Esperienze e pratiche

Computer and chemistry: Facilitating the learning process of the infrared spectra of water and carbon dioxide

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Abstract
A computational laboratory is proposed for secondary school students to facilitate the learning process of the Infrared (IR) spectra of water and carbon dioxide. In the context of the greenhouse effect, which is the macroscopic phenomenon related to the rate of cooling of our planet in response of being warmed by the sun, students can learn its molecular origin with the support of computer through the simulation of the vibrational spectra of water and carbon dioxide. Input files as well as data are provided so that the laboratory can be proposed even when computational facilities are not available. In particular, the role of computer in chemistry teaching and learning is established because molecular models let the students visualize the subnanometric world which remains elusive in daily experience.
Keywords*:* carbon dioxide, computational activity, greenhouse effect, infrared, Johnstone's triangle, water.

First submission: 28/09/2023; accepted: 08/11/2023
Available online: 13/12/2023

Introduction

'Chemistry is difficult' is the frequent complaint of students. 'It's hard to teach chemistry' is commonly reported by chemistry teachers at all levels.

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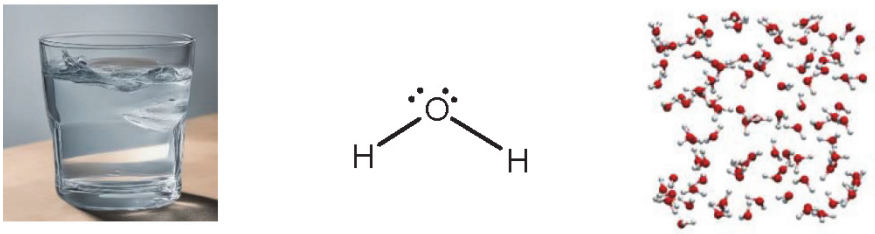
Il contributo è frutto di un lavoro condiviso in ogni sua parte.
Ringraziamenti.

Excellence and Innovation in Learning and Teaching (ISSNe 2499-507X), 2023, 2

Doi: 10.3280/exioa2-2023oa16829

Johnstone (Reid, 2019, 2021) has well contextualized the difficulties in learning chemistry by observing that chemists can see things at three levels. Matter can be described in terms of its properties and behavior, which are observed with the senses. This is the approach children learn in their early childhood. But chemistry has a peculiar symbolic language which is used to describe these observations and this coding is part of chemistry educational programs. Finally, chemists draw explanations for the observed phenomena using atoms and molecules, which are not visible, because they belong to the subnanometric world. The invisible structure and organization of matter makes understanding a challenging effort. These three aspects of chemical knowledge are connected like the corners of a triangle (Jonhstone's triangle), but it is not trivial to establish such links and, in particular, the rationalization of phenomena through particle-level interpretation creates a true cognitive barrier for the students and represents perhaps the major challenge in chemistry learning (Johnstone, 2010).

Figure 1 - (a) Liquid water; (b) Chemical formula of water; (c) Snapshot from a Molecular Dynamics simulation of a sample of liquid water



(a) (b) (c)

In Figure 1, the case of water is shown: on the left, liquid water can be seen; in the middle, the chemical formula of water is written, which encodes in a universal language the message that water is a chemical substance characterized by identical composition independently from the different samples in which it is present, i.e., a drink, swamp mud or sweat. Finally, on the right, a snapshot of an atomistic simulation of water is shown, from which macroscopic physico-chemical properties of water can be inferred such as its liquid state at room temperature and pressure, its density, and its boiling point.

Also, for this simple and universally known example, it is not straightforward to link the three descriptions. In particular, Figure 1 (a) and 1 (c) show water at a different length scale, and the macro-sub nano transition is performed using computer modeling. Nowadays there are experiments that allow to 'see' atoms and molecules, thus providing a proof of concept to the particle nature of matter, but computer simulations have proved to be faithful

and reliable tools to represent the features of the sub nanometric world. Yet, one should not forget that they are based on mathematical and physical equations and rely also on a well-defined coding. While the former can be almost ignored, at least at school level, the latter aspect deserves some attention because it can generate confusion and misconception, In Fig. 1 (c), each water molecule is formed by three spheres representing the three constituent atoms i.e., two hydrogens and one oxygen, connected by two identical segments representing the chemical bonds between each hydrogen and oxygen, The non-linear structure and the connectivity H-O-H (rather than H-H-O as erroneously suggested by the chemical formula H_2O) stem from complex physical concepts (quantum mechanics) or, alternatively, from an elegant chemical formalism (Lewis formulas, Figure 1 (b)) which allows to write chemical structures identifying the position and connectivity of atoms in a molecule without solving the electronic problem using quantum mechanical equations. In addition, the ball and stick representation and the color itself of the atoms are potential sources of misconception because they may erroneously suggest that atoms are colored spheres, bonds are rigid sticks, hydrogen is white and oxygen is red, and so on. Thus, the simulation allows to see the sub nanometric structure of water in a snapshot in analogous way to observing the fluid at macroscopic level, but the students must be aware of the representation code employed.

The example of water is a very simple case and is useful in the context of this work. In addition, it encompasses the great potential as well as the relevant issues related to the use of the computer in learning chemistry. Indeed, teachers can use the computer and technology in the class to stimulate curiosity and approach difficult concepts of chemistry at all three levels of Johnstone's triangle and this is the topic of the present work, which illustrates an example focused on the molecular vibrations of water and carbon dioxide through which they can take advantage of the computer in the class. This activity has been proposed on several occasions in the past years by the authors in very different circumstances, both to students from the secondary school and to chemistry undergraduates attending computational chemistry courses, after basic courses of physical chemistry. The level of detail was of course modulated on the level of knowledge of the students, but the approach is identical and includes the observation of the phenomenon, its representation, and its correct explanation; notably, not all three levels of Johnstone's triangle are necessarily introduced in the computational laboratory, depending on the age and chemistry background of the students, but are here discussed for completeness. Very recently, an accurate similar laboratory for undergraduates, including experimental and computational tasks, has been proposed by Hall and co-workers (Hall & Gunning, 2023).

In this work, we will describe the computational activities as they can be proposed to secondary school students, who are less familiar with radiations and have no knowledge of quantum mechanics, providing all necessary data and advice to run the simulations also when not all computational facilities are available.

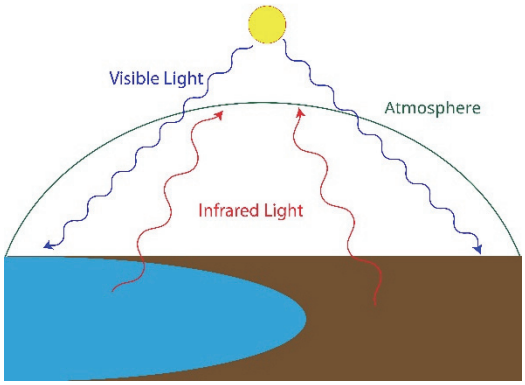
Discussion

The computational laboratory is intended for secondary school students (aged 16-18). It takes approximately four hours and should be organized in a computing room (or online). Students can work in small groups of 2-3 people. Ideally the teacher should introduce the topic of greenhouse effect, better if using open questions or brainstorming, or showing a video, or even involving the students in the construction of a small green house (one hour). In addition, due to its importance in modern society, global warming and its short and long-term consequences are a central topic of many scientific and political discussions and should be included in the introductory presentation. Quite often, global warming and the greenhouse effect are erroneously considered to be the same. On the contrary, the greenhouse effect is a natural phenomenon, which has allowed life on earth, whereas global warming is an effect caused by human emissions of greenhouse gases. Moreover, the greenhouse effect is explained to kids as well as to young learners who remain most of the times unaware of the physical chemistry behind it. Furthermore, quite often, it is related exclusively to carbon dioxide and/or to minor greenhouse gases, neglecting that the most important greenhouse gas is water vapor. The greenhouse effect is summarized in Figure 2 showing the sun radiation which passes through the atmosphere and warms the oceans and the lands, which in turn radiate infrared (IR) energy (heat) back to the atmosphere. Some gases can trap this energy, which remains inside the atmosphere. If the concentration of these gases in the atmosphere increases, more IR energy is trapped by the atmosphere, and this causes the global warming effect.

A second hour should be dedicated to the physical-chemical description using the symbolic language of chemistry. Focusing on water and carbon dioxide, the teacher should recall their chemical formulas and structure, introduce their three-dimensional geometry with molecular models, investigate the possible deformations from the equilibrium structure and their representations, review the electromagnetic spectrum and in particular the infrared region and the thermal effects of the infrared radiation. All these concepts are found in the school textbooks. It’s the ability of the teacher to

summarize them or to organize a more active lesson based for example on flipped classroom.

Figure 2 - The greenhouse effect



Finally, in the last two hours the students work in the computing room and through the guided protocol, which will be illustrated in this paper, visualize, interpret, and understand the molecular structure and vibrations of water and carbon dioxide molecules, from which the greenhouse effect originates.

Approaching chemical problems at macroscopic level

The teacher can introduce the topic by showing some images or videos or by proposing a brainstorming, aiming at defining what a greenhouse is and why it is used to cultivate crops and plants. Numerous examples can be found on the Web, but these are mostly videos which include 'the whole story' of the greenhouse effect, with an explanation adapted to the target public. The observation may efficiently be limited to the phenomenon which can be reproduced in a greenhouse, enforcing the concept that *the greenhouse effect is natural* and focusing on water vapor and carbon dioxide. When presenting the activity, the brainstorming approach seems suitable to let students share their thoughts and misconceptions emerge. The teacher can also involve the students in building a small greenhouse with jars or plastic bags, to let them reproduce the warming effect ("Modelling the greenhouse effect"). In Table 1, examples of general questions about the macroscopic problem are listed with their connection to scientific evidence and knowledge required to interpret properly the phenomenon.

Table 1 - General questions to start the introductory discussion

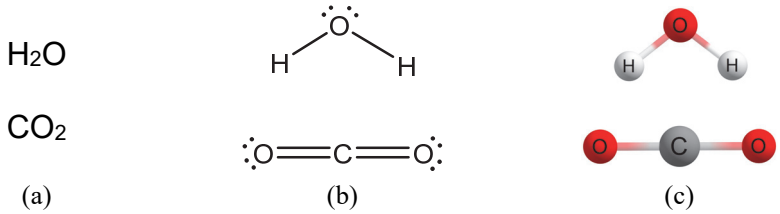
What is a greenhouse?	In a greenhouse, the temperature is higher and favors plants' lifecycle.
The electromagnetic spectrum	The sun light is an electromagnetic radiation. Bodies with higher temperature emit radiations with higher energy.
Infrared radiation and heat	Infrared radiation can be used to transfer energy in the form of heat
What is the role of atmosphere?	The atmosphere is like the glass of the greenhouse. It contains gases (including water vapor and carbon dioxide) which let the sun (body at higher temperature) radiation reach the planet, but trap (absorb) the IR radiation (heat) emitted by the earth.

Within this description, the greenhouse effect is apparently not related to molecular aspects and, although correct, the scientific knowledge remains a bit vague. The computational laboratory experience we have set up aims at explaining HOW the greenhouse effect results in trapping infrared radiation emitted from our planet and trapped by some gases in the atmosphere, focusing on water vapor and carbon dioxide.

Approaching the symbolic language of chemistry

When describing matter at molecular level, chemists use formulas i.e., a symbolic language which encodes different information. In basic chemistry courses, both at school and at the university, students learn to handwrite and sketch different chemical formulas of different complexity. In Figure 3, different chemical formulas of water and carbon dioxide are shown. Molecular formulas show the actual number of atoms within each molecule, while structural formulas represent how atoms are connected in the molecule. The strongest limitation is that the three-dimensional aspect of the molecules is lost. The computer is thus a valuable tool to visualize molecules as 3D objects and this aspect of this laboratory may inspire other activities, i.e., facilitate the 3D representation of molecules. Anyway, although 3D molecular representation is not the focus, it is important to stress that ball-and-stick models are not exactly a snapshot of the molecule, i.e., they are models which can be accurate and useful, but are representations of the real molecules. Thus, students must be aware of the information coding they are using, like atom colors, which are assigned based on Hofmann's croquet ball models (1865) and currently employed in the Corey-Pauling-Koltun (CPK) notation (Corey & Pauling, 1952; Koltun, 1965), stick representation of bonds, ball size, stick length and overall molecular shape which are rigid while real molecules at room temperature vibrate. Despite their simplicity, we can describe water and carbon dioxide and the procedure leading from their molecular formula to their 3D structure.

Figure 3 - Molecular formula (a), structural formula (b), and ball-and-stick representation of water and carbon dioxide



H_2O and CO_2 are the chemical formulas of water and carbon dioxide, respectively. Knowledge of the fundamentals of chemical bonding and Lewis theory, which is explained also in the textbooks of the secondary school, is mandatory to move from the molecular formula to the structural formula. Lewis representation gives reason also of the bent structure of water and the linear structure of carbon dioxide, respectively. Finally, the 3D structure can be built using the computer. The students can use the molecular editor Avogadro (Hanwell et al., 2012, 2023), which is a free software available for all platforms, and draw with the mouse each molecule in separated sessions. It is not important that the molecule is drawn with precision: Avogadro allows the pre-optimization of molecular structures, i.e., the automated modification of bond lengths, angles and dihedrals leading to the most stable structure.

Then, the molecular structure can be determined with increased accuracy by running a geometry optimization using quantum chemistry methods (DFT). For students at the secondary school, these methods can be used as a black box, because the formalism of quantum mechanics is beyond the curricula of their studies.

Approaching the sub-nanometric nature of matter

The third corner of Johnstone's triangle regards the sub-nanometric nature of matter i.e., its composition of atoms and molecules. This is the area in which the use of the computer can have the strongest impact as it allows to visualize 3D structures of atoms and molecules that compose matter. This experience aims at teaching students how to understand the role of water and carbon dioxide in the greenhouse effect through the analysis of their calculated IR absorption spectra.

Introductory notions on light and matter should be qualitatively explained based on the level of knowledge of the participants (Table 2). In particular, the students must understand that IR absorption is associated to energy transfer as heat and involves the interaction of light with matter. It causes rotations of the molecules of a sample and vibrations i.e., deformation of their structure, and is

thus strictly related to the chemical nature of the sample. This interaction with the IR radiation explains the spectroscopic signals and the greenhouse effect as well. In fact, the greenhouse gases like water and carbon dioxide absorb the IR radiation emitted form the earth and the oceans and in turn re-emit it so that heat remains trapped in the atmosphere. The accumulation of heat causes the well-known warming, a phenomenon which has allowed the development of life on earth and still makes it possible but can lead to excessive raise of the temperature if the amount of greenhouse gases increases in an uncontrolled way. Thus, the resonance frequencies (vibrational energy) of the greenhouse gases fall in the IR energy range. At molecular level, not all vibrations are excited by (absorb) the IR radiation, but only those which are accompanied by a change of the molecular dipole moment. Therefore, elements of molecular symmetry showing the most common types of normal modes (symmetric and asymmetric stretching and bending, Figure 4) should be presented and their effect on the molecular dipole moment clarified.

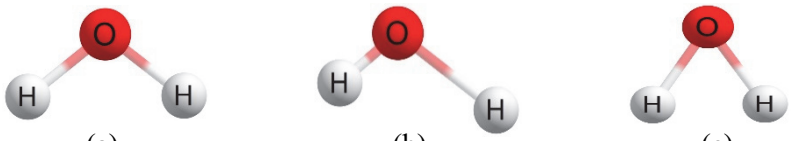
Table 2 - Basic notions needed to understand the proposed activity.

Topic	Explanation
Molecular motion	Molecules are not fixed in space but move around by translating, rotating and vibrating. Each of these motions mode is made up of discrete (quantized) levels that can be visited by the molecule.
Normal Modes	A different set of coordinates. Each coordinate, instead of describing the position of an atom, describes a motion mode i.e., a particular translation, rotation, or vibration.
Molecular dipole moment	The vectorial sum of all bonds' dipole moments. Bond dipole moments can be defined recalling the electronegativity of the different atoms.
IR absorption	IR absorption involves energies that target molecular vibrations. It is detected only if the targeted vibration involves a change in the molecular dipole moment. It can be measured or calculated.

A full step-by-step procedure of the computational lab activity is reported in the Supporting information with all the inputs and outputs necessary. First, the free software Avogadro can be employed to draw and pre-optimize the molecules of water and carbon dioxide. If the computational software Gaussian (Frisch et al., 2016) is available, the students can carry out the calculations of the spectra inserting the coordinates obtained from the pre-optimization in the provided input templates (see Supporting Information) and calculate the IR spectra. In case computational facilities are not available, we have provided the results of the calculations (see Supporting Information). The obtained outputs can be visualized with the software ChemCraft (Andrienko, 2023) that shows the calculated molecular vibrations and the obtained IR spectrum. Each group can then analyze the different vibrational modes obtained from the calculation

(Figure 4). Table 3 shows an example datasheet that can be used to collect the results. The teacher can then proceed to discuss the results of one of the two compounds. Additional details on the physical properties of the vibrations can be highlighted and confirmed by the numbers obtained e.g., the fact that bendings are found at lower energies than stretchings or that normal modes that are equivalent by symmetry have the same energy. The second compound should be left as a test for the students to do on their own.

Figure 4 - Vibrational modes of water. In the stretching vibrational mode, the OH bond lengths can change in a symmetric fashion (a) or asymmetrically (b); the bending vibrational mode affects the HOH angle amplitude (c)



(a) (b) (c)

Table 3 - Example datasheet for the analysis of the calculated results

Compound				
Vibration nr.	Wavenumber	Intensity	Mode type	Visible in spectrum?
1				
2				
3				
4				

Evaluation and assessment

The evaluation of the activity is carried out by grading the report sheets (see an example in Table 3) for both compounds for each group. One point is given if the field is correct, none if not. A passing score of 60% of correct answers and an excellence score of 90% were used in the test sessions for the activity. We evaluated the activity on two classes of 21 and 24 students and in both around 90% of the students passed, with more than half exceeding the excellency level. The most common mistakes involved mainly the second compound that was carried out by the students without the teacher's guidance and regarded the recognition of the mode type. The aggregated results should be shared with the students to assess which were the most common errors and try to understand why the underlying concepts were not fully understood.

Finally, an open discussion should conclude the activity to put the calculations into the greenhouse effect context. Students should be asked to try

and make a connection between the calculated IR spectra and the macroscopic greenhouse effect exerted by water and carbon dioxide. The teacher should act as a guide to make sure that the link between the molecular properties and the macroscopic effect they have in the greenhouse effect is clearly outlined. If there is a good response from the class, the discussion can be furthered asking the students to make predictions on the possibility of some of the other substances present in the atmosphere to be or not to be (this is the case of the abundant molecular oxygen and molecular nitrogen) greenhouse gases. Since typically students enjoy looking at molecular vibrations, exercises can be proposed to classify them for different molecules and predict if they are IR active. To this purpose, at the end of the lab, the teacher can propose to install an app on the mobile phone, MolAr ("MolAR"), which allows to visualize the vibrational normal modes of a lot of molecules with their classification and eventually prepare interactive exercises.

Conclusions and perspectives

The greenhouse effect is a good example of a pressing environmental challenge that can be used in a secondary school activity to explore all three levels of chemistry (Reid, 2019, 2021). Our computational laboratory aims at explaining the origin of this phenomenon through the calculation of the IR spectra of two fundamental components of the atmosphere, water and carbon dioxide, using a robust protocol. The procedure can directly show, using the symbolic language of chemistry, how the macroscopic atmospheric effects are caused by the intrinsic properties of microscopic objects.

The use of all three levels of chemistry in the same experience is often hard to find in secondary school curricula that usually focus on only one of the aspects, leaving students with a series of uncorrelated pieces of knowledge that are hard to assimilate. With the combination of calculations, that give access to the elusive microscopic world, and the introduction of more interactive teaching strategies actively involving students, we believe that it will be possible to create more effective chemistry programs encompassing all the corners of Johnstone's triangle that will result in enhanced competence and likely in students saying 'Chemistry is fun!' and teachers replying, 'It's a pleasure to teach chemistry!'.

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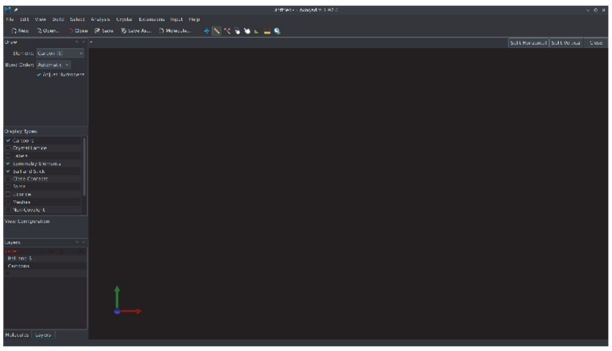
Appendix

IR Spectra calculation procedure

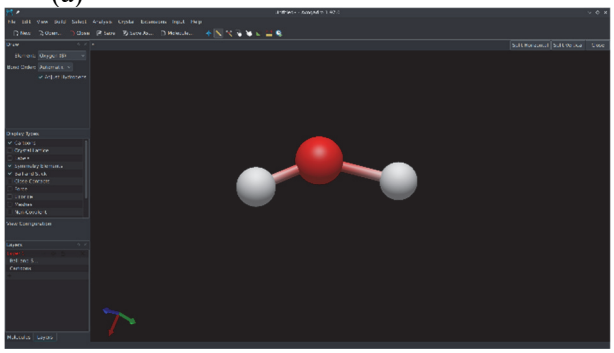
To calculate the IR spectrum of water or carbon dioxide the first step is to create the 3D model of the molecule. The free software Avogadro (https://www.openchemistry.org/projects/avogadro2/) will be used to draw the spatial structure of the molecule and then pre-optimize the geometry with the in-built force field engine. After launching, Avogadro presents a black window where molecules can be drawn (Figure S1, a). Using the pencil tool atoms of different elements can be added (Figure S1 b). As the drawn molecular structure is usually not good, a pre-optimization is carried out that should bring the molecule closer to its equilibrium geometry (Figure S1, c). The coordinates of

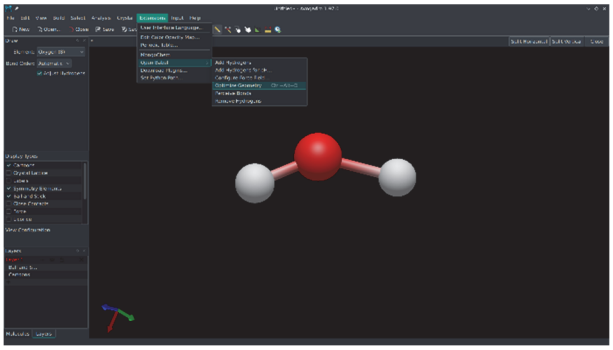
the pre-optimized structure can be extracted and used for the DFT calculation using Gaussian (Figure S1, d).

Figure S1 - Avogadro 2 steps to obtain the initial pre-optimized coordinates of water. Initial Avogadro 2 screen (a); Drawing tool to insert the required atoms (b); Force field geometry optimization menu (c), and cartesian coordinates editor (d)

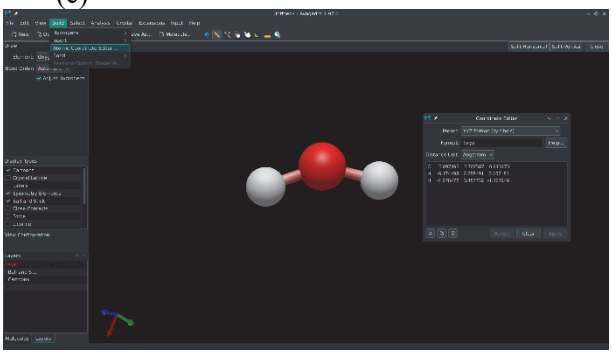


(a)





(c)



The actual IR spectrum is calculated at the DFT level with Gaussian. The template input for the calculation is the following:

```
%mem=8GB
%nprocshare=8
%chk=opt.chk
#p b3lyp/6-311G(d,p) opt freq

title

0 1
O    -0.032562940    0.000000000   -0.421603299
H    -0.032562940    0.759337000    0.174439701
H    -0.032562940   -0.759337000    0.174439701
```

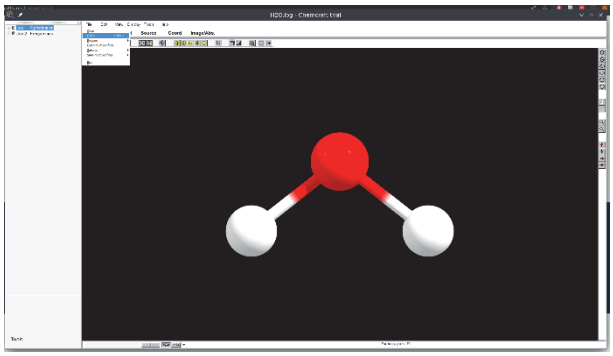
The first line is the amount of RAM requested for the calculation, the second the number of CPUs, and the third the name of the checkpoint file that will be created. These can be changed in relation to the available computational resources. The line starting with #p is the so-called *route* and it contains all the

parameters for the calculation. In this case the functional B3LYP and the basis set 6-311G(d,p) are chosen. In addition, a geometry optimization (opt) and a frequency calculation (freq) are requested. The route line is followed by a blank space, the title line that contains the name of the calculation, and by the molecule specification. The latter starts with a line containing the charge (0) and the multiplicity (1 for a singlet) of the molecule and is followed by the molecular coordinates. In this example the coordinates for a molecule of water are reported. They can be substituted with the coordinates of the molecule for which the IR spectrum must be calculated. **IMPORTANT:** the use of blank lines in Gaussian is very precise and exactly one blank line must separate route from title and title from molecule specification. Moreover, the input file must always end with a blank line otherwise the calculation will not run.

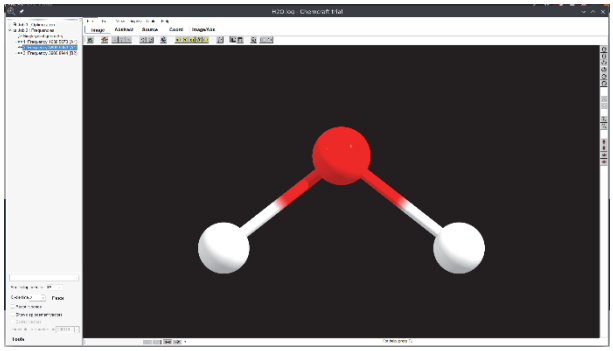
The gaussian calculations can be run by executing the g16 command on the created input file. It will create a text file with .log extension. If the calculation correctly ended, the last line of the .log file should read "Normal termination of Gaussian". In case the Gaussian software is not available we have provided the output files as supplementary material.

The outputs can be opened with the software ChemCraft (https://www.chemcraftprog.com) to visualize the molecular vibrations and the IR spectrum. ChemCraft is a paid software that offers a trial period and can therefore be downloaded and used for free for a period of 150 days. The main steps needed to open the Gaussian results and visualize the vibrations and IR spectrum are reported in Figure S2.

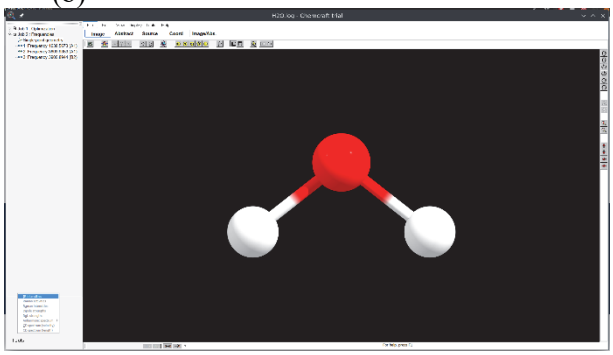
Figure S2 - ChemCraft steps to visualize the molecular vibrations and the IR spectrum. Initial ChemCraft screen and open file menu (a), molecular vibrations list under Frequency section in the left-hand side of the screen (b), the spectra visualization menu available when the entry Frequencies on the left hand side is selected (c), and the IR spectrum visualized from ChemCraft (d)



(a)



(b)



(c)