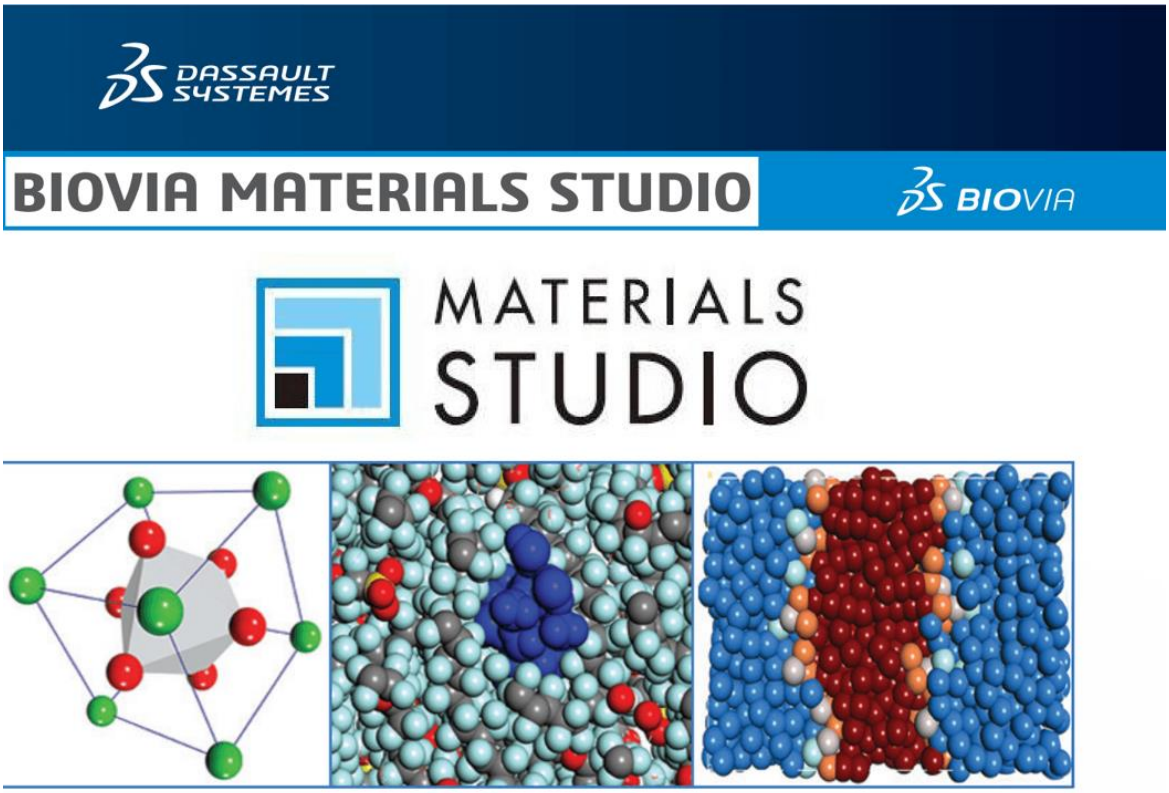
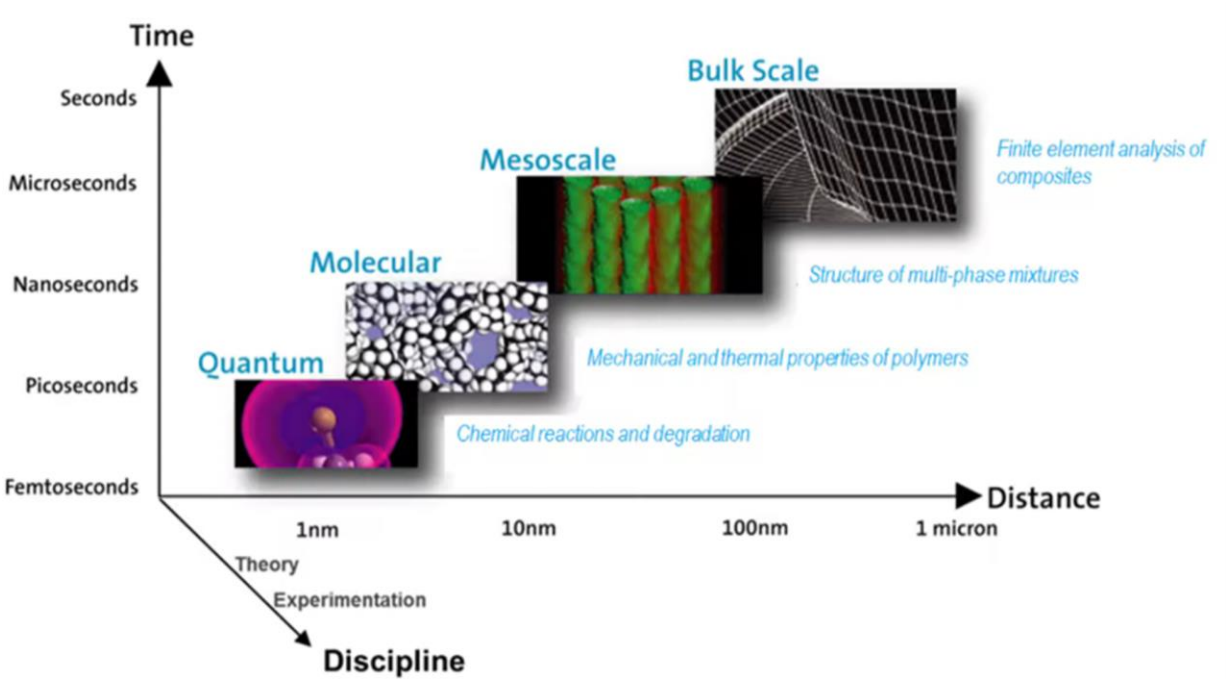
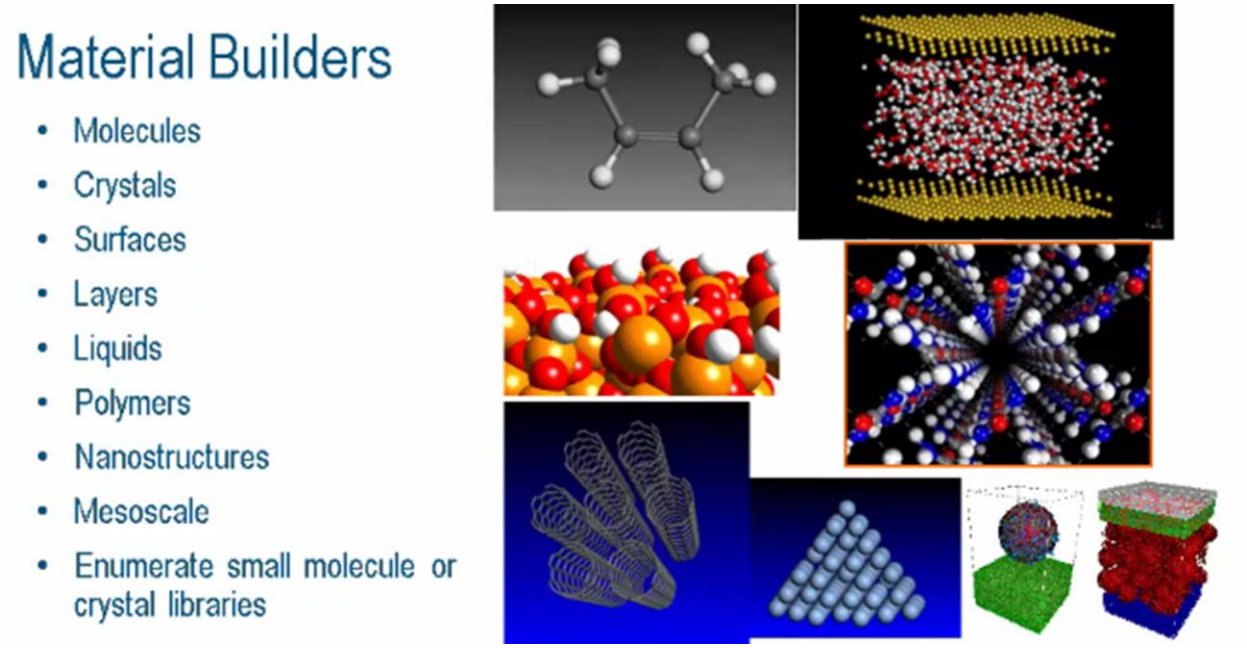
Instructions for Materials Studio 2025



Software Overview:





The development of new materials requires a fundamental understanding of the relationship of a material's atomic and molecular structure with its properties and behavior. Using Materials Studio (MS), researchers in many industries are engineering better performing materials of all types including catalysis, polymers, composites, metals & alloys, batteries & fuel cells, and more. Materials development is accelerated by the use of simulation methods at a range of linked scales from the atomistic and molecular scale in order to predict bulk chemical reactivity in the development of catalysts and material properties to more coarse-grained simulations of mixtures to predict the structure and properties of blends and composites. Ultimately, these models can structure property input for engineering scale simulations in order to predict the bulk properties of composites. The development of catalysts with high reactivity, specificity and long life is an important R&D activity in the chemicals and petrochemicals industries through the use of simulation tools in materials studio catalyst structures can be quickly screened in order to identify relationships between chemical structure and catalytic activity about 20% of the energy consumed in the U.S. is for powering chemical reactors and improved catalysts providing a 1% efficiency gain in energy consumption can lead to savings of hundreds of millions of dollars. Prediction of electronic and optical properties of materials has driven the development of new candidates in the field of photonics and solar cells. MS provides the ability to screen potential photo active dyes for improving solar cell efficiency by prediction of the emission energy and current voltage relationships for new materials. Modeling and simulation software will allow researchers working with specialty chemical companies to predict and understand how chemical structure can be modified to reflect different colors. Researchers must also know how their modifications can in turn affect a material's property and behavior.

MS provides a complete range of simulation capabilities from quantum, atomistic, mesoscale, statistical, analytical and crystallization tools. Its' broad range of solutions enables researchers to evaluate materials at various particle sizes and time scales in order to predict properties more accurately and evaluate performance in the shortest time possible.

QUANTUM TOOLS

Materials Studio provides a range of density functional theory based solvers and semi-empirical methods to predict properties of molecular and solid state materials from electronic structure, It also includes specialized solvers for using quantum mechanical derived energies and properties in chemical reaction.

Product	Description
Materials Studio CANTERA	Cantera [www.cantera.org] is a solver for chemical rate equations. Materials Studio Cantera provides environment for configuring the thermodynamic input, and for executing these calculations. Cantera Reaction Editor enables users to introduce new species and reactions, optionally with reaction rates determined from Materials Studio DMol³, into complex reaction schemes with existing experimentally determined thermodynamic data.
Materials Studio CASTEP	Materials Studio CASTEP simulates the properties of solids, interfaces, and surfaces for a wide range of materials including ceramics, semiconductors, and metals using a plane-wave density functional method.
Materials Studio DMol³	Materials Studio DMol³ is used to model the electronic structure and properties of organic and inorganic molecules, molecular crystals, covalent solids, metallic solids, and infinite surfaces using DFT.
Materials Studio DFTB+	Materials Studio DFTB+ is a semi-empirical module for simulating electronic properties of materials. It uses a tight-binding approach based on density functional theory to enable quantum mechanical accuracy on larger system sizes.
Materials Studio FlexTS	The Materials Studio FlexTS module is a robust tool for identifying the minimum energy path between reactant and products in chemical reactions (location of transition states). FlexTS requires DMol³ or DFTB+ in order to supply the system energy of each configuration.
Materials Studio KINETIX	BIOVIA Materials Studio KINETIX is a general purpose program for simulating the competing chemical and physical adsorption, desorption and diffusion processes taking place at surfaces. This provides unique insights such as the role of species diffusion in catalyst activity and poisoning, and surface coverage of species at up to microscales.
Materials Studio NMR CASTEP	Materials Studio NMR CASTEP predicts NMR chemical shifts and electric field gradient tensors from first principles. The method can be applied to compute the NMR shifts of both molecules and solids for a wide range of materials including ceramics and semiconductors.
Materials Studio ONETEP	Materials Studio ONETEP is a linear scaling DFT code, enabling accurate, first principles calculations on systems of up to thousands of atoms.
Materials Studio QMERA	Materials Studio QMERA employs QM/MM method combining the accuracy of a quantum with the speed of a forcefield calculation. This approach makes it possible to perform accurate calculations on very large systems for substantially less effort.
Materials Studio VAMP	Materials Studio VAMP is capable of rapidly predicting many physical and chemical properties for molecular organic and inorganic systems using a semi-empirical molecular orbital method. Materials Studio VAMP is an ideal intermediate approach between forcefield and first principles methods.

CLASSICAL SIMULATION TOOLS

Materials Studio offers a very wide range of methods based on classical interactions between atoms and molecules. These include Molecular Dynamics, Lattice Dynamics and various Monte Carlo based methods as well as the provision of forcefields.

Product	Description
Materials Studio Adsorption Locator	Materials Studio Adsorption Locator finds low-energy adsorption sites for molecules on both periodic and non-periodic substrates
Materials Studio Amorphous Cell	Materials Studio Amorphous Cell is a suite of computational tools that allow you to construct representative models of complex amorphous systems and to predict key properties.
Materials Studio Blends	Materials Studio Blends predicts phase diagrams and interaction parameters for liquid-liquid, polymer-polymer, and polymeradditive mixtures, phase equilibria, and separations technology.
Materials Studio Conformers	Materials Studio Conformers provides conformational search algorithms and analysis tools to characterize molecular conformation and flexibility.
Materials Studio COMPASS	Materials Studio COMPASS is a forcefield which enables accurate prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation and in condensed phases, and under a wide range of conditions of temperature and pressure. This includes access to the latest COMPASS III parameters (https://doi.org/10.1080/08927022.2020.1808215) - highly validated and covering the widest range of materials
Materials Studio Forcite Plus	Forcite Plus offers molecular mechanics and dynamics methods for molecules and periodic systems. The tool includes a wide range of analysis features to predict mechanical properties, diffusivity, local structure, density variations, cohesive energy density, dipole autocorrelation functional and more. Supported forcefields are Materials Studio COMPASS, CVFF, PCFF, Dreiding, and Universal. Forcite Plus also supports execution on GPUs for accelerated performance.
Materials Studio GULP	GULP is a method for optimization, property calculation and dynamics of materials. It includes a wide range of forcefields for metals, oxides, minerals semiconductors, as well as molecular mechanics forcefields for covalent systems. Forcefield fitting tools are also provided to develop parameters for custom materials.
Materials Studio Sorption	Sorption provides a means of predicting fundamental properties needed for investigating adsorption and separations phenomena, such as sorption isotherms and Henry's constants.

MESOSCALE SIMULATION TOOLS

Mesoscale methods in Materials Studio are based on two coarse-graining approaches (1) where groups of atoms are replaced by beads or (2) where or regions of materials are represented by density fields. Using these approaches it is possible to extend the accessible length and time scales by several orders of magnitude over classical simulations.

Product	Description
Materials Studio MesoDyn	MesoDyn is a classical density functional method for studying the long length- and time-scale behavior of complex fluid systems, in particular the phase separation and structure of complex polymer systems.
Materials Studio Mesocite	Mesocite is a coarse-grained simulation module for the study of materials at length scales ranging from nanometers to micrometers and time scales from nanoseconds to microseconds. Materials Studio Mesocite can provide structural and dynamic properties of fluids in equilibrium, under shear or in confined geometries.
Materials Studio PhaseField	Materials Studio PhaseField is a module providing predictions of microstructure in hard materials such as grain structure in complex metal alloys through simulation of solidification and grain growth. This module is run using protocols provided by Pipeline Pilot Materials Studio Collection.

STATISTICAL TOOLS

Statistical tools are ideal to screen compounds quickly by relating molecular traits directly to experimentally observed quantities.

Product	Description
Materials Studio QSAR	QSAR's (Quantitative Structure-Activity Relationships) integration in Materials Studio provides access to a wide range of descriptors and advanced analysis capabilities to help generate high quality structure activity relationships. QSAR includes a wide range of descriptors including topological and electro-topological descriptors. Also, Jurs descriptors enable charge distribution on solvent surfaces to be examined; VAMP Descriptors further extend the range of 3D descriptors into those including electronic interactions; and GFA applies a sophisticated genetic algorithm method to calculate quantitative structure-activity relationships.
Materials Studio QSAR Plus	QSAR Plus adds the power of the DMol^3 Descriptors for calculating reactivity indices and accurate energies to QSAR. Also included are Neural Networks to build non-linear models and models that are more resistant to noisy datasets than other model building methods. It can also be used with datasets that have some missing values, and can be used to build weighted models to predict multiple physical properties.
Materials Studio Synthia	Synthia calculates properties of homo- and copoplymers using advanced Quantitative Structure-Property Relationships (QSPRs). It allows researchers to rapidly screen candidate polymers for a wide range of properties.

ANALYTICAL & CRYSTALLIZATION TOOLS

Analytical and crystallization tools are employed to investigate, predict, and modify crystal structure and crystal growth.

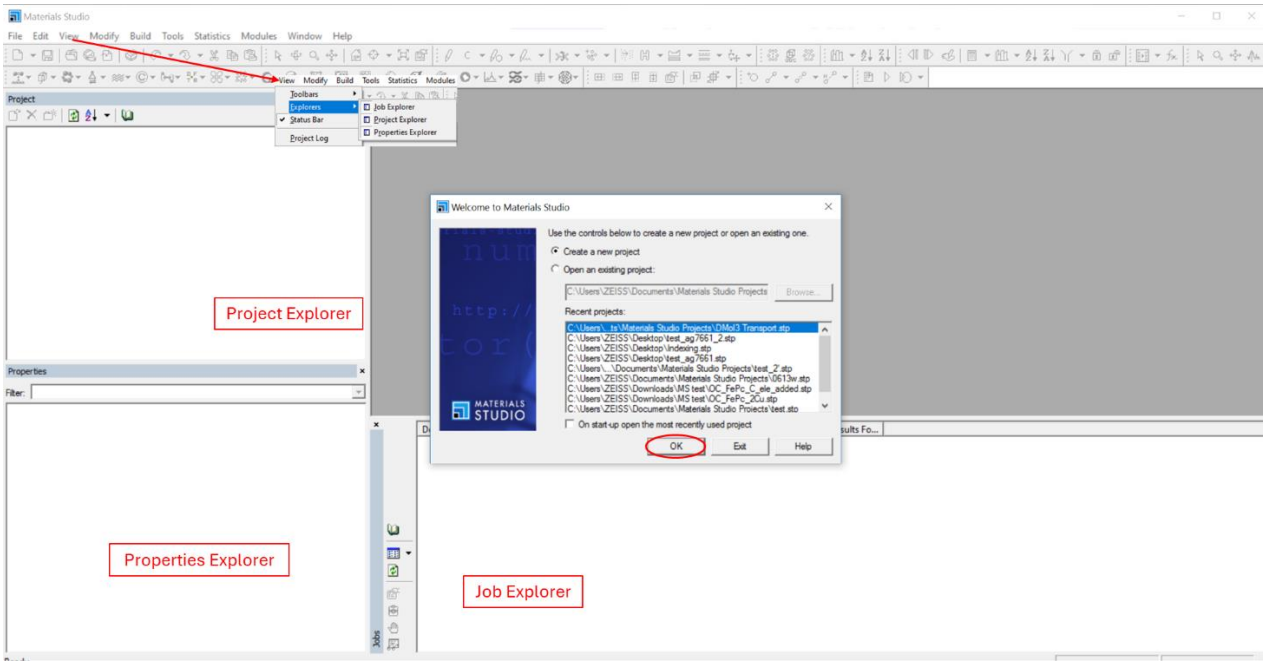
Product	Description
Materials Studio Morphology	Morphology allows you to predict crystal morphology from the atomic structure of a crystal. Morphology allows for the prediction of crystal shape, the analysis of crystal surface stability, the development of tailor-made additives, and the control of solvent and impurity effects.
Materials Studio Polymorph Predictor	Polymorph Predictor has been developed for use with fairly rigid, non-ionic or ionic molecules composed primarily of carbon, nitrogen, oxygen, and hydrogen. The approach is based on the generation of possible packing arrangements in all reasonable space groups to search for the low-lying minima in lattice energy.
Materials Studio Motif	Motif analyzes connectivity information in molecular crystals, providing a qualitative and quantitative analysis method of hydrogen bond topologies. Combined with the predictive capabilities of Polymorph, Motif allows for categorization and statistical scoring of proposed structures. It interfaces with the Cambridge Structural Database exploiting Cambridge Crystallographic Data Centre's Mercury functionality.
Materials Studio Reflex	Reflex simulates X-ray, neutron, and electron powder diffraction patterns based on models of crystalline materials. Reflex Plus offers a complete package for the determination of crystal structures from medium- to high-quality powder diffraction data.
Materials Studio Reflex QPA	Reflex QPA extends the Reflex functionality for quantitative phase analysis, allowing for the determination of the relative proportion of different phases, including both inorganic as well as organic systems, in a mixture based on powder diffraction data.
Materials Studio X-Cell	X-Cell is an efficient, indexing algorithm for medium- to high-quality powder diffraction data. X-Cell uses an extinction-specific dichotomy procedure to perform an exhaustive search of parameter space to establish a complete list of all possible unit cell solutions.

How to Run:

1. Location of the Workstation (**pmi-versalabdct**): IAC Room 027D

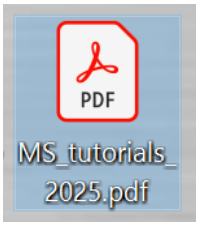
2. Open Materials Studio (click the icon from the taskbar)

3. Select either "**Create a new project**" or "**Open an existing project**" (please save all projects in your own folder: DATA(D:)>SharedDATA>(Your name)). The UI of MS 2025 looks like the following:

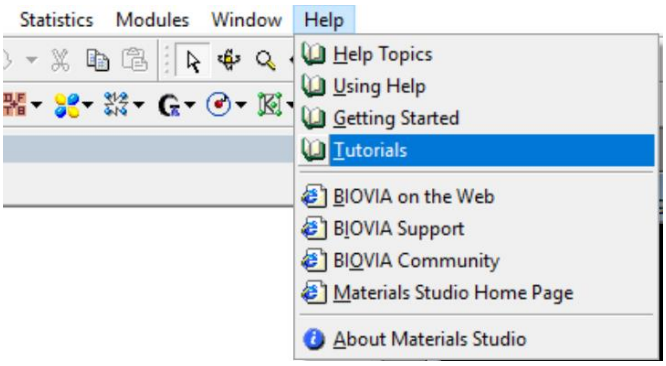


Sometimes, users may accidentally close a window (or Explorer) and then aren't sure how to bring it back. In that case, go to **View → Explorers** to open or close specific windows.

Also, the latest MS tutorials file (MS_tutorials_2025.pdf) is available on the desktop:



Note: This file only contains selected functions from some modules. If the types of simulation you want to perform are not included in this file, you can find more information under **Help** (see below).



5. Before you start:

Since this Workstation is publicly accessible, ALWAYS reset all settings before use as you won't know what changes previous users made. To do this, go to "**Tools → Settings Organizer →** select your project name → click "**Reset**"

6. Depending on what kind of calculation you want to run, find the corresponding chapter and follow it step by step. Once you are familiar with the software, you can build your own models.

Hands-on Example using CASTEP

Adsorption of CO onto a Pd(110) surface

Purpose: Introduces the use of CASTEP for calculating the adsorption energy of a gas onto a metal surface.

Modules: Materials Visualizer, CASTEP

Time:

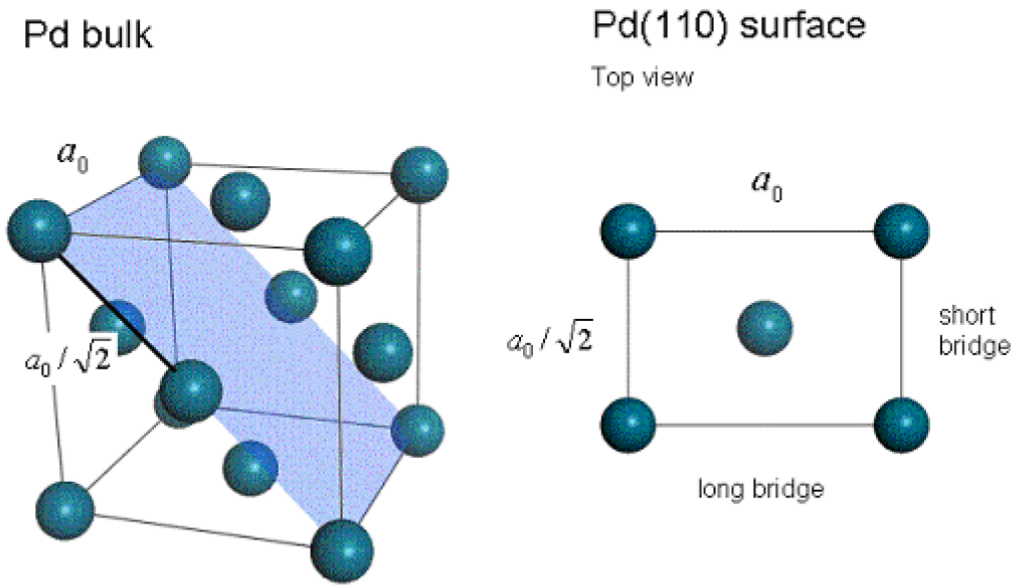
Prerequisites: Using the crystal builder Visualizer Tutorial

Background

In this tutorial you will examine the adsorption of CO on Pd(110). The Pd surface plays a crucial role in a variety of catalytic reactions. Understanding how molecules interact with such surfaces is one of the first steps to understanding catalytic reactions. In this context, DFT simulations can contribute to this understanding by addressing the following questions:

- Where does the molecule want to adsorb?
- How many molecules will stick to the surface?
- What is the adsorption energy?
- What does the structure look like?
- What are the mechanisms of adsorption?

You will focus on one adsorption site, the short bridge site, as it is known to be energetically preferred at fixed coverage. At 1 ML coverage the CO molecules repel each other preventing them from aligning exactly perpendicular to the surface. You will calculate the energy contribution of this tilting to the chemisorption energy by considering a (1×1) and (2×1) surface unit cell.



Pd bulk and a top view on the Pd(110) surface. The (110) cleave plane is highlighted in blue. a_0 is the bulk lattice constant, also known as the lattice parameter.

Introduction

In this tutorial, you will use CASTEP to optimize and calculate the total energies of several different systems. Once you have determined these energies, you will be able to calculate the chemisorption energy for CO on Pd(110).

This tutorial covers:

- Getting started
- To optimize bulk Pd
- To build and optimize CO
- To build the Pd(110) surface
- To relax the Pd(110) surface
- To add CO to the 1 × 1 Pd(110) surface and optimize the structure
- To set up and optimize the 2 × 1 Pd(110) surface
- To analyze the energies
- To analyze the density of states (DOS)

Note: In order to ensure that you can follow this tutorial exactly as intended, you should use the Settings Organizer dialog to ensure that all your project settings are set to their BIOVIA default values. See the Creating a project tutorial for instructions on how to restore default project settings.

1. Getting started

Begin by starting Materials Studio and creating a new project.

Open the **New Project** dialog and enter **CO_on_Pd** as the project name, click the **OK** button.

The new project is created with *CO_on_Pd* listed in the Project Explorer.

This tutorial consists of five distinct calculations. To make it easier to manage your project, you should begin by preparing five subfolders in your project.

Right-click on the root icon in the Project Explorer and select **New | Folder**, repeat this four more times. Rename the folders **Pd bulk**, **Pd(110)**, **CO molecule**, **(1x1) CO on Pd(110)** and **(2x1) CO on Pd (110)**.

2. To optimize bulk Pd

The crystal structure of Pd is included in the structure library provided with Materials Studio.

In the Project Explorer, right-click on the **Pd bulk** folder and select **Import...** to open the Import Document dialog. Navigate to **Structures/metals/pure-metals** and import **Pd.xsd**.

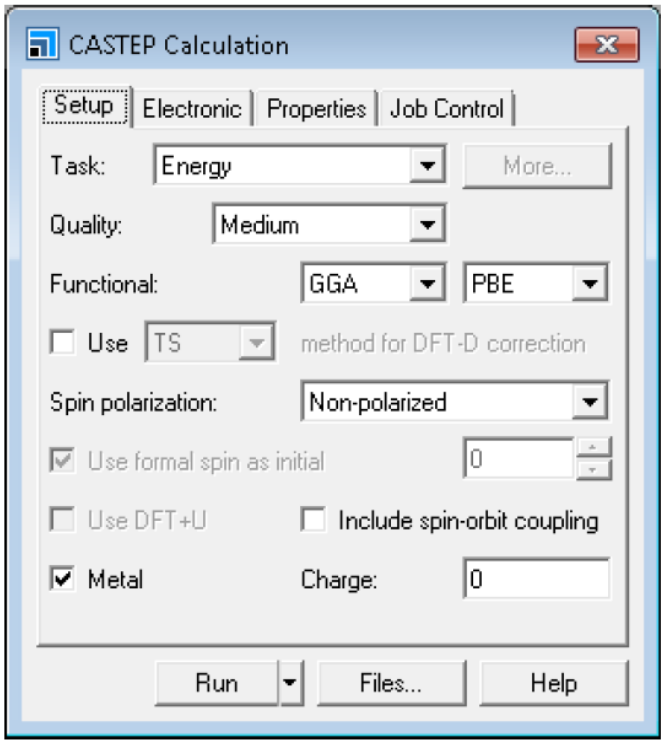
The bulk Pd structure is displayed. You can change the display style to ball and stick.

Right-click in the **Pd.xsd** 3D Viewer and select **Display Style** to open the Display Style dialog. On the **Atom** tab, select **Ball and stick** and close the dialog.

Now optimize the geometry of the bulk Pd using CASTEP.

Click the **CASTEP** button on the **Modules** toolbar then select **Calculation** or select **Modules | CASTEP | Calculation** from the menu bar.

This opens the CASTEP Calculation dialog.



CASTEP Calculation dialog, Setup tab

Cell optimization of crystals requires more accurate calculations than those performed with default settings.

Change the **Quality** from Medium to **Fine**.

To maintain consistency across the calculations that you are going to perform, you should make some changes on the Electronic tab.

Select the **Electronic** tab and click the **More...** button to open the CASTEP Electronic Options dialog. On the **Basis** tab check the **Use custom energy cutoff** checkbox and make sure that the field value is **570.0** eV. This ensures that all calculations in the tutorial use the same energy cut-off.

The default values for geometry optimization do not include optimization of the cell.

Change the **Task** from Energy to **Geometry Optimization**. Click the **More...** button to open the CASTEP Geometry Optimization dialog. Select **Full** from the **Cell optimization** dropdown list and close the dialog.

Click the **Run** button. A message dialog about conversion to the primitive cell is displayed. Click the **Yes** button.

The job is submitted and starts to run. You should proceed to the next section and build the CO molecule but return here when the calculation is complete to display the Lattice Parameters.

When the job has finished, you must convert the primitive cell result back to a conventional cell representation in order to proceed with building the Pd(110) surface in step 4.

In the Project Explorer, open **Pd.xsd** located in the **Pd CASTEP GeomOpt** folder. Select **Build | Symmetry | Conventional Cell** from the menu bar.

You should now save your project files.

Select **File | Save Project**, then **Window | Close All** from the menu bar. In the Project Explorer, re-open the optimized **Pd.xsd**.

Right-click in the 3D Viewer and select **Lattice Parameters**.

This opens the Lattice Parameters dialog. The value of *a* should be approximately 3.962 Å, compared with the experimental value of 3.89 Å.

Close the **Lattice Parameters** dialog and **Pd.xsd**.

3. To build and optimize CO

CASTEP will only work with periodic systems. To optimize the geometry of the CO molecule, you must put it into a crystal lattice.

In the Project Explorer, right-click on the **CO molecule** folder and select **New | 3D Atomistic Document**. **Rename** the new document **CO.xsd**.

An empty 3D Viewer is displayed. You will use the Build Crystal tool to create an empty cell and then add the CO molecules to it.

Select **Build | Crystals | Build Crystal...** from the menu bar to open the Build Crystal dialog. Choose the **Lattice Parameters** tab and change each cell **Length a**, **b**, and **c** to **8.00**. Click the **Build** button.

An empty cell is displayed in the 3D Viewer.

Select **Build | Add Atoms** from the menu bar to open the Add Atoms dialog.

The C-O bond length in the CO molecule has been determined experimentally as 1.1283 Å. By adding the atoms using Cartesian coordinates you can create your CO molecule with exactly this bond length.

Select the **Options** tab and ensure that the **Coordinate system** is set to **Cartesian**. On the **Atoms** tab click the **Add** button.

A carbon atom is added at the origin of the cell.

Change the **Element** to **O**, leave the **x** and **y** values as **0.000**. Change the **z** value to **1.1283**. Click the **Add** button and close the dialog.

You are now ready to optimize your CO molecule.

Open the **CASTEP Calculation** dialog.

The settings from the previous calculation have been retained. However, you do not need to optimize the cell for this calculation.

Open the **CASTEP Geometry Optimization** dialog. Select **None** from the **Cell optimization** dropdown list and close the dialog.

On the **Properties** tab of the CASTEP Calculation dialog check the **Density of states** checkbox. Change the **k-point set** to **Gamma** and check the **Calculate PDOS** checkbox. Click the **Run** button.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation starts. You can move onto building the Pd(110) surface as you will analyze the energy at the end of the tutorial.

4. To build the Pd(110) surface

This section of the tutorial uses the optimized Pd structure from the Pd bulk part of the tutorial.

Select **File | Save Project**, then **Window | Close All** from the menu bar. Open **Pd.xsd** in the **Pd bulk/Pd CASTEP GeomOpt** folder.

Creating the surface is a two step process. The first step is to cleave the surface and the second is to create a slab containing the surface and a region of vacuum.

Select **Build | Surfaces | Cleave Surface** from the menu bar to open the Cleave Surface dialog. Change the **Cleave plane (h k l)** from -1 0 0 to **1 1 0** and press **TAB**. Increase the **Fractional Thickness** to **1.5**. Click the **Cleave** button and close the dialog.

A new 3D Viewer is opened containing the 2D periodic surface. However, CASTEP requires a 3D periodic system as input, this is obtained using the Vacuum Slab tool.

Select **Build | Crystals | Build Vacuum Slab...** from the menu bar to open the Build Vacuum Slab Crystal dialog. Change the **Vacuum thickness** from 10.00 to **8.00** and click the **Build** button.

The structure changes from 2D to 3D periodic and a vacuum is added above the atoms. Before continuing, you must reorient the lattice.

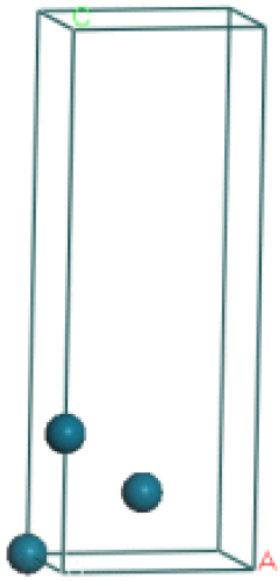
Open the **Lattice Parameters** dialog and select the **Advanced** tab, click the **Re-orient to standard** button. Close the dialog.

You should also change the lattice display style and rotate the structure so that the z-axis is vertical on the screen.

Open the **Display Style** dialog and select the **Lattice** tab. In the **Display style** section, change the **Style** from Default to **Original**. Close the dialog.

Press the **UP** arrow key twice.

The 3D view shown below is displayed:



The Pd atom with the largest z-coordinate will be called "the uppermost Pd layer".

Later in this tutorial, you will need to know the bulk interlayer spacing d_o. You can calculate this using the atom coordinates.

Select **View | Explorers | Properties Explorer** from the menu bar. Select the Pd atom with **FractionalXYZ x = 0.5** and **y = 0.5**. Note the **z** value of this atom from the **XYZ** property.

The z value should be 1.401 Å and this is the interlayer spacing. This z value refers to the Z coordinate from the (Cartesian) XYZ property and not FractionalXYZ.

Note: For an fcc(110) system, d_0 can be calculated as:

$$d_0 = \frac{a_0}{\sqrt{8}}$$

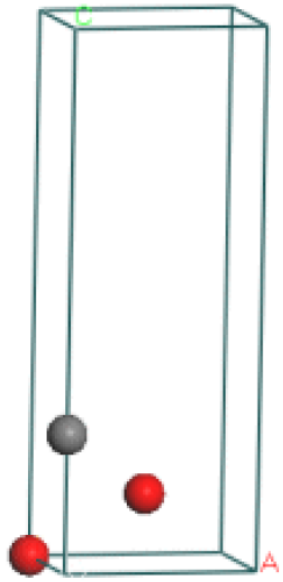
Before you relax the surface, you must constrain the Pd atoms in the bulk as you only need to relax the surface.

Hold down **SHIFT** and select all the Pd atoms except the uppermost Pd layer. Select **Modify | Constraints** from the menu bar to open the Edit Constraints dialog. Check the **Fix fractional position** checkbox and close the dialog.

The bulk atoms have been constrained. You can see the constrained atoms by changing their display color.

In the 3D Viewer, click anywhere to deselect the atoms. Open the **Display Style** dialog and select the **Atom** tab. Change the **Color by** option to **Constraint**.

This 3D view is now displayed:



Change the **Color by** option back to **Element** and close the dialog.

This structure is needed for the Pd(110) surface relaxation and also as a starting model for (1x1) CO on Pd (110) optimization.

Select **File | Save As...** from the menu bar. Navigate to the **Pd(110)** folder and click the **Save** button.

Hold down **CTRL** and drag the document into the **(1x1) CO on Pd(110)** folder. Rename the document **(1x1) CO on Pd(110)**.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

5. To relax the Pd(110) surface

Now you are ready to optimize the Pd (110) surface.

From the Project Explorer, open **Pd (1 1 0).xsd** in the **Pd(110)** folder. Open the **CASTEP Calculation** dialog and then the **CASTEP Geometry Optimization** dialog. Ensure that **Cell optimization** is set to **None** and close the dialog.

You should also calculate the density of states for the system.

Select the **Properties** tab on the CASTEP Calculation dialog. Check the **Density of states** and **Calculate PDOS** checkboxes and change the **k-point set** to **Fine**.

You are ready to run the calculation.

Click the **Run** button and close the CASTEP Calculation dialog.

When asked about converting to higher symmetry, click the **No** button to proceed with the current symmetry.

The calculation will take some time to run and so you will perform the analysis at the end. You should move on and construct the next set of surfaces.

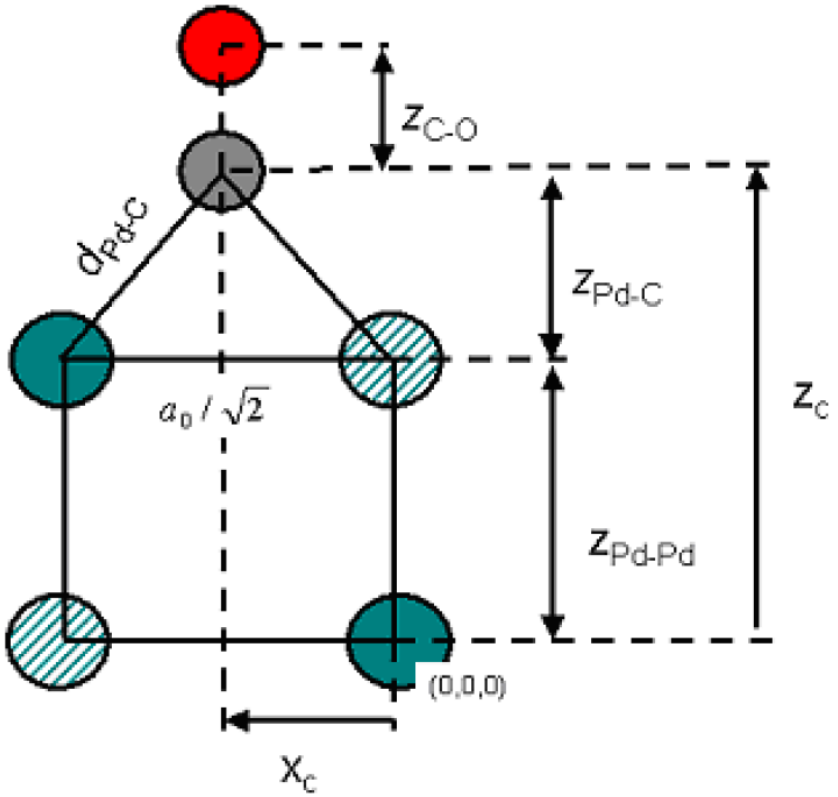
Select **File | Save Project** then **Window | Close All** from the menu bar.

6. To add CO to the 1 × 1 Pd(110) surface and optimize the structure

Now you are going to work with the structure in the `(1x1) CO on Pd(110)` folder.

In the Project Explorer, open **(1x1) CO on Pd(110).xsd** in the **(1x1) CO on Pd(110)** folder.

Now add the CO molecule above the short bridge position. You will make use of the fact that for CO on Pd(110), bond lengths have been experimentally determined.



Geometry of CO on Pd(110) in the yz-plane. Hatched atoms are not displayed in Lattice: Original display mode.

The first step is to add the carbon atom. The Pd-C bond length (denoted above as $d_{Pd\text{-}C}$) should be 1.93 Å. When you use the Add Atom tool you can enter either Cartesian or fractional coordinates but in this case you will use fractional coordinates, x_C, y_C, and z_C. x_C and y_C are simple as y_C = 0.5 and x_C = 0.

However, determination of z_C is slightly more difficult. You will construct it from the two distances $z_{Pd\text{-}C}$ and $z_{Pd\text{-}Pd}$.

$z_{Pd\text{-}Pd}$ is simply the lattice parameter a_0 divided by $\sqrt{2}$ (it should be 2.80 Å).

$z_{Pd\text{-}C}$ is obtained from the formula:

$$z_{Pd-C} = \sqrt{d_{Pd-C}^2 - \frac{1}{8}a_0^2}$$

It should be 1.33 Å.

Add $z_{Pd\text{-}C}$ and $z_{Pd\text{-}Pd}$ to obtain z_C (it should be 4.13 Å). Now convert this distance into a fractional length. You do this using the Lattice parameters.

Right-click in the 3D Viewer and select **Lattice Parameters** from the shortcut menu. Note the value of **c**.

To calculate the fractional z coordinate, you divide z_C by the c lattice parameter (you should obtain 0.382).

Open the **Add Atoms** dialog and choose the **Options** tab. Check that the **Coordinate system** is **Fractional**. On the **Atoms** tab change the **Element** to **C**, change **a** to **0.0**, **b** to **0.5**, and **c** to **0.382**. Click the **Add** button.

If you want to confirm that you have set up the model correctly, use the Measure/Change tool.

Click the **Measure/Change** arrow  on the toolbar and select **Distance** from the dropdown list. Click on the Pd-C bond.

The next step is to add the oxygen atom.

On the **Add Atoms** dialog, change the **Element** to **O**.

Experimentally, the C-O bond length has been determined as 1.15 Å. In fractional coordinates this is 0.107, adding this value to the fractional z-coordinate of carbon (0.382), the z-coordinate of oxygen is 0.489.

Change the value of **c** to **0.489** and click the **Add** button. Close the dialog.

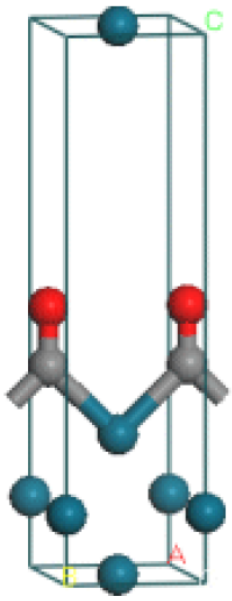
The calculations for the Pd surface model were carried out using P1 symmetry. However, the system has a higher symmetry, even after the addition of the CO molecule. You can find and impose symmetry, using the Find Symmetry tool, to speed up further calculations.

Click the **Find Symmetry** button  on the **Symmetry** toolbar to open the Find Symmetry dialog. Click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMM2.

Open the **Display Style** dialog and select the **Lattice** tab. Change the **Style** to **Default**. On the **Atom** tab, select the **Ball and stick** display style and close the dialog.

The structure should look similar to this:



Before you optimize the geometry of the structure, you should save it in the (2x1) CO on Pd(110) folder.

Select **File | Save** from the menu bar to save the 1x1 system. Then also select **File | Save As...** from the menu bar, navigate to the **(2x1) CO on Pd(110)** folder and save the document as **(2x1) CO on Pd (110).xsd**.

You are now ready to optimize the structure.

Select **File | Save Project**, then **Window | Close All** from the menu bar.

In the Project Explorer, open **(1x1)CO on Pd(110).xsd** in the **(1x1)CO on Pd(110)** folder.

Open the **CASTEP Calculation** dialog.

The parameters from the previous calculation should have been retained.

Click the **Run** button and close the dialog.

Once again, you can move onto building the final structure while the calculation progresses.

7. Setting up and optimizing the 2 × 1 Pd(110) surface

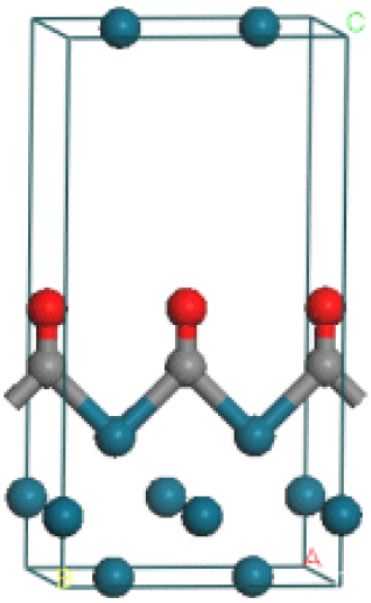
The first step is to open the 3D Atomistic document in the (2 × 1) CO on Pd(110) folder.

In the Project Explorer, open **(2x1) CO on Pd(110).xsd** in the **(2x1) CO on Pd(110)** folder.

This is currently a 1 × 1 cell so you need to use the Supercell tool to change it to a 2 × 1 cell.

Select **Build | Symmetry | Supercell** from the menu bar to open the Supercell dialog. Increase **B** to **2** and click the **Create Supercell** button and close the dialog.

The structure should look like this:



(2 × 1) Cell of CO on Pd(110)

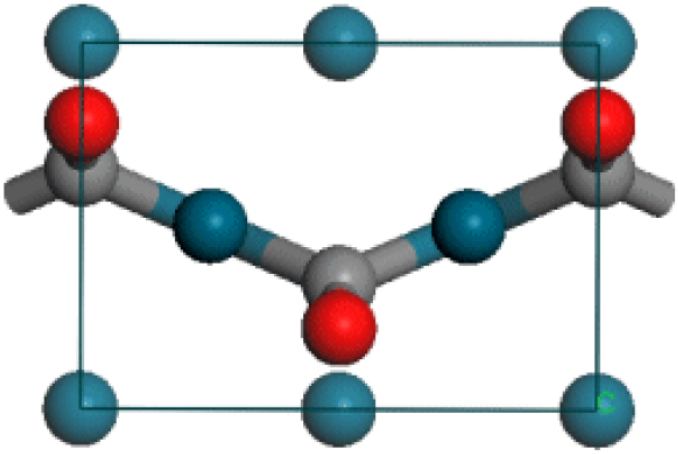
Now tilt the CO molecules with respect to each other. To simplify this operation, identify the CO molecule at y = 0.5 as molecule A and the one at y = 0.0 as molecule B.

Select the **carbon** atom of molecule B. In the Properties Explorer, open the **XYZ** property and subtract **0.6** from the **X** field. Repeat this for the **oxygen** atom of molecule B but subtract **1.2** from the **X** field.

Now repeat this for molecule A.

Select the **carbon** atom of molecule A. In the Properties Explorer, open the **XYZ** property and add **0.6** to the **X** field. Repeat this for the **oxygen** atom of molecule A but add **1.2** to the **X** field.

The view down the z-axis of the molecule should look like this:



However, you will notice that the Pd-C and C-O bond lengths have changed from their original values.

Select the **carbon** atom in molecule A and use the Properties Explorer to change the **Z** field of the **FractionalXYZ** property to **0.369**. Repeat this for molecule B.

This corrects the Pd-C bond length. You can use the Measure/Change tool to correct the C-O bond length.

Click the **Measure/Change** button  on the **Sketch** toolbar and select **Distance** from the dropdown list. Click on the **C-O** bond for molecule A.

Choose the 3D Viewer **Selection Mode** tool  on the **3D Viewer** toolbar and select the monitor. In the Properties Explorer, change the **Filter** to **Distance**.

Change the **Distance** property to **1.15** Å. Repeat this for molecule B.

Now recalculate the symmetry of the system.

Open the **Find Symmetry** dialog and click the **Find Symmetry** button then the **Impose Symmetry** button.

The symmetry is PMA2. The view of the unit cell changes from 3 CO molecules on the Pd surface to only 2. You are now ready to optimize the geometry of your system.

Open the **CASTEP Calculation** dialog and click **Run**.

The calculation starts. When the calculation finishes, you will need to extract the total energy of the system as detailed in the next section. You can move onto the next section to extract the energies from the previous calculations.

8. To analyze the energies

In this section you are going to calculate the chemisorption energy ΔE_{chem}. This is defined as:

$$\Delta E_{chem} = 0.5E_{(2\times1)CO\ on\ Pd(110)} - E_{Pd(110)} - E_{CO\ molecule}$$

Allowing the CO atoms to tilt against each other, hence reducing the self repulsion of the CO molecules, should result in a gain in energy. The repulsion energy can be calculated from:

$$\Delta E_{rep} = 0.5E_{(2\times1)CO\ on\ Pd(110)} - E_{(1\times1)CO\ on\ Pd(110)}$$

To calculate these properties, you need to extract the total energies from CASTEP text output documents for each simulation.

In the Project Explorer, open **CO.castep** in the **CO molecule/CO CASTEP GeomOpt** folder. Press **CTRL + F** and search for **Final Enthalpy**. Note down the value that appears in that line. Repeat the procedure to find the total energies of the other systems and so complete the table.

Simulation	Total Energy (eV)
CO molecule	
Pd(110)	
(1×1)CO on Pd(110)	
(2×1)CO on Pd(110)	

Once you have the energies, simply use the above equations to calculate ΔE_{chem} and ΔE_{rep}. These should have values of approximately -1.79 eV and -0.06 eV, respectively.

9. To analyze the density of states (DOS)

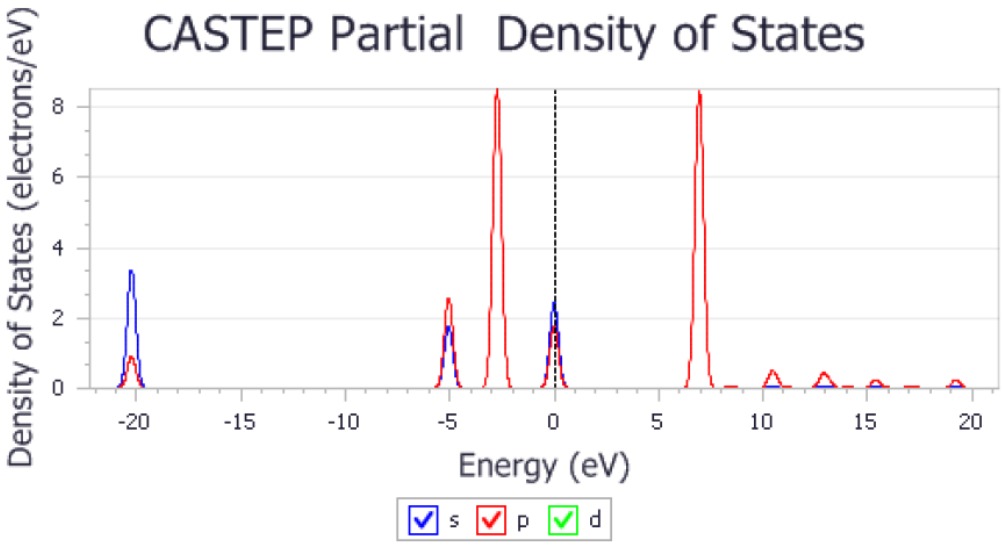
Next, you will examine the changes in the density of states (DOS). This will allow you to obtain an insight into the bonding mechanism of CO on Pd(110). To do this, you need to display the density of states of the isolated CO molecule and of (2x1) CO on Pd(110).

In the Project Explorer, open **CO.xsd** in the **CO molecule/CO CASTEP GeomOpt** folder.

Click the **CASTEP** button  on the **Modules** toolbar, then select **Analysis** to open the CASTEP Analysis dialog.

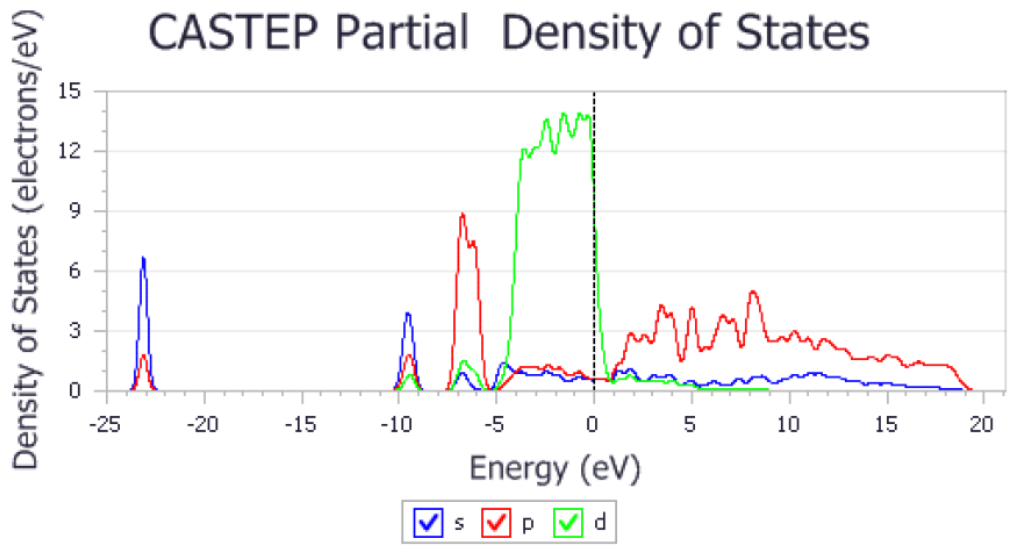
Select the **Density of states**. Click the **Partial** radio button and uncheck the **f** and **Sum** checkboxes. Click the **View** button.

A chart document is displayed showing the PDOS for the CO molecule.



PDOS of CO molecule

Repeat the above for **(2x1) CO on Pd(110).xsd**.



PDOS of (2x1) CO on Pd(110)

It is clear that the electronic states of the isolated CO molecule at approximately -20, -5, and -2.5 eV are considerably lowered in energy as the CO binds to the surface.

Note: The default pseudopotential for Pd, `Pd_2017R2.otfg`, treats 4s and 4p semicore states as valence. This results in sharp peaks in the calculated DOS at about -84 and -49 eV. The chart above excludes those states; this can be achieved by using Properties Explorer to change the maximum and minimum values along X and Y axes.

As an independent exercise you can analyze PDOS further by investigating contributions to the PDOS of the adsorbate complex that arise from the C and O atoms.

Hold down **SHIFT** and select all C and O atoms in the **(2x1) CO on Pd(110).xsd** document. Generate partial DOS as described above - the chart shows the effect of hybridization with Pd states which manifests itself as broadening of the energy levels and their general shift towards lower energies.

There are a number of additional experiments that can be carried out as an independent exercise, for example:

- Investigate the accuracy of the results by checking convergence with respect to calculation parameters:
  1. Repeat the chemisorption calculation with a significantly higher value for the vacuum thickness (for example, 15 Å instead of 8 Å).
  2. Repeat the chemisorption calculation with a more accurate k-point sampling; on the *CASTEP Electronic Options* dialog, *k-points* tab, use a *Separation* of 0.03 1/Å to produce a denser k-point grid. This step can be repeated with few more values until the chemisorption energy is converged to the desired accuracy.
  3. Similar to the previous step, repeat the calculations by increasing the energy cutoff on the *CASTEP Electronic Options* dialog, *Basis* tab; check *Use custom energy cutoff* to enable this step.

- The number of substrate layers can affect the result substantially; you can repeat this tutorial with more Pd layers by using a higher value for the *Fractional Thickness* when generating the surface.
- Surface calculations in a slab geometry often benefit from application of a dipole correction, especially when there is a pronounced dipole moment - as in the CO molecule.

  CASTEP allows you to apply such a correction by selecting a *Self-consistent* option for the *Apply dipole correction* on the *CASTEP Electronic Options* dialog, *SCF* tab. Repeat calculations with this setting to check whether it affects the energetics of CO adsorption.

  Tip: It is recommended to use the *All Bands/EDFT* option for the *Electronic minimizer* setting in this tutorial (on the SCF tab of the CASTEP Electronic Options dialog). The default *Density Mixing* option exhibits convergence problems for the elongated thin cells that are used in these calculations.

  You could additionally examine electrostatic potential by using the *Potentials* selection on the *CASTEP Analysis* dialog. A chart of the average profile of the electrostatic potential will be created when the *Import* button is clicked.

  Tip: There is a difference between the charts generated for calculations with and without a dipole correction applied.

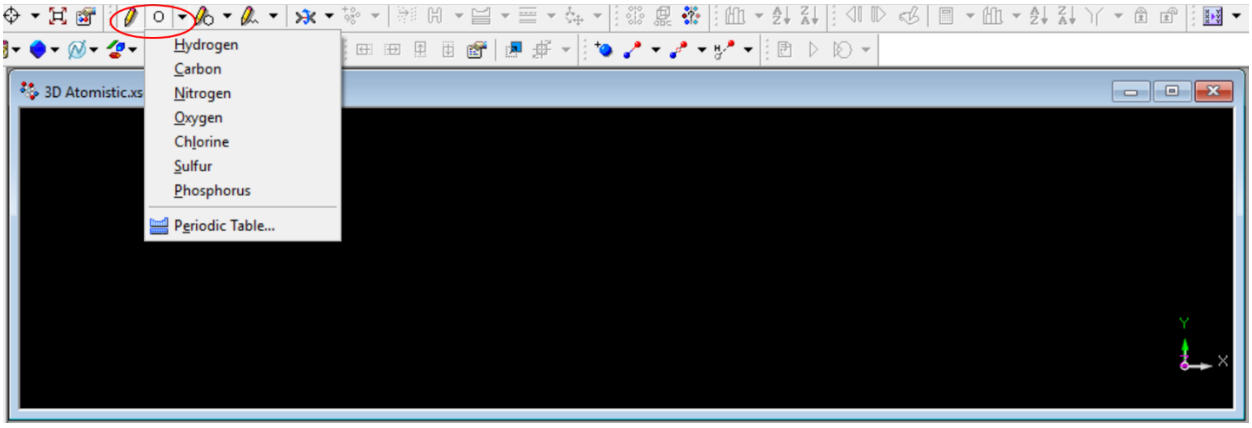
Note: Vacuum width has to be greater than 8 Å in order to generate the chart of electrostatic potential, so this last exercise can be performed only by increasing the vacuum thickness.

This is the end of the tutorial.

Common Q&A (continuously updated with new questions):

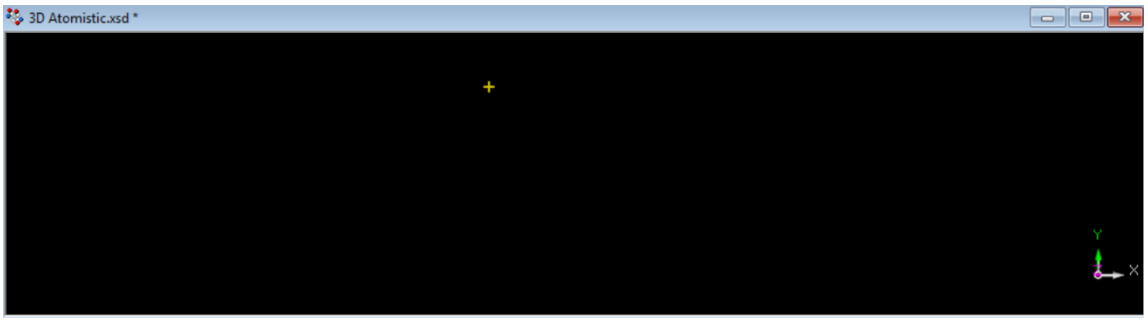
Q1: Where can I find the sketching tool? How can I create a molecule from scratch?

A1: First, go to **File → New →** double-click **3D Atomistic →** the sketching tool is on the toolbar



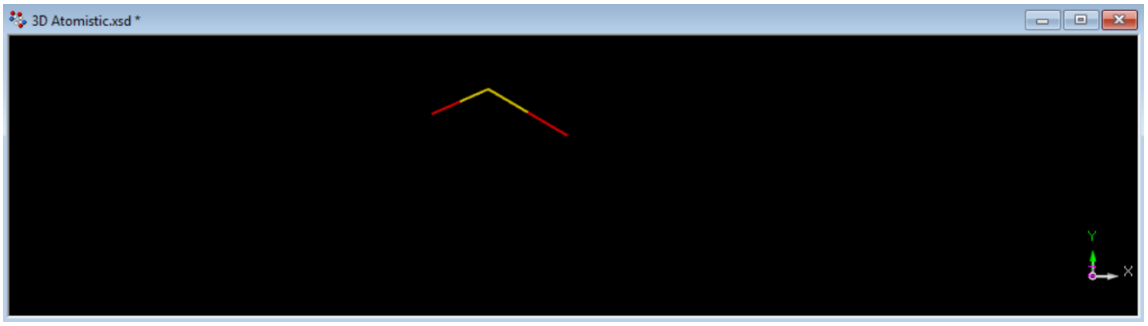
Common elements are listed here. You can also add any element you like by clicking "**periodic table**."

To add an atom (e.g., sulfur), select "Sulfur" from the list, left-click in the "3D Atomistic.xsd*" window, and then right-click or press "Esc" to confirm. Here, the "+" symbol indicates the S atom.



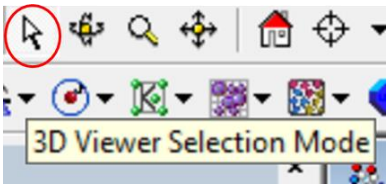
To build a molecule (e.g., SO_2), manually add two O atoms bonded to S. Select "Oxygen" from the list, left-click near the S atom, then left-click on S to form the bond.

Next, add the second O atom on the opposite side:

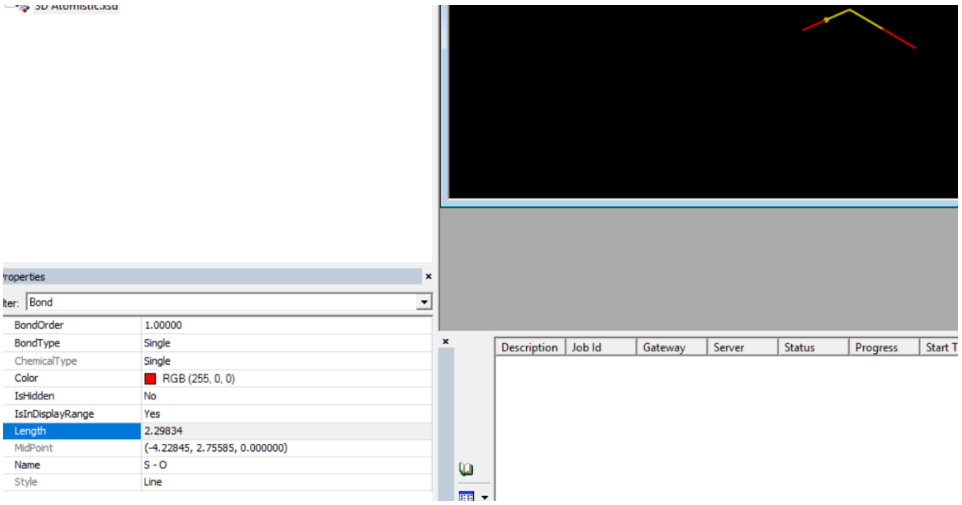


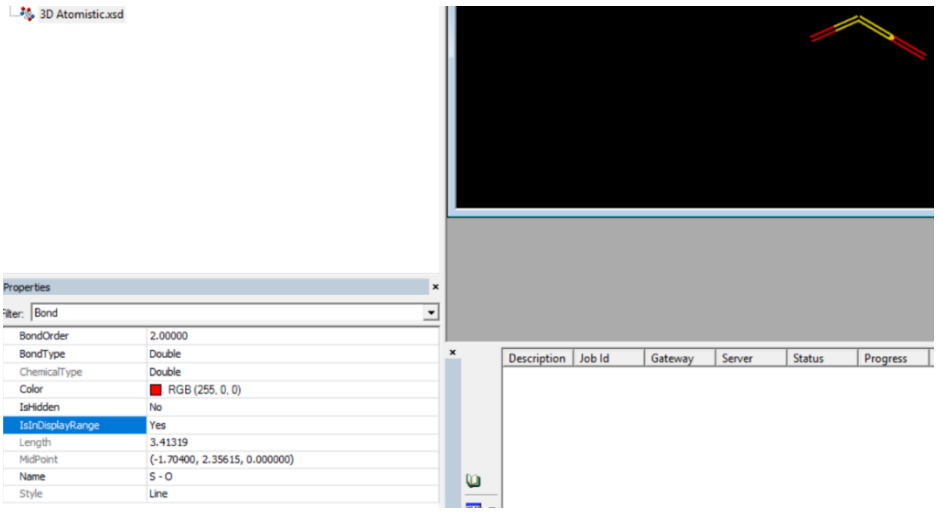
Apparently, the two S=O bonds are not equivalent. This is normal. We will address this in a later step.

Next, select the “3D Viewer Selection Mode,”

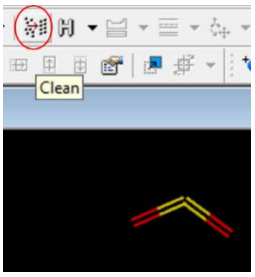


Since SO_2 has double bonds, click the middle of one bond, manually change the bond order from 1 to 2, and set the bond type from single to double.

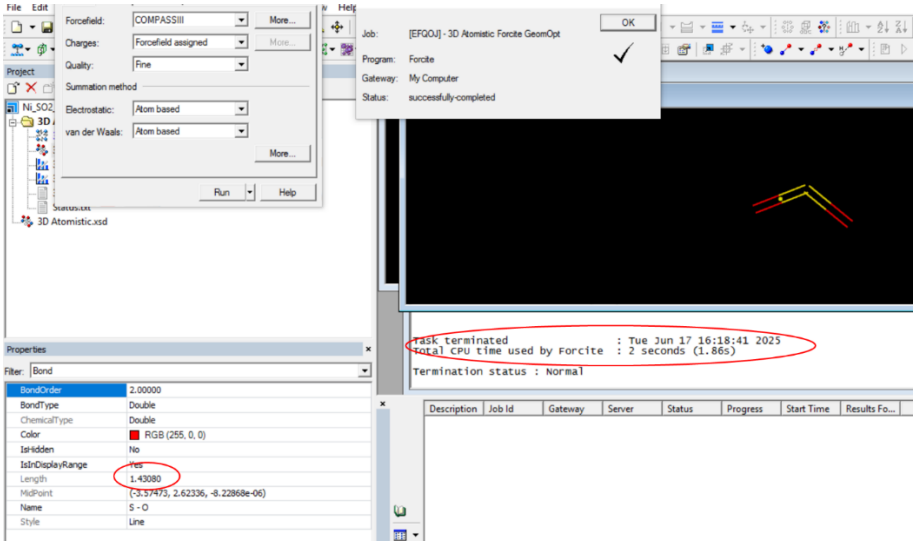




Now, let's make the structure look better. Simply click "**Clean**."

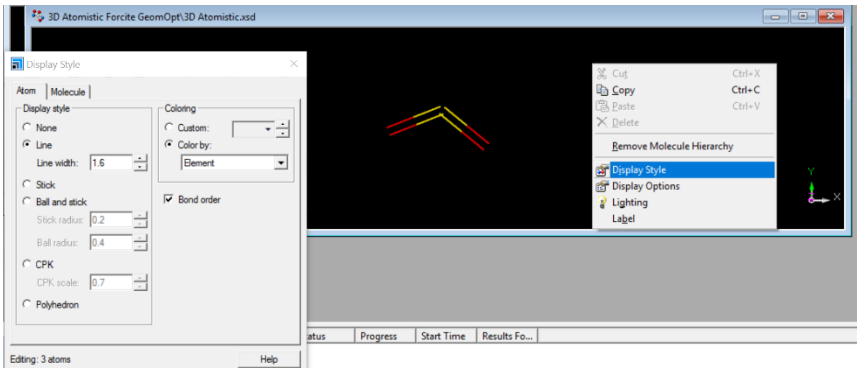


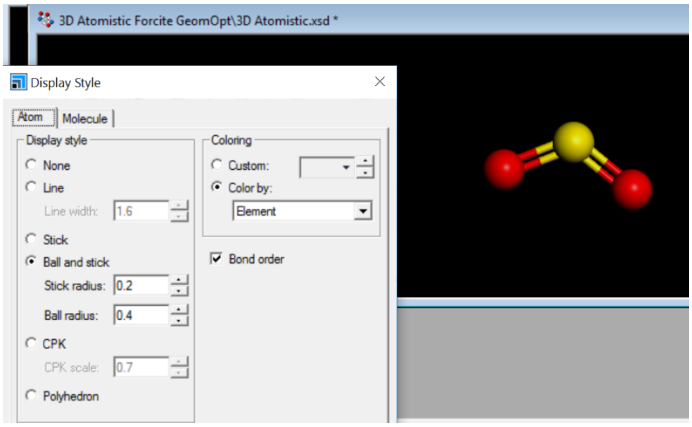
Finally, to optimize the structure, select **Module → Forcite → Calculation** from the menu bar to open the Forcite Calculation dialog. On the **Setup** tab, change the *task* to **Geometry Optimization** and the *Quality* to **Fine**. Select the **Energy** tab and change the *Forcefield* to **COMPASSIII**. Click **Run**.



Here, the calculated bond length is 1.43080 Å, in good agreement with the experimental value of 1.43 Å.

Finally, if you don’t like the display style, right-click in the structure window, and select **Display Style**, then you can choose any style you like, e.g., **Ball and stick**:





Q2: The tutorial mentions “ensure xxx is the active document” and “make xxx the active document” many times, what do they mean? What should I do?

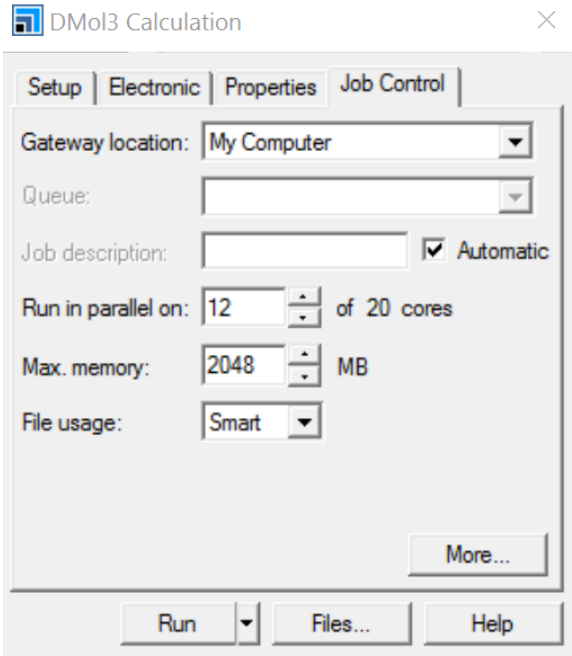
A2: Simply left click the document.

Q3: Where are the example documents? I cannot find them.

A3: C:\Program Files (x86)\BIOVIA\Materials Studio 25.1\share

Q4: How can I request more cores/processors to speed up my calculations?

A4: Parallel calculations may not always be available. If they are, go to **Job Control**, adjust the # of cores. For this specific workstation, the maximum # of cores you can request is 20. However, for small jobs (e.g., optimizing a small molecule), using more cores can sometimes slow down the calculations.



Q5: After I imported my model, I accidentally rotated the view to a random angle with the mouse. How can I reset it back to the default view?

A5: See below:

Q6: I noticed that MS's default diffraction data format is .xcd, which differs from the format of the data I collected at IAC (.raw). How should I convert my data so that MS can read it correctly?

A6: MS can directly read the .raw format and will automatically convert it to .xcd. See below: