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CRYSPLOT: A new tool to visualize physical and chemical properties of molecules, polymers, surfaces, and crystalline solids

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CRYSPLOT: a new tool to visualize physical and chemical properties of molecules, polymers, surfaces and crystalline solids

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ABSTRACT

CRYSPLOT is a web-oriented tool (http://crysplot.crystalsolutions.eu) to visualize computed properties of periodic systems, in particular, as computed with the CRYSTAL code. Along with plotting, CRYSPLOT also permits the modification and customization of plots to meet the standards required for scientific graphics.
CRYSPLOT has been designed with advanced and freely available graphical Javascript libraries as Plotly. The programming language used is Javascript. The code parses the input files, reads the data and organizes them into objects ready to be plotted with the plotly.js library. It is modular and flexible so that it is very simple to add other input data formats. The new graphical tool is presented in details along with selected applications on metal-organic frameworks to show some of its capabilities.

Introduction

Visualization tools are becoming more and more important to analyze, help in understanding and present scientific data[1]. Nowadays, this is particularly true in the realm of computational molecular and solid state chemistry for which a paramount number of data can be obtained from more robust and multipurpose computational codes and through the accessibility of powerful computing facilities. In the world of computational solid-state chemistry several different software exist for the ab-initio study of physical and chemical properties of periodic systems as polymers, surfaces and crystalline solids. Among them a prominent role is played by the CRYSTAL code[2-7], a software developed since mid-seventies of the last century by the Theoretical Chemistry Group of the University of Torino and later in collaboration with the Computational Materials Science Group at Daresbury Laboratory (U.K.). While CRYSTAL has recently shown a tremendous improvement in terms of advanced and powerful algorithms[4,6], particularly, for speeding up calculations of the two parallel versions[8-10] and for extending the number of properties that can be computed[7], the graphical tools for the analysis and visualization of the predicted results have remained at a less developed stage. To fill this gap, a new project, CRYSPLOT, has started to provide end users with a modern, web-oriented, machine independent, quick and easy-to-use visualization environment. In the following, we discuss in details technical aspects and features of CRYSPLOT (i.e. how it works, what it does, …) along with selected examples to show the capabilities of the new graphical tool.

Why a new visualization tool?

The CRYSTAL package performs ab initio calculations of the ground state energy, electronic wave function and properties of

periodic systems at the HF and DFT level of theory[7]. Presently, graphical tools available to analyse data computed with the CRYSTAL code are not unique and in some cases obsolete. Some of the computed properties and related data can be plotted by means of Gnuplot[11]. Gnuplot is a widespread tool for plotting scientific data. It was originally created to allow scientists and students to visualize mathematical functions and data interactively, but nowadays it has grown to support many non-interactive uses such as web scripting. For instance, CRYSTAL can create files that can be read by gnuplot to plot simulated vibrational spectra. Other properties like band structure and density of states can be plotted with the homemade CrGra package whose latest release dates back to 2006. The development of the CrGra suite of programs started almost thirty years ago by the CRYSTAL team to create graphic plots in the PostScript language that could be easily printed. CrGra2006 processes data written by CRYSTAL in the Fortran unit "fort.25"[7]. The CrGra suite is comprised of three modules: maps06 to draw contour maps (e.g. charge and spin density, electrostatic potential), bands06 to plot band structures and doss06 to plot total and projected density of states. However, the code was not updated for plotting data related to other properties that are now available from CRYSTAL (e.g. simulated IR/Raman spectra, topological analysis related quantities and electron conductivity).

In addition to these plotting tools, also other graphical tools are available to visualize data from CRYSTAL such as DLV[12] and XCRYSDEN[13]. Even if they provide a more extended graphical interface to the code (e.g. visualization of the crystalline structure and related features, animation of vibrational frequencies, and so on, see ref. 12 and 13 for further details) they are currently not fully updated to the last release of the code and not available for all operating systems.

Therefore, we decided to create an up to date modern web-oriented visualization tool to be machine independent, easy to use and freely accessible to users from all over the world through Internet browsers. Briefly, CRYSPLOT extends over the capabilities of CrGra to plot additional data (e.g. simulated IR/Raman spectra) and to manage multiple datasets. It also allows users to customize plots as detailed in the next section.

CRYSPLOT: What it does and how it works

CRYSPLOT is available online at http://crysplot.crystalsolutions.eu/.

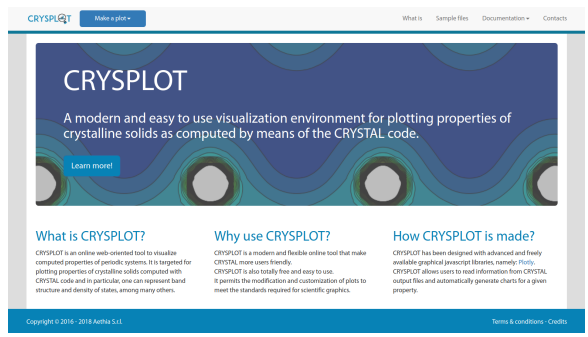

Figure 1. Screenshot of the CRYSPLOT home page

In Figure 1, a screenshot of the CRYSPLOT web page is shown. Basically, CRYSPLOT allows users to visualize Band Structure, Density of States, Electron Charge Density and electrostatic potential maps, Simulated Vibrational Spectra, Topological Analysis, Phonon Dispersion and Transport Properties computed with CRYSTAL on a machine independent platform. It also aims at offering users with easy-to-use options to modify and customize plots in order to meet standards required for scientific publications. It is worthy to note that, although CRYSPLOT is targeted to CRYSTAL the same properties as computed from other programs could be plotted by simply converting raw data to the CRYSTAL format as described in the Appendix of the CRYSTAL User's Manual[7].

At the design stage of CRYSPLOT, we decided to create a cross platform tool for making it easily accessible to the largest number of

users. For this reason we decided to organize CRYSPLOT as a website and develop it as a web application by using HTML5 markup language, CSS3 style sheet language, BOOTSTRAP front-end framework and the Javascript programming language. BOOTSTRAP is a free front-end framework for faster and easier web development that includes HTML and CSS based design templates for typography, forms, buttons, tables, navigation, modals, image carousels and many other, as well as optional JavaScript plugins. In addition, BOOTSTRAP has the ability to easily create responsive designs, i.e. web sites that automatically adjust themselves to look good on all devices, from small smartphones to large desktops. BOOTSTRAP is easy to use and compatible with all modern browsers (Chrome, Firefox, Internet Explorer, Safari, and Opera). For the graphical part we have chosen PLOTLY[14]. It is a high-level, declarative charting library, built on top of d3.js and stack.gl. In CRYSPLOT, we use its javascript version named plotly.js. Plotly.js uses stack.gl for high performance 2D and 3D charting and the charts are shipped with zoom, pan, hover, and click interactions like click-and-drag to zoom into a region, double-click to autoscale, click on legend items to toggle traces. Plotly.js ships with 20 chart types, including 3D charts, statistical graphs, and SVG maps; it abstracts the types of statistical and scientific charts that one would find in packages like matplotlib, ggplot2, or MATLAB. The charts are described declaratively as JSON objects and every aspect of the charts, such as colors, grid lines, and the legend, has a corresponding set of JSON attributes.

CRYSPLOT web page

The CRYSPLOT website (see Figure 1) has a descriptive part (homepage and "What is"), an operative one ("Make a plot") and user dedicated services ("Contacts"). The "Make a plot" button is the heart of CRYSPLOT. It opens a cascade menu from which user can select the property to be plotted as shown in Figure 2.

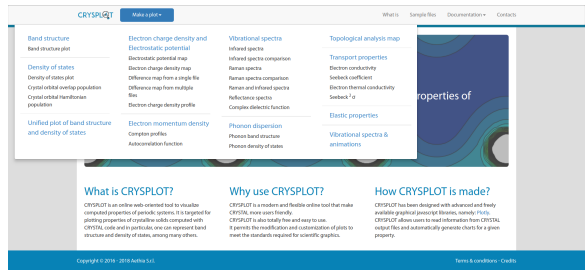

Figure 2. “Make a plot” cascade menu

In addition, the header of the web page contains links to the pages described above: "CRYSPLOT" brings to the homepage, "What is" links to a page on the main features of CRYSPLOT and "Contacts" to the contact page. Then, under the header there is a tab in which the selected property will be plotted. Figure 2 also shows the list of available properties, namely: band structure, density of states, crystal orbital overlap population, crystal orbital Hamiltonian population, electron charge density maps and profiles, electrostatic potential maps, Compton profiles, autocorrelation function, infrared, Raman, reflectance and complex dielectric spectra, phonon band structure and density of states, topological analysis, electron conductivity, Seebeck coefficient and electron thermal conductivity. There is also the possibility to plot elastic properties through the link to the Elate web site[15], a web tool for the analysis of elastic tensors, developed by F. X. Coudert and co-workers.

In each property tab, users may choose the output file from their local PC (see button ”Choose file”) to upload the data for the selected property as previously computed by CRYSTAL. All data to be plotted are written in a formatted way (i.e. plain ASCII) either on the Fortran unit 25 (fort.25) or in separate files (e.g. BAND.DAT, IRSPEC.DAT, ...). The list of properties and the corresponding name of the auxiliary files is listed in Table 1 in the Supporting Information.

Notably, since in crystalline systems many properties are tensors and anisotropic, CRYSPLOT also allows the simultaneous plot of multiple datasets as for the simulated Raman spectra of a single crystal model for

which six sets of data are available for the six independent orientation of the Raman tensor (i.e. *xx, yy, zz*, *xy, yz*, *xz*) as will be shown later on.

The ”Plot settings” lateral menu (hidden on the left of the CRYSPLOT web page) contains a palette of options for customizing the plot shown on the screen. CRYSPLOT has independent pages for every property and these pages have a specific ”Plot settings” set of options.

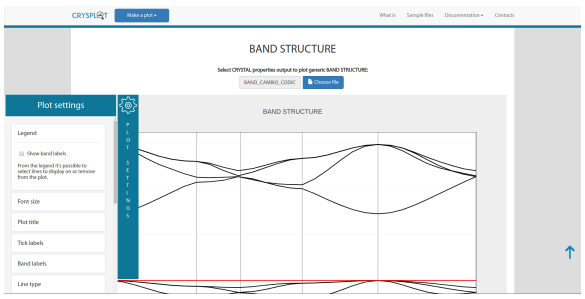

Figure 3. Example of plot settings palette as for the band structure plotting

For instance, Figure 3 shows an example of the “plot settings” menu for the band structure. Some of the available options to modify the plot are described in the following:

- *Legend* allows one to show or hide the legend,
- *Font size* permits to decide the size of the plot and axis titles font, selecting from four sizes,
- *Plot title* permits to change the chart title,
- *Tick labels* allows to change the labels of the k points on the x-axis,
- *Band labels* allows users to change the name of each band (i.e. electronic level),
- *Line type* permits to decide which type of line is adopted for plotting the bands, namely: plain line, only markers or both,
- *Y-axis unit* controls the y-axis unit to be either Hartree (default) or eV,
- *Different layout for open shell case* enables user to change the appearance of the plot to have the band structure for alpha and beta electrons on the same graph or on two separate plots,
- *Shifting Y-axis* allows to shift values for the value of Fermi Energy,
- *Fermi Energy line* allows one to show or hide the line of Fermi Energy,
- *Axis range* allows to selected a sub-region of the plot by axis values,
- *Data on hover* allows to change the visualization of data on the plot
- *Grid* allows one to show or hide the grey grid of the plot
- *Background color* modifies the color of the plot background from grey (default) to white
- *Plot layout* allows to select the size of the plot

In the case of the density of states, users can change line colors, and for spin polarized systems one can decide whether painting α and β lines in pairs or with different colors. Also, total and projected density of states can be plotted either on the same graph or on different charts.

Finally, at the bottom of the page there is an ”Export” section to save the actual plot as a picture. After selecting the file format (i.e. jpeg, png and svg) users must simply write the plot name and click on ”Download Plot”.

CRYSPLOT: Under the hood

The programming language used for CRYSPLOT is javascript. Our code parses the input files, checks if the uploaded files are correct and, if they are, it reads the data and organizes them into objects ready to be plotted with plotly.js library. A peculiar feature of CRYSPLOT is to keep separate the import code from the plotting one. Indeed, different import filters for each supported file format have been created, but the code that transfers data to plotly.js is always the same. When importing the data, the code checks

whether the file format is correct, if not, an error message appears. After data have been re-organized, it is straightforward to visualize them through the common code for plotting. For instance, data for band structure can be imported either from BAND.DAT (or filename.BAND) file or the Fortran unit fort.25 (or filename.f25). In that case, the code has two different import functions: one for .BAND or .DAT format and another one for fort.25. Therefore, even if data are organized and formatted very differently, after importing them, users get the same javascript object that can be passed to plotly.js through the general plotting code for the final representation of the graph.

This structure makes CRYSPLOT modular and flexible so that it is very simple to add other input data formats. In fact, it is just a matter of creating a new import filter that organizes the values in the proper way.

Finally, it is worth noting that CRYSPLOT does not need any third party libraries. It has been tested with most common browsers on different operating systems by using standard test cases of the CRYSTAL code, sample tests included in the CRYSTAL Tutorial project and on-purpose designed tests.

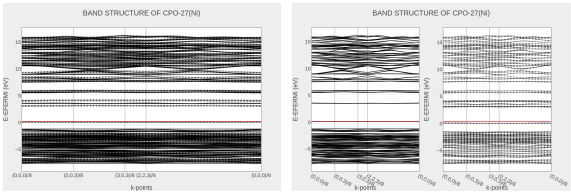

Figure 4. Example of a band structure plot for the metal-organic framework CPO-27-Ni. Alpha and beta electronic bands are represented as continuous and dashed lines, respectively. The Fermi level is indicated with a red line.

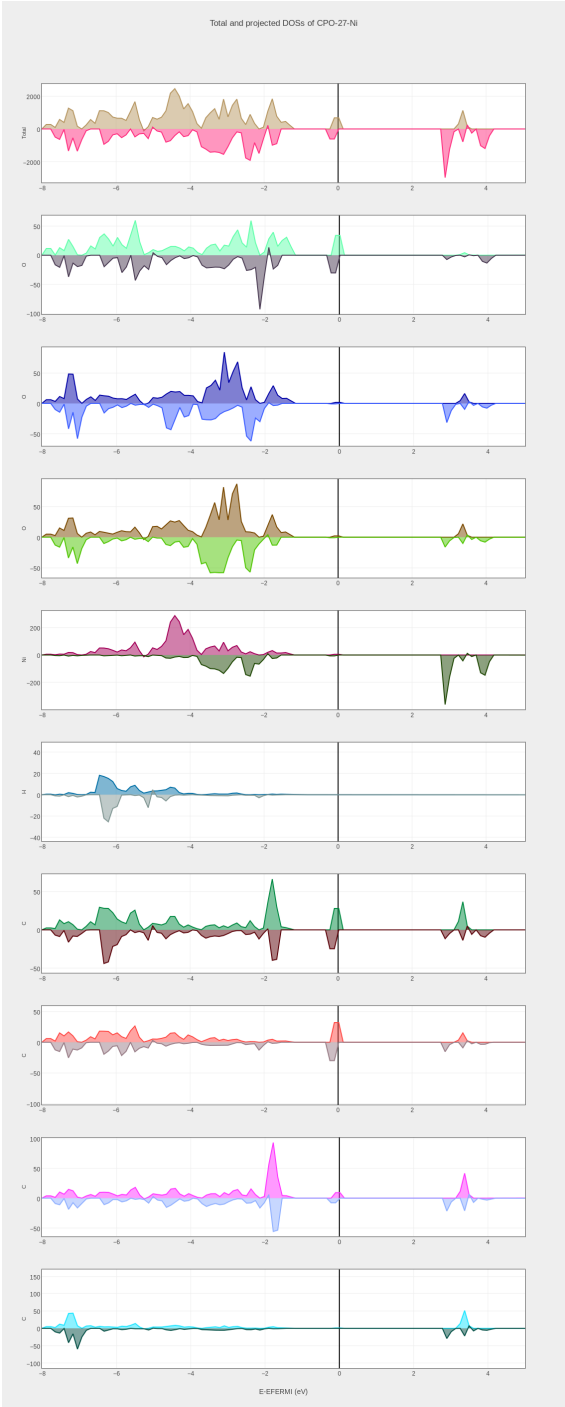

Figure 5. Example of total and projected density of states plot for CPO-27-Ni. Projected DOSs are plotted for all non-symmetry related atoms in the unit cell.

CRYSPLOT at work: Selected case studies

In this section, metal-organic frameworks (MOFs) are used as case studies to show some of the capabilities of CRYSPLOT. MOFs

are a relatively new class of hybrid inorganic-organic materials that are comprised of an inorganic cluster (or metal) and an organic linker acting as secondary building units of a tridimensional and usually porous framework.[16] Due to their peculiar structure, MOFs are interesting for several applications ranging from gas adsorption, separation and capture to catalysis and drug delivery. Recently, they have become of interest for other technologically relevant applications such as sensoring, lighting and optoelectronics.[17-19]

Band structure and density of states

As a first case study, we discuss the electronic structure of CPO-27-Ni. This MOF consists of metal-containing helical chains connected throughout space by the organic linker (i.e. 2,5-dihydroxyterephthalic acid) to form a honeycomb-like framework[20-21]. The resulting structure shows one-dimensional channels in which unsaturated metal sites are exposed at the inner surface. Due to the presence of unpaired electrons on the metal, CPO-27-Ni is a spin-polarized system. Results refer to a ferromagnetic configuration with Ni in a high-spin state. Reported data have been obtained with the M06-D method[22] with a TZVP basis set[23].

In Figure 4, the band structure of CPO-27-Ni is shown. CRYSPLOT can automatically manage spin-polarized systems by plotting band structure for alpha and beta electrons together or separately in two graphs.

The total and the projected density of states have been plotted for all atoms in the asymmetric unit (i.e. 9 projected DOSs) is shown in Figure 5. As it can be seen, the colored filled area plot is very effective in highlighting the role of alpha and beta electrons and multiple plots allow users to compare total and projected DOSs.

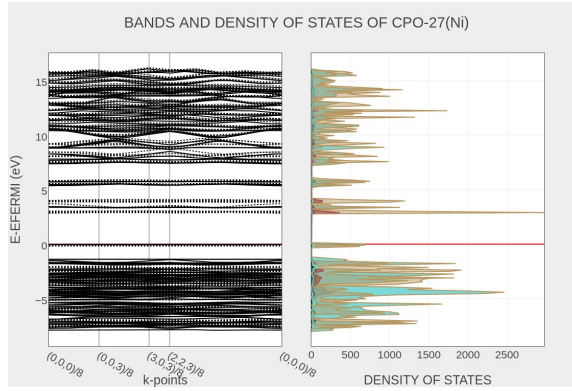

Figure 6. Example of a combined band structure and density of states plot for CPO-27-Ni.

With CRYSPLOT, band structure and density of states can be also easily visualized in a combined plot. Figure 6, shows the band structure of CPO-27-Ni along with its total and projected density of states, that is the combination of Figures 4 and Figure 5. By default, the two plots are aligned to the Fermi level at 0 eV. From this graph, users can easily visualize which atom contributes to the corresponding electronic band. For instance, for CPO-27-Ni, it can be readily seen that the top of the valence band corresponds to orbitals of the organic linker while the bottom of the conduction band is mainly dominated by the metal, thus suggesting a possible ligand-to-metal electronic transition.

Electron charge density maps

As an example of the plotting of 2D maps, the total electron density of a carbon monoxide molecule adsorbed on the inner surface of CPO-27-Ni is shown in Figure 7. Results have been computed at the M06-D/TZVP level of theory. The CO molecule strongly interacts with the Ni atoms that are exposed in the one-dimensional channels oriented along the *c*-axis.[24] The interaction is dominated by electrostatics and charge transfer effects due to the back-donation between the diffuse molecular orbitals of carbon monoxide and the unoccupied *d*-orbitals of the metal. To better appreciate the redistribution of the charge density upon the formation of the

metal-CO interaction, it is then useful to plot the deformation charge density as shown in Figure 8.

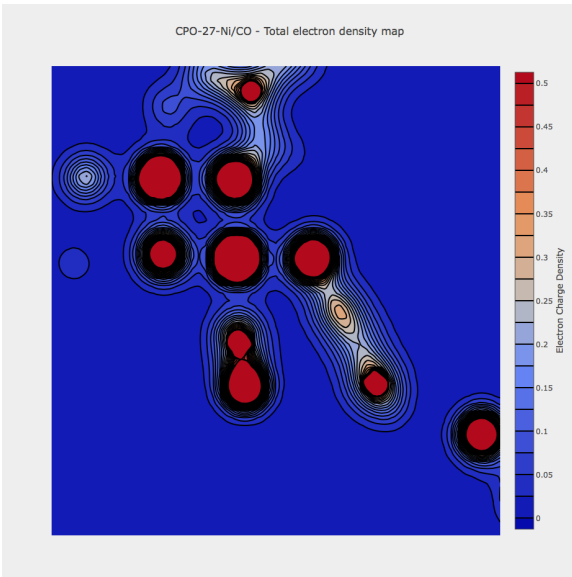

Figure 7. Contour plot of the total electron charge density map of a CO molecule adsorbed in the inner channels of CPO-27-Ni.

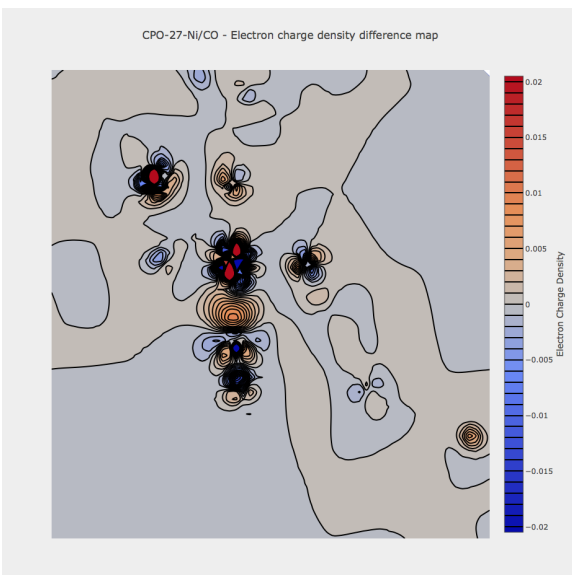

Figure 8. Plot of the electron charge density deformation map of CO molecule adsorbed in CPO-27-Ni. Blue and red lines correspond to negative and positive values, respectively.

CRYSPLOT can easily manage multiple sets of data and combine them to obtain a new map that corresponds to the difference (or sum) of the uploaded datasets. For instance, Figure 8 shows the deformation of the charge density when a CO molecule is adsorbed on top of the metal in CPO-27-Ni. The plot is obtained as a combination of the total electron charge densities of three systems, namely: the target system (i.e. CPO-27-Ni/CO) and the two separated subsystems (i.e. an array of CO molecules and the CPO-27-Ni alone). The electron density deformation map in Figure 8 shows positive values, in red, that correspond to charge accumulation while negative values, in blue, show where a depletion of charge occurs. As evident from Figure 8, upon interaction the electron charge density of the CO molecule is polarized towards the metal with a significant charge transfer between CO and Ni.

Simulated vibrational spectra

To show the capabilities of CRYSPLOT in plotting vibrational spectra, we compare the two phases of the bi-stable MOF known as MIL-53-Al.[25-26] The MIL-53 family of MOFs shows a flexible framework that can undertake a phase transition driven by external stimuli as temperature, pressure and gas adsorption.[27] The structure of MIL-53-Al consists of infinite chains of corner-sharing $AlO_4(OH)_2$ octahedra linked through the organic ligands (i.e. 1,4-benzendicarboxylic acid) to form flexible one-dimensional channels.[25] For MIL-53-Al, it was shown that, by changing the temperature, a phase transition occurs between a low-T narrow-pore (NP) structure and a high-T large-pore (LP) phase. [25-26]

It has been recently shown that the two phases exhibits unique vibrational fingerprints from dielectric function spectra[28] and IR/Raman spectra[29]. With CRYSPLOT simulated IR and Raman spectra as computed by CRYSTAL can be easily visualized. In addition, up to five IR (or Raman) spectra can be plotted together to highlight differences in the vibrational modes and distinguish between different phases. This is very useful when comparing vibrational spectra of

different polymorphs as for molecular crystals, or different phases as for the case of MIL-53-Al.

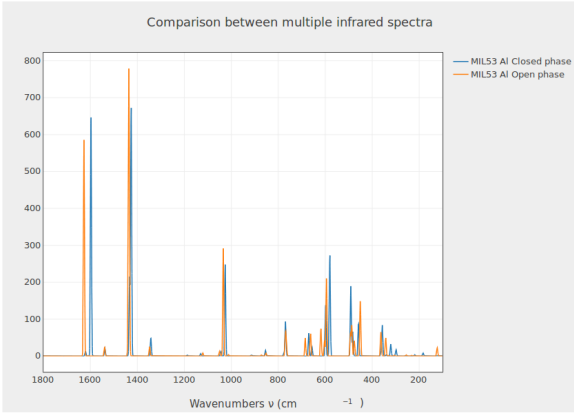

Figure 9. Comparison between IR spectra of the NP (blue) and LP (orange) phases of MIL-53-Al.

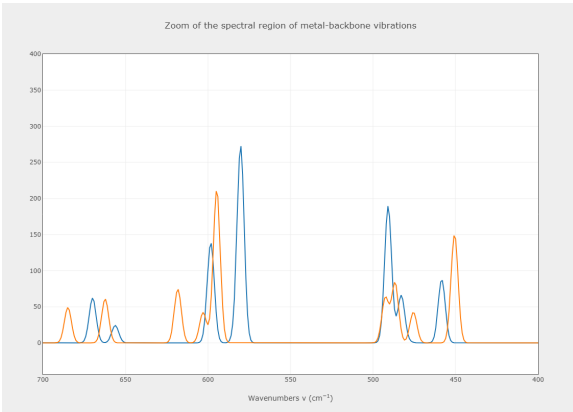

Figure 10. Details of the spectral region between 400 and 700 cm^{-1} of the IR spectra of the NP (blue) and LP (orange) phases of MIL-53-Al.

In Figure 9 and 10 the comparison between the simulated IR spectra, respectively, of the NP and CP phases of MIL-53-Al is shown. Results have been obtained with the B3LYP functional[30-32] augmented with the Grimme's D3 dispersion correction[33-34] in combination with a triple-zeta quality basis set[35]. It can be clearly seen that the two phases show several spectral shifts of the peaks from a few to twenty wavenumbers. In particular, by zooming into the plot with CRYSPLOT one can also visualize in more detail the spectral regions that show the largest variations because they can reveal the presence of vibrational fingerprints. For instance, in Figure 10 the IR region between 400 and 700 cm^{-1} of the two phases is highlighted. According to a recent work by Hoffman *et al.* [16] this corresponds to the region of metal-oxide backbone vibrations that are more influenced by the phase transition.

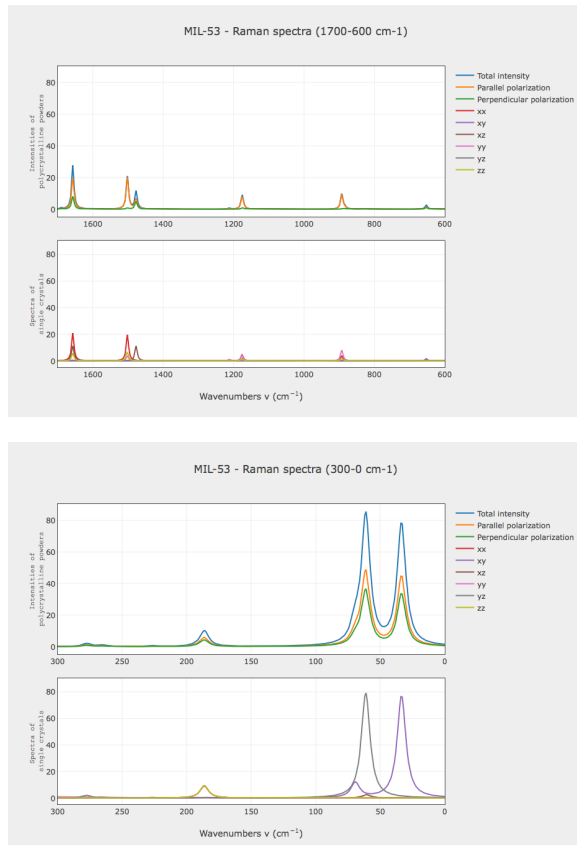

Figure 11. Raman spectra of the LP phase of MIL-53-Al in the region (top) 1700-600 cm^{-1} and (bottom) 300-0 cm^{-1}. The two graphs show the simulated Raman spectra as for a polycrystalline material (3 components) and a single crystal (6 components) respectively. See text for details.

As an additional example, the simulated Raman spectra of MIL-53 large pore phase are shown in Figure 11. CRYSTAL permits to simulate the Raman spectra of solids either as a polycrystalline powder or a single crystal[36-37]. In the former case, the total spectrum is

predicted along with two components in the parallel and perpendicular directions. For the latter, the six spectra originate from the corresponding independent components of the second-order electric susceptibility tensor (i.e. *xx,xy,xz,yy,yz,zz*). For instance, Figure 11 has been obtained by using the unscaled vibrational frequencies and a Lorentzian profile with a FWHM of 8 cm^{-1}. For this kind of plot, CRYSPLOT permits to visualize all spectra simultaneously. A nice feature is that by clicking on the items in the legend, one can hide (or show) the corresponding spectrum in the plot. This option allows users to analyze the data and highlight the Raman spectrum along a given direction. From Figure 11 (bottom), it is evident that the two peaks at very low frequency in the THz region (i.e. 300-0 cm^{-1}) are polarized in different directions, i.e. *xy* and *xz*, thus making easier the comparison with single-crystal Raman spectra from experimental works. On passing, it is worthy to note that the simulated total Raman spectrum of MIL-53(LP) as a crystalline powder (see Figure 11, top) nicely agrees with the experimental one reported by Hoffman *et al.* [16]

Conclusions

CRYSPLOT is a user-friendly web-oriented tool that is freely available to CRYSTAL users. It allows the visualization of many properties in a few seconds by reading information from auxiliary files created by CRYSTAL.

CRYSPLOT has been highly optimized with just a common function that is called multiple times and different import filters for each property to be plotted. In this respect, it is also highly modular because it can be easily modified to visualize new kinds of property that will be available in next release of the CRYSTAL code. Since CRYSPLOT reads data from formatted text files, it can be considered a versatile and general tool because, in principle, it is not limited to visualize data computed with CRYSTAL. Indeed, one could obtain results from another software, reorganize raw data according to the proper format (see the CRYSTAL User's Manual[7]) and then plot the results with CRYSPLOT.

CRYSPLOT is an easy-to-use web platform that has been designed as a very intuitive graphical tool, a low entry-level interface to all types of users: from beginners (i.e. students) to expert researchers. It is also a sufficiently advanced and powerful tool that enables users to customize graphs in such a way that results could be used in scientific publications. This has been shown for selected applications taken from the study of metal-organic frameworks. Its ease-of-use makes CRYSPLOT also very useful for educational purposes.

From a general perspective, CRYSPLOT is under development and a bunch of other features will be included in future releases. It will be extended to visualize more computed properties (e.g. simulated X-ray powder diffraction and inelastic neutron scattering spectra[7]) and some facilities on the server side. In particular, we would like to provide each user with a personal page in which they can save and store plots created with CRYSPLOT. A more advanced graphical user interface for CRYSTAL is also under development with enhanced capabilities like a structure visualizer, a wizard to prepare input files and tools to manage calculations. When ready, CRYSPLOT will be fully encoded in the new graphical interface to enable users to promptly analyze and visualize computed properties.

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Keywords: GUI, CRYSTAL, solid state, periodic systems

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