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RAMAN SPECTRA WITH CRYSTAL14[*]

Lorenzo Maschio, Roberto Dovesi
Dipartimento di Chimica,
and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces)
Università di Torino
lorenzo.maschio@unito.it

A new, fully analytical method for simulating Raman spectra in periodic systems has been recently implemented in the CRYSTAL code, that uses a local basis set. We review the features of this development, and document its accuracy in reproducing the experimental spectrum of Metal-Organic frameworks.

The simulation of vibrational spectra of crystalline materials is of diffuse interest in both fundamental and applied research. Raman spectroscopy is one of the most effective experimental techniques in mineralogy, solid state physics and chemistry and materials science. Its popularity is due to its high sensitivity to structural changes and defects, and to the relative simplicity of the experimental setup. On the other hand, as the relative intensity of Raman peaks ranges over 5 orders of magnitude, great care and skills are required in order to extract all the available information the spectrum can provide. In this connection the availability of *ab initio* simulated spectra can be of great value in the calibration and interpretation of the experiment.

CRYSTAL[1,2] is a well known program for the *ab initio* study of crystalline systems at the Hartree-Fock and Density Functional Theory (DFT) level. Its development started in Torino in the Seventies of the last century and a new version, CRYSTAL14, has recently been released. A main feature of CRYSTAL is the choice of a Gaussian basis set, as opposite to plane waves (PW) that are by far the most common choice in quantum programs aimed at the solid state.

There are several advantages in adopting a local basis in periodic systems: (i) the same language, tools and algorithms as in molecular quantum chemistry can be used; (ii) the treatment of 1D, 2D and 3D systems can be performed on the same footing, thus avoiding the *horror vacui* typical of PWs; (iii) hybrid functionals like B3LYP can be used easily, since their computational cost is not significantly higher than that of GGA functionals; (iv) all electron basis sets can be used.

Among the drawbacks one can list the need of defining a basis set, a step that can be time consuming and requires some experience, and the basis set superposition error.

The implementation of complex algorithms in a local basis presents a lot more difficulties than in the case of PWs. This is due to the much simpler analytical form of PWs; a second crucial difference is due to Pulay forces[3], that arise because of the atomic orbital (AO) basis moving together with the atoms. The treatment of long-range summations and the correct handling of Ewald-type infinite summations are delicate points as well[4].

For these reasons the implementation in CRYSTAL of a full package capable of computing infrared and Raman spectra, including peak position, intensities, and the LO-TO splitting in the case of 3D systems, was delayed with respect to PW packages[5,6].

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Energy gradients were included in the CRYSTAL98 release[7], while the calculation of vibrational frequencies was made available in CRYSTAL03[8]. The Coupled-Perturbed Kohn-Sham (CPKS) formalism needed for dealing with electric field terms in the Hamiltonian was then developed[9] and included in CRYSTAL09, and only recently the adaptation of such treatment to the calculation of infrared and Raman intensities was completed[10,11,12].

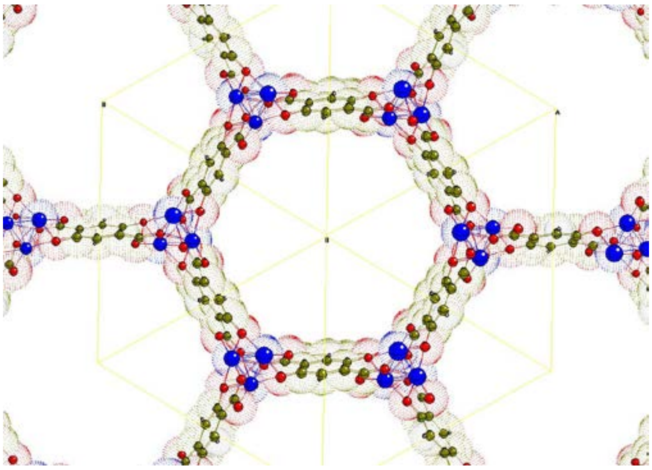

Fig. 1 - Structure of the Ni-CPO27 crystal

The above mentioned intensities require the evaluation of mixed derivatives of the total energy with respect to atomic displacements (once) and to an external electric field (once for IR, twice for Raman). The analytical formulation of such derivatives, though much harder to be formally derived and implemented compared to treatments that perform numerically one or more of the differentiations, has great advantages in terms of efficiency and numerical stability.

A fully analytical formulation for Raman intensities in a local basis set has been developed for molecules nearly 30 years ago[13]. Such a derivation for crystals has been long delayed, both due to the increasing difficulty in treating the above mentioned Pulay forces when going to periodic systems, and due to the phase problem that arises when the electric field operator is reformulated to take into account the periodicity of the lattice (a derivative with respect to reciprocal space vector *k* is introduced, and its combination with other derivatives is not trivial. The interested reader can find a detailed discussion in[10,11,14].

We have recently presented the formal aspects of such a treatment, validated the method by testing its consistency in the treatment of molecules, polymers, slabs and bulk systems, and demonstrated its good performances in reproducing Raman spectra that are significantly close to the experiment[12,14]. Here we further demonstrate the efficiency of our implementation by applying it to the study of CPO-27-Ni.

CPO-27 is one of the most well-known and widely studied among Metal-Organic Framework structures. It is characterized by channels (honeycomb structure with a section of about 12 Å) containing unsaturated metal sites organized in helicoidal chains (see Fig. 1).

Its complete characterization has been possible also through joint synergic effort of experimental[15,16,17] and computational[18] groups. The model used here for CPO-27-Ni is the same as in Ref. 19. Space group is R-3, with 6 symmetry operators. There are 54 atoms in the unit cell. We also adopted the same computational conditions used there, with a TZVP basis set and a *hybrid* B3LYP functional complemented by a -D2 empirical dispersion correction specifically tuned for solids[19].

In Fig. 2 the simulated spectrum of CPO-27-Ni is compared to the experimental one (that is the same as published in [15], Fig. 1) in the 1,200-1,800 cm^{-1} range. Both spectra have been normalized to the tallest peak, and as a consequence the intensity is reported in arbitrary units. A

Lorentzian broadening of 5 cm^{-1} has been used in the simulated spectrum. The position of the simulated peaks has been shifted by a factor 0.99 to match the experiment.

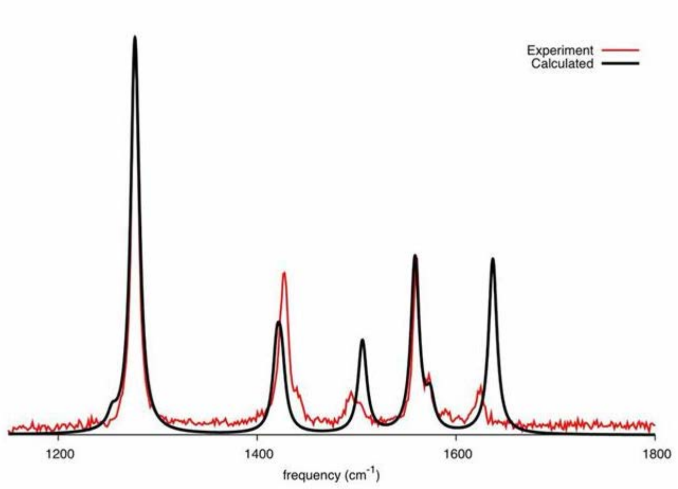

Fig. 2 - Simulated and experimental Raman spectra of CPO27

The reported part of the spectrum is most interesting and characteristic, where the fingerprint bands of the organic ligands are found. We quote from [18]: *"...the bands at 1,625 and 1,561cm^{-1} can be ascribed to stretching modes of the benzene ring. [...] The fingerprint of the linker also is the doublet at 1,501 and 1,427 cm^{-1} due to the (COO-)asym and (COO-)sym of the carboxylates, while the strong band at 1,278 cm^{-1} can be attributed to (C-O) vibration of the deprotonated species derived from the hydroxyl group."*

This has to be compared with the data in Tab. 1. We see that both peaks at 1,636 and around 1,558 cm^{-1} are a convolution of modes of Ag and Eg symmetry. But the calculated intensities permit to confirm that the Eg (asymmetric) mode dominates the former peak, while Ag (symmetric) mode is more evident in the latter. The other doublet, with (computed) peaks at 1,505 and around 1,424 cm^{-1}, is also a composite peak, but in this case modes have a comparable intensity, thus it is questionable whether one can be able to uniquely assign a peak to a symmetric or asymmetric vibration.

Tab. 1 - Computed Raman frequencies and intensities

Frequency (cm^{-1})	*Symmetry*	*Intensity (a.u.)*
1,254	Ag	9.9
1,254	Eg	28.2
1,276	Ag	1000.0
1,280	Eg	133.9
1,419	Eg	102.9
1,424	Ag	167.0
1,505	Ag	121.9
1,506	Eg	139.1
1,558	Ag	483.7
1,573	Eg	88.8
1,636	Ag	27.0
1,636	Eg	458.1

The intensity of some stretches is quite well reproduced by our simulation, while other intensities are considerably overestimated. This could be due to the presence of defects such as missing or substituted ligands in the measured sample. On the other hand effects due to the incompleteness of the basis set are possible. We have already documented[12] that the choice of Hamiltonian has small effects on intensities.

The computational cost is 33 hours on 256 processors (Intel Xeon, 2.6 GHz) using the replicated-memory parallel CRYSTAL14 executable. The most time is dedicated to CPKS equations (that presently do not fully exploit point symmetry) that require 3.4 and 20.8 hours for the solution of first and second order equations, respectively. The construction of IR and Raman tensors is considerably faster (30 minutes) while about 8 hours were needed for the frequencies.

In conclusion, in this contribution we have highlighted how, thanks to our recent work on the development and implementation of Raman intensities in CRYSTAL, it is possible to efficiently simulate ab initio Raman spectra of complex crystals such as CPO-27-Ni, an open-shell microporous compound containing 54 atoms (including nickel) in the unit cell, using an all-electron basis set and a hybrid functional.

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