



# DEPARTMENT OF CHEMISTRY SEMINAR SERIES

## Characterizing the infrared spectra of minerals through ab initio simulation

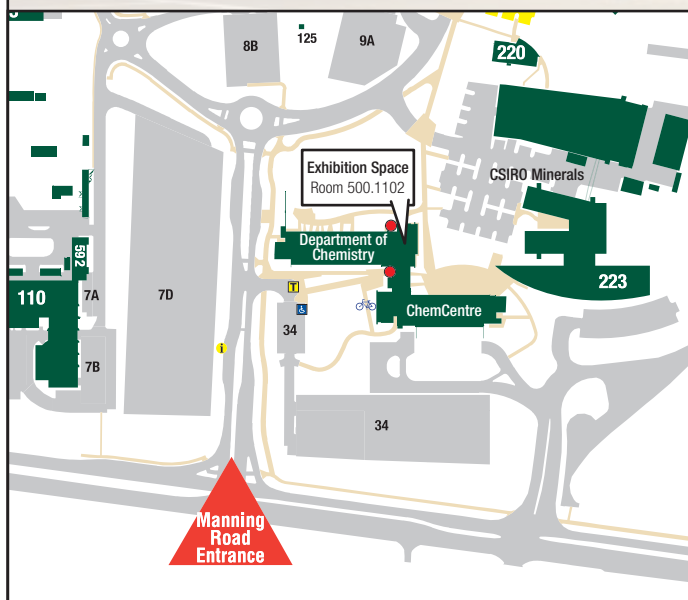
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Ab initio quantum-mechanical simulation has nowadays reached a high level of accuracy in the prediction of infrared (IR) properties, namely frequencies and intensities, of crystalline solids [1,2]. Two advanced case studies are here presented, involving the use of hybrid Hartree-Fock / Density Functional Hamiltonians and localized Gaussian-type basis sets.

A novel approach has recently been proposed [3,4], that makes large use of symmetry to reduce the computational cost for the simulation of disordered structures and mineral solid solutions, with potential applications in the fields of materials science and geochemistry. We here present the investigation of the infrared vibrational spectrum of the Andradite-Grossular garnet solid solution  $\text{Ca}_3\text{Fe}_x\text{Al}_{2-x}\text{Si}_3\text{O}_{12}$  [5]. Relationships can be established between IR properties (frequencies and intensities) and variables such as structural parameters, chemical composition, short-range cation order. Effective comparisons with experimental observations are made possible.

Accurate IR data as obtained from ab initio simulation may represent the starting point for a synergistic approach to characterization of experimental IR reflectance spectra [6,7]. These spectra contain a high amount of information, which is accessible through the mathematical relations among reflectance spectrum, dielectric function and frequencies/intensities of the vibrational modes. Extraction of these data from the experimental spectra requires a delicate best-fit process involving a large number of parameters. Simulation here plays a crucial role, providing the full set of fundamental modes with accurate frequencies and intensities, which is the ideal starting guess for the best-fit. Low intensity fundamentals are identified, whereas peaks not corresponding to fundamental computed modes are recognized as combinations or overtones. Interpretation of almost all the spectral features of the spectra is enabled through a straightforward scheme.



Friday, 20th September 2013 at 4:00 PM  
Exhibition Space, Building 500, Room 1102

For more details about the  
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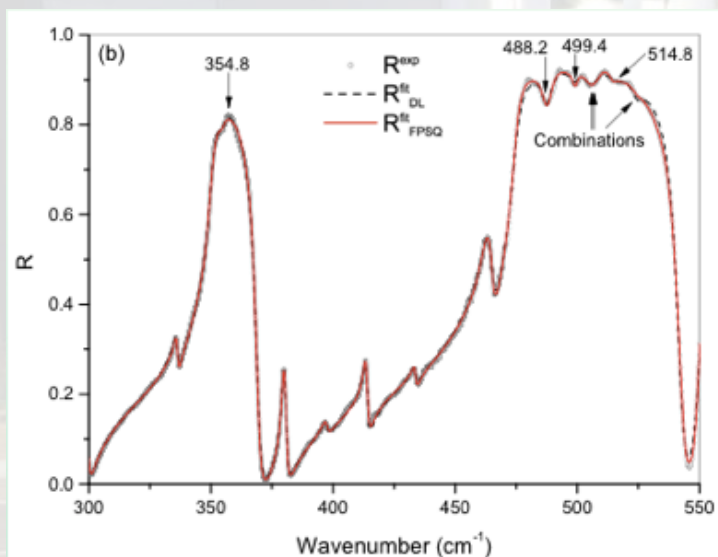
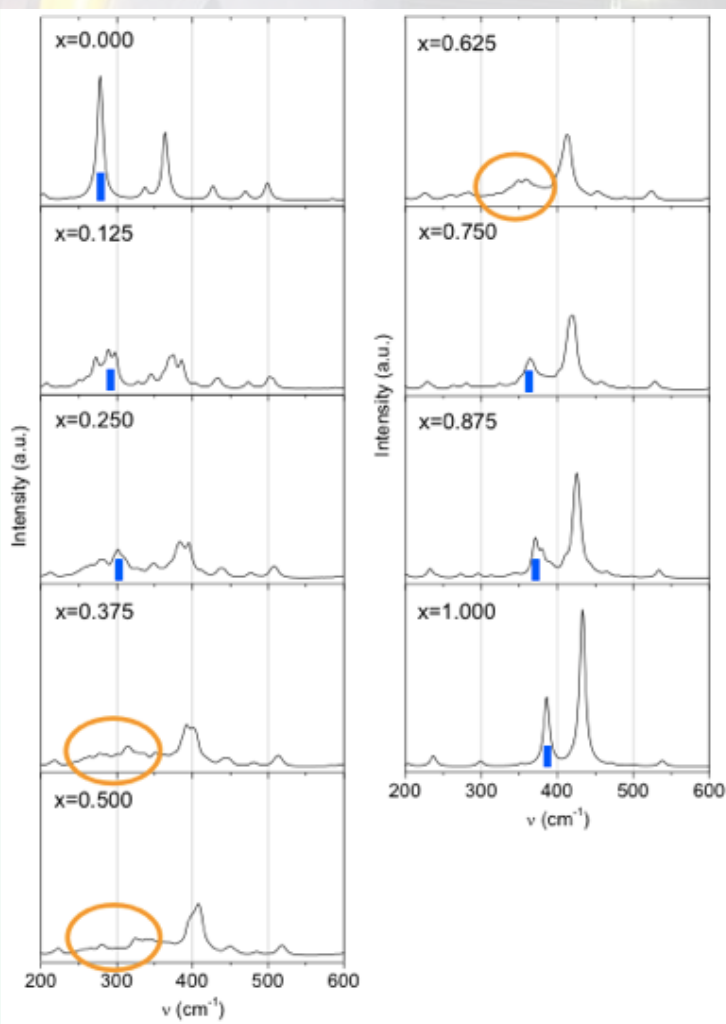
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## References

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- [2] R. Dovesi, M. De La Pierre, A. M. Ferrari, F. Pascale, L. Maschio, C. M. Zicovich-Wilson (2011) *Am. Miner.* 96, 1787-1798.
- [3] S. Mustapha, Ph. D'Arco, M. De La Pierre, Y. Noël, M. Ferrabone, R. Dovesi (2013) *J. Phys.: Condens. Matter* 25, 105401 (16 pp.).
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- [7] M. De La Pierre, C. Carteret, R. Orlando, R. Dovesi (2013) *J. Comput. Chem.* 34, 1476-1485.

**Figure 1 (left).** Behaviour of a low-frequency IR peak of the Andradite-Grossular solid solution with respect to composition.

**Figure 2 (right).** Characterization of the IR reflectance spectrum of ortho-enstatite along the b axis; the 300-550 cm<sup>-1</sup> range is shown. Frequency labels indicate additional IR modes identified using simulation.



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