{-1}.

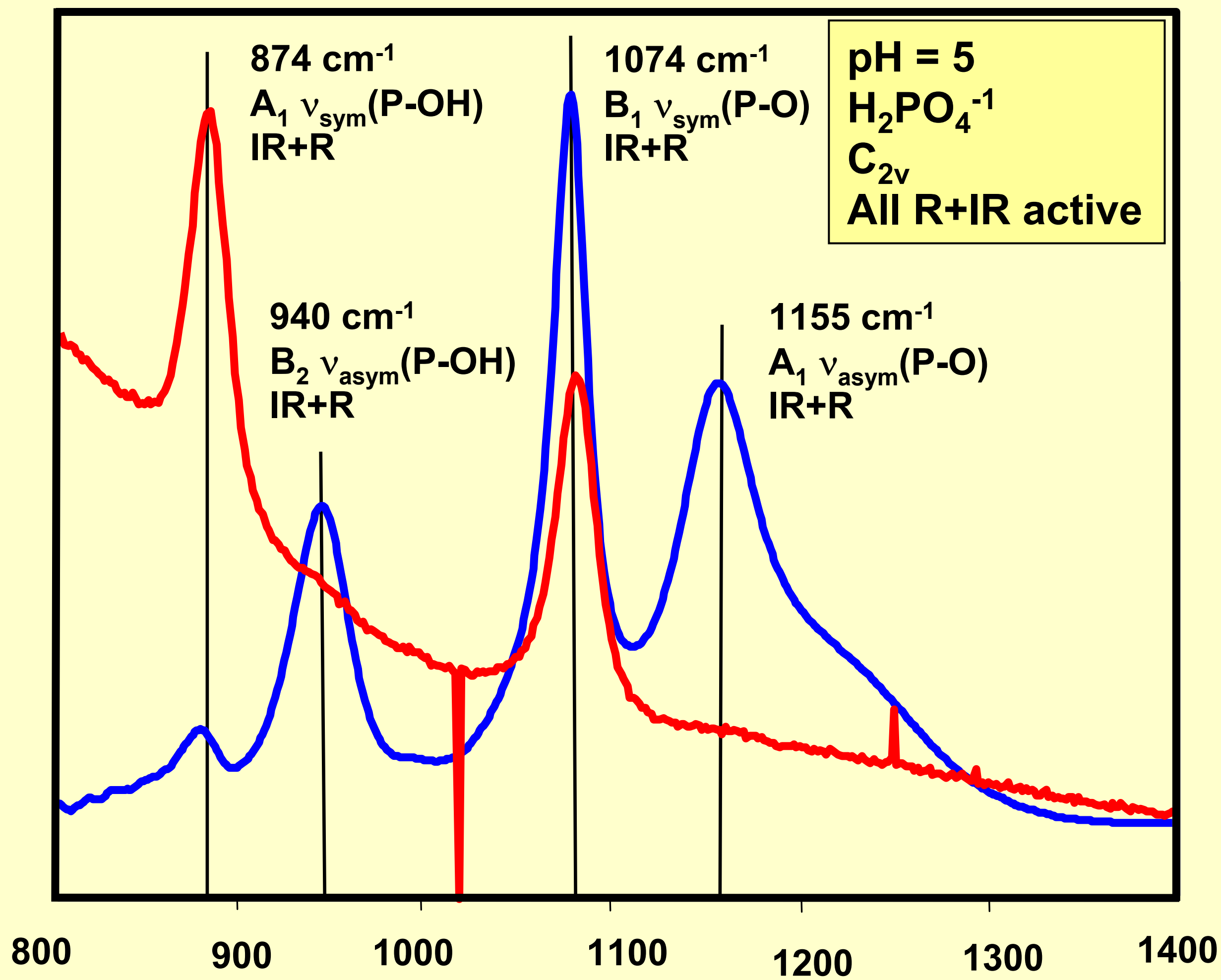
Raman spectra of 50 mM KH_2PO_4 – Non-polarized



ATR-FTIR spectra of 100 mM PO_4



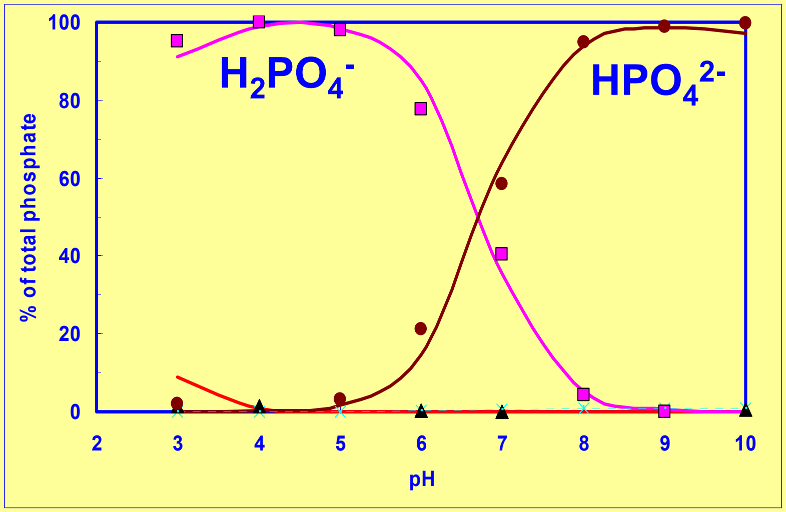
Complementary relationship between Raman and IR data; absorption bands sensitive to phosphate protonation.

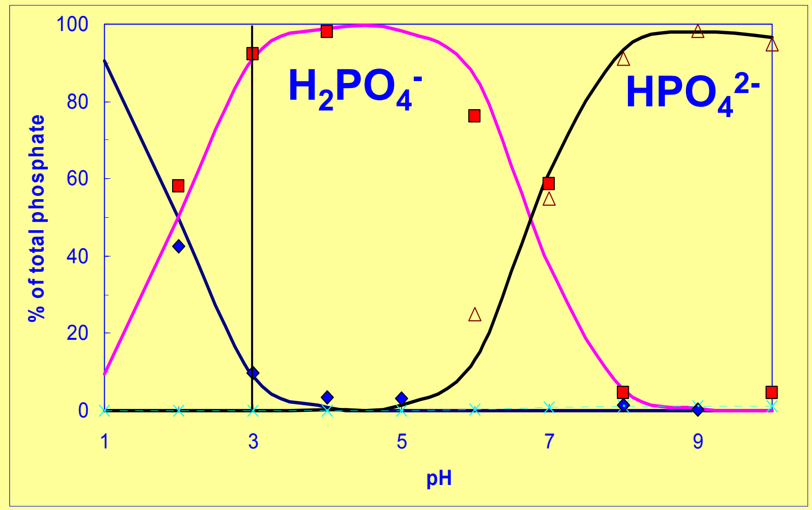


Raman (red) and ATR-FTIR (blue) spectra at pH 5 (C=100 mM)

Partial Least Square fits for ATR-FTIR & Raman spectra

(Lines represent predicted chemical speciation; data points correspond to spectroscopic predictions)



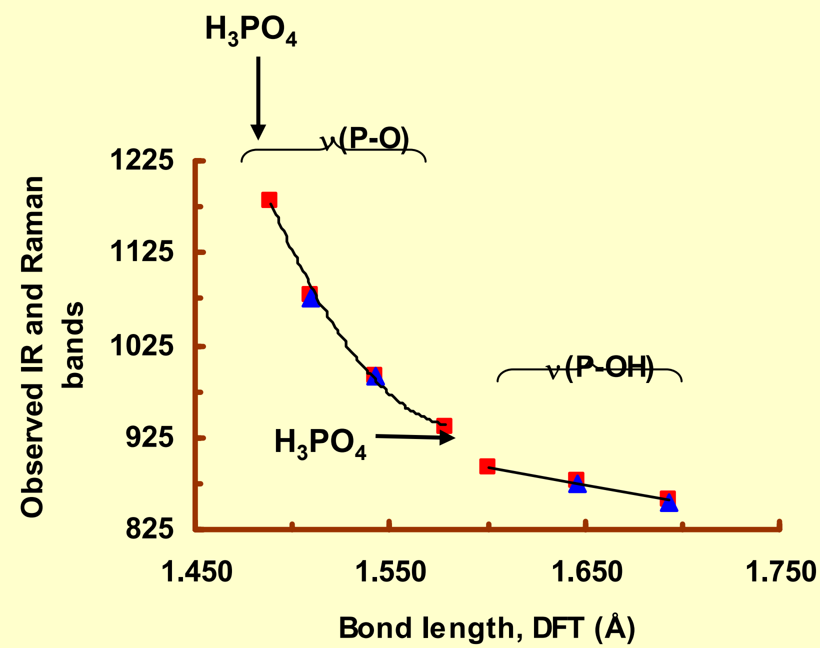


- **Excellent agreement between phosphate speciation obtained by spectroscopic data and chemical species obtained by geochemical model**

DFT bond lengths and observed IR/Raman band positions

Species	Avg P-O	Raman	IR
H_3PO_4	1.489	1182	
H_2PO_4	1.510	1079	1076
HPO_4	1.543	992	990
PO_4	1.578	937	

Species	Avg P-O	Raman	IR
H_3PO_4	1.600	892	
H_2PO_4	1.646	877	874
HPO_4	1.694	857	854



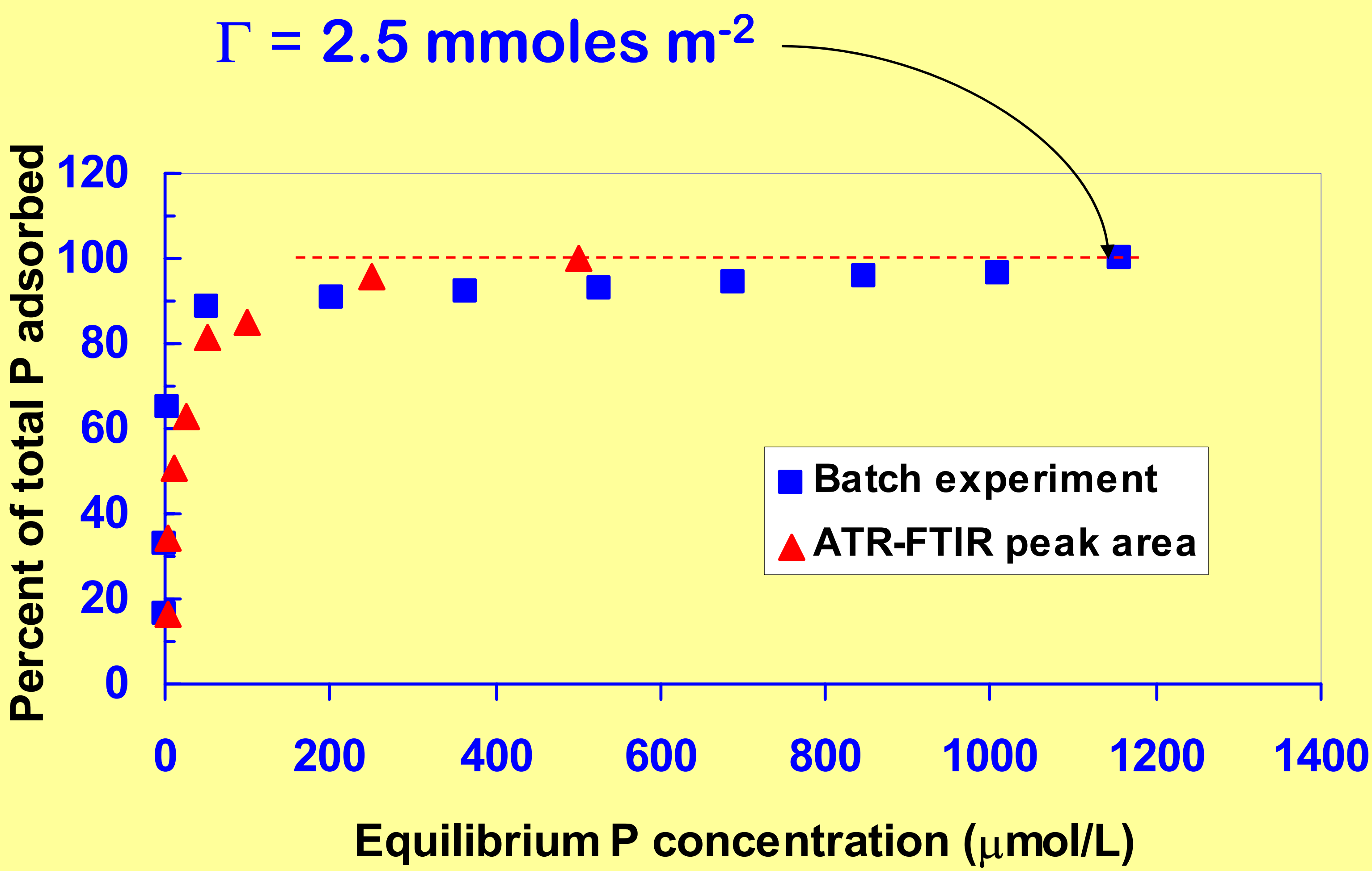
Solution spectroscopy and DFT calculations: summary

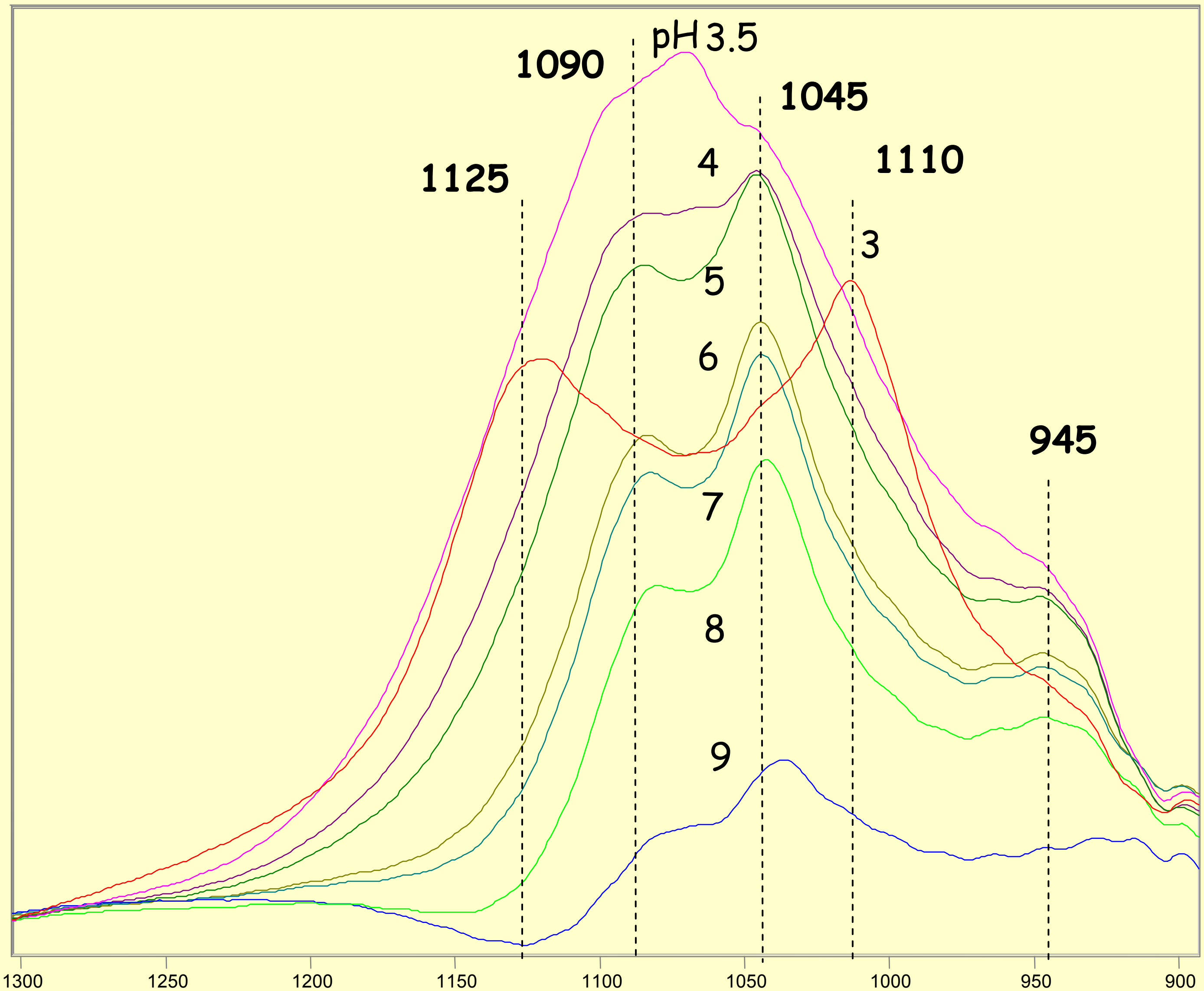
- Complementary data obtained from Raman and IR spectroscopies.
- Pronounced changes in IR and Raman bands in the two vibrations (P-O and P-OH) upon phosphate protonation.
- Bond length increases with increasing negative charge (ie increasing pH) of phosphate species.
- Observed position of bands (IR and Raman) decreases with increasing bond lengths for P-O and P-OH bands.

In situ ATR-FTIR experiments

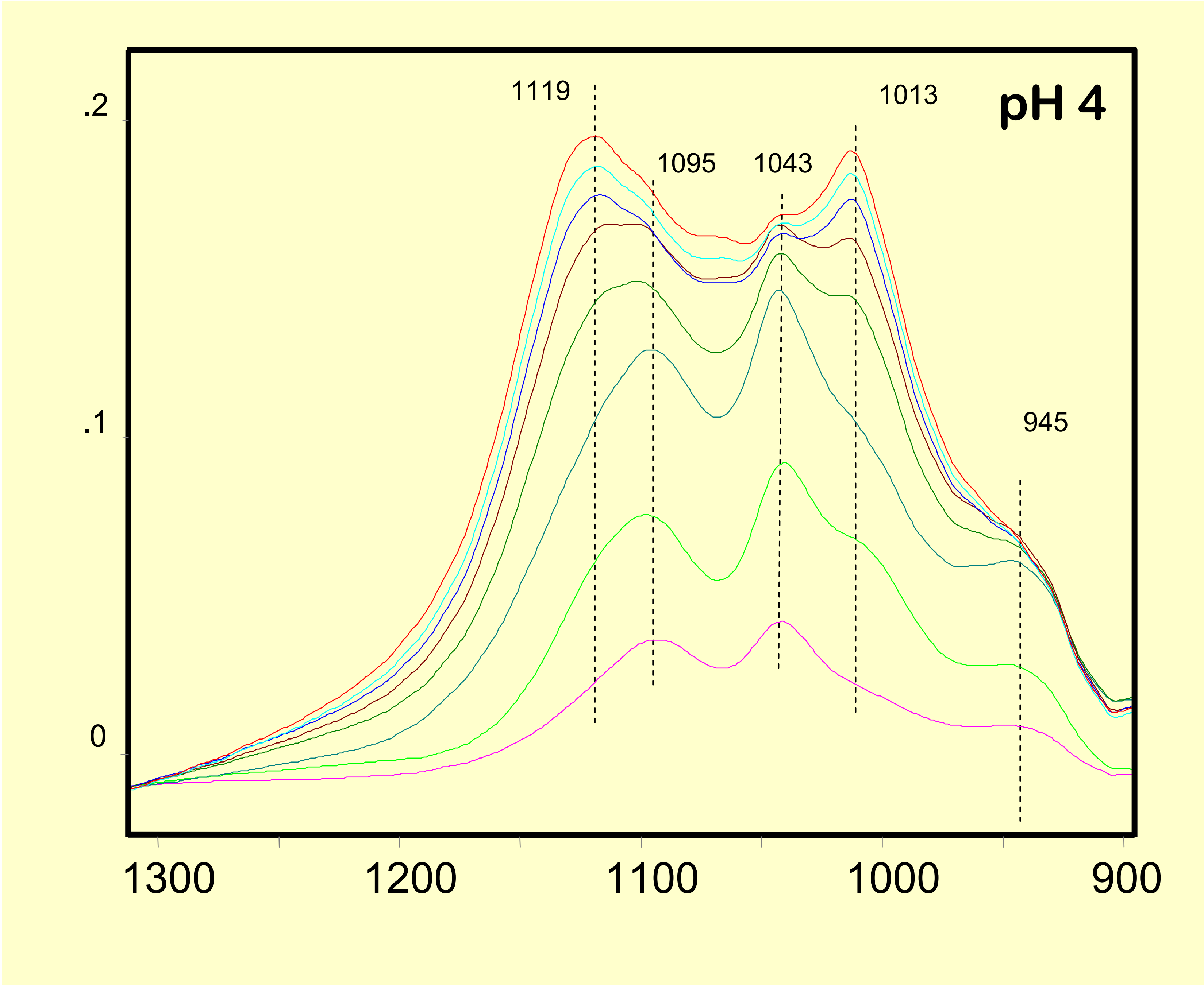
- 2.5 mg deposit of goethite on ZnSe internal reflection element (N_2 cooled MCT detector)
- Equilibrated goethite deposit with 0.01 M NaCl at pH 4 (no loss of goethite observed).
- Introduced PO_4 at pH 4 (concentration varied from 2.5 to 500 mM); flow rate of 1.4 mL min^{-1}. Experiment lasted ~ 36 hours.
- pH was continuously monitored to ± 0.02 pH units
- For adsorption envelope - initial PO_4 concentration was 25 mM at pH 10 and pH was sequentially lowered to 3 in one-unit pH increments.
- Integrated intensity and band between 1335 and 805 cm^{-1} were considered.

In situ ATR-FTIR data perfectly follow the trend observed in the batch adsorption experiment.





pH 3.5
1090
1045
1125
4
1110
3
5
6
945
7
8
9
1300
1250
1200
1150
1100
1050
1000
950
900



pH 4
1119
1095
1043
1013
945
.2
.1
0
1300
1200
1100
1000
900

IR frequencies observed for orthophosphate species adsorbed at different equilibrium P concentrations (2.5-500 µm) at pH = 4; and at different pH values (3-10) in equilibrium with 25 µm P.

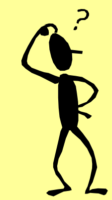
Equilibrium P (µM)	IR band frequency (cm^{-1})							
2.5		1095	1042	1011	943		852	
5	1124	1097	1043	1014	942		849	
10	1133	1096	1044	1015	943		858	
25	1130	1098	1045	1015	943		858	
50	1127	1088	1044	1008	953	932	854	
100	1128	1090	1042	1009	964	935	855	
250	1129	1092	1042	1009	967	936	871	840
500	1129	1095	1048	1009	955	932	871	838
Equilibrium pH								
3	1130	1095	1046	1011	947		865	
4	1122	1090	1046		946	861		
5		1090	1042	1003	942	851		
6		1090	1043		941	856		
7		1089	1043	1009	942			
8		1087	1043		944			
9		1082	1042	1009	945			
10		1080	1041	1009	926			

In situ ATR-FTIR study of PO_4 sorption to goethite modified IRE

- **Phosphate molecules symmetry is lowered upon adsorption to goethite; and with increasing loading and decreasing equilibrium pH.**

- **The data in good agreement with the solution spectroscopic data, ie pronounced changes in the vibrations (P-O and P-OH) upon phosphate protonation, (and bond length increases and position of bands decreases with increasing solution pH).**

Adsorption mechanisms ?



Kwon and Kubicki (2004): MO/DFT calculations

(ATR-FTIR data from Arai & Sparks (2001) and Persson et al. (1996)

- **pH 4.2-5.7: diprotonated bidentate complex (Persson et al. (1996) interpreted diprotonated mondentate complex)**
- **pH 7.9-12.8: monoprotonated and diprotonated monodentate complexes**

Rahnemaie et al. (2007): MO/DFT and CD model

(ATR-FTIR data from Tejedor-Tejedor & Anderson (1990)

- **Low pH : protonated monodentate complex (loading dependent)**
- **High pH: monoprotonated bidentate complex**

- **We identified two distinct complexes at different pH and phosphate loadings; however**
- **couldn't distinguish between monodentate and bidentate complexes ?**

Acknowledgements

- Gnanasiri Premachandra (Purdue University) for his help in FTIR and Raman spectroscopy work;
- Clay Minerals Group of the Mineralogical Society for the travel grant.