Invited keynote lecture:

Quantum Mechanical Simulation of the Raman and IR spectrum of Crystalline compounds. The case of Garnets

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Pyrope garnet ($Mg_3Al_2Si_3O_{12}$, cubic, 80 atoms/unit cell) is used to illustrate how quantum-mechanical simulation can be used for the classification and interpretation of the vibrational spectra of crystalline compounds, and then how it can be used as a tool complementary to experimental techniques.

The reducible representation built on the basis of the atomic Cartesian coordinates (80x3-3=237) can be decomposed as follows:

$$\Gamma=3A_{1g}+5A_{2g}+8E_g+14F_{1g}+14F_{2g}+5A_{1u}+5A_{2u}+10E_u+18F_{1u}+16F_{2u}$$

There are 25 Raman ($A_{1g}+E_g+F_{1g}$) and 17 IR (F_{1u}, one mode of this symmetry corresponds to translations) active modes, some of which of low intensity. For this reason the proposed experimental sets are incomplete, or characterized by some large discrepancy with respect to simulation.

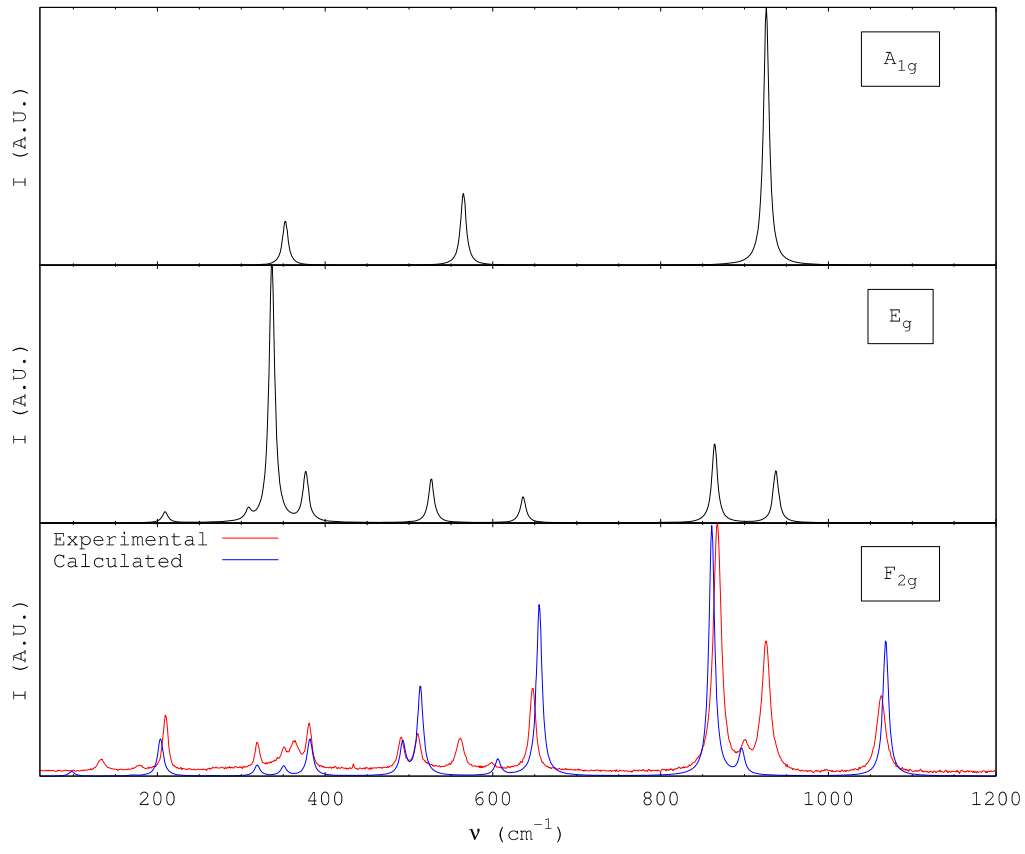

Fig. 1. *Calculated Raman spectra for A_g, E_g and F_{2g} modes in pyrope, the latter compared with observed bands.*

Ab initio quantum-mechanical calculations have been performed by using an all electron gaussian-type basis set and the hybrid B3LYP functional, as implemented in the CRYSTAL code (Dovesi et al, 2009). Complementary tools such as isotopic substitution and graphical animation of the modes are available (http://www.crystal.unito.it/prtfreq/jmol.html). They permit an easy interpretation of the modes (translations of the cations, rotations of sub-units, bending, stretching, and so on).

The frequencies of the 25 Raman active modes are in excellent agreement with the corresponding experimental data (Hofmeister and Chopelas 1991; Chaplin et al. 1991; Kolesov and Geiger 1998; 2000), the mean absolute difference spanning from 5 to 8 cm^{-1}. The intensity, calculated here for the first time for a member of the garnet family, can be compared only qualitatively with the experimental data, that are not tabulated and have been obtained from the plot of the spectra (Kolesov and Geiger 1998). The simulated spectrum permits to characterize the missing modes of the tabulated experiments as very low intensity modes. When attributed a frequency on the basis of interpolation from different sources/experiments, these modes can be affected by a large error (up to 30–40 cm^{-1} difference with respect to simulation).

Figure 1 shows the simulated spectrum for the A_{1g}, E_g and F_{2g} symmetry. The last is compared with the experimental spectrum. In Table 1 the modes showing the most relevant isotopic shift in the simulation or in the experiment (Kolesov and Geiger 1998) are reported; it turns out that the agreement is quite satisfactory for most of the modes, with a couple of exceptions that will be discussed during the conference.

Table 1. *List of calculated positions of Raman bands of pyrope garnet, and their isotopic shifts.*

	Calculated			Kole-Geig 1998
Symm.	ν	$\Delta\nu(cm^{-1})$	$\Delta\nu(\%)$	$\Delta\nu\%$
A_g	352.5	0.0	0.00	0.03
E_g	205.5	3.7	1.80	1.33
	308.2	0.3	0.08	3.52
	331.7	4.8	1.44	1.45
F_{2g}	94.8	3.1	3.27	3.68
	201.9	1.8	0.89	0.85
	318.7	0.3	0.09	0.09
	492.5	0.1	0.03	0.08
	513.3	0.2	0.04	0.06
	655.1	0.2	0.03	0.09
	1067.8	0.5	0.05	0.02

References:

Chaplin T, Price GD, Ross NL (1998) Computer simulation of the infrared and Raman activity of pyrope garnet and assignement of calculated modes to specific atomic motions. Am Mineral 83:841–847

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