

Lab 7

Electronic Spectroscopy

7.1 Overview

In this lab we will consider how to deal with excited states using an extension of DFT called time-dependent density functional theory or TDDFT. We will look at calculating excitation energies and intensities and use this data to simulate spectra. We will analyze the spectra with a graphical tool and we will also consider how to assign excitations in terms of orbital excitations. Finally, we will look at how to deal with Rydberg excitations.

7.2 Density Functional Theory and Excited States

Excited electronic states play an important role in chemistry. An excited state can be populated when a molecule absorbs a large amount of energy. A typical example of this process is the absorption of a photon from the ultraviolet region of the spectrum. The interaction between a photon and a molecule can lead to chemical reactions a part of chemistry often called photochemistry. Many spectroscopic techniques involve excited electronic states. Understanding these processes requires some understanding of the nature of the excited states. The experimental study of a molecule in an excited state is difficult because they are generally very short lived and low in concentration. Theoretical methods don't suffer from these problems.

The most obvious way to determine the properties of an excited state theoretically is to calculate the wavefunction of the state of interest directly. This is the most common approach used in non-DFT methods. When considering the basic theories of DFT you may have noticed that they don't say anything about excited states. The Hohenberg-Kohn theorem applies to the ground state only.

Is there any way we can learn something about excited states using DFT? We can use *Response Theory*. In response theory we study how a system responds to a perturbation. It turns out that from the response of the ground state of a molecule we can obtain a lot of information about its excited states. The particular form of response theory most useful for the study of excited states with DFT is time-dependent density functional theory or TDDFT. It is beyond the scope of this course to go into response theory or TDDFT. You should just recall that we actually calculate the ground state of a system and the response of that system to a perturbation.

From a TDDFT calculation we can obtain useful information that is directly related to absorption spectra. In particular, the calculation gives the difference in energy between

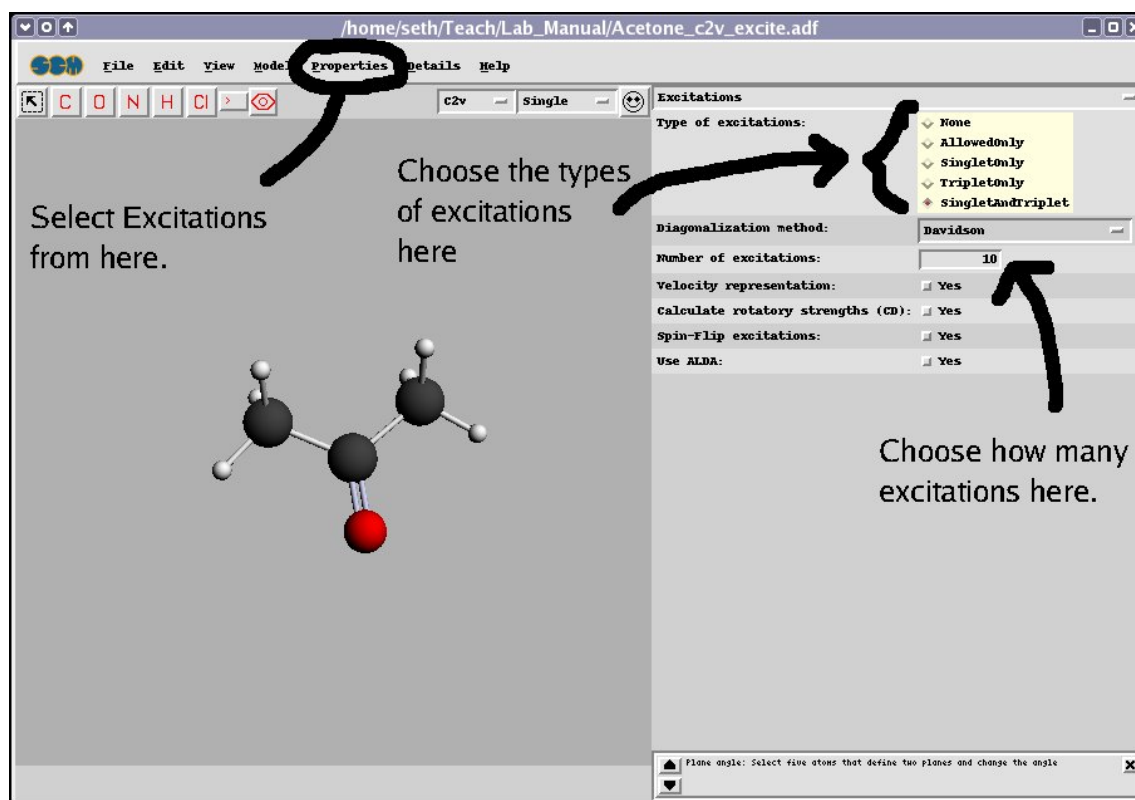


Figure 7.1: The Excitations options.

the ground state and excited states (i.e. the excitation energies) and the intensities of the transitions from the ground state. With this information at hand it is possible to make a simulated spectrum from the calculated data.

7.3 Excited States and ADF

To choose to calculate excitation energies and intensities select the *Properties: Excitations* menu option. Doing so will bring up a series of options on the right-hand side of the ADFIN-PUT window (see figure 6.1).

The default of the “Type of excitations” to be calculated is “None” i.e. don’t calculate excitations. Other than “None” you have several options as to which excitations to calculate. You may recall from previous chemistry lectures that there are some selection rules attached to electronic spectroscopy. One selection rule is that spin is conserved so that a transition from a singlet state will go to another singlet state, a doublet to a doublet and so on. If the molecule has some symmetry, there may be further selection rules depending on the symmetry of the ground and excited states involved. For example, if a molecule has C_{2v} symmetry and the ground state has A_1 symmetry then transitions to states with A_1 , B_1 and B_2 symmetry are allowed and transitions to states with A_2 symmetry are forbidden.

Thus, you can select that ADF will calculate only excitations to states that are allowed according to the selection rules (“AllowedOnly”), only excitations to states that are singlets (“SingletOnly”), only excitations to states that are triplets (“TripletOnly”) or excitations to both (“SingletandTriplet”). It should be noted that higher spin states are not accessible. Further, we will only consider here molecules with closed shell (singlet) ground states. If we are dealing with a molecule that has unpaired electrons the situation is more complicated.

Calculating a forbidden transition may seem pointless or even impossible but just because an excitation is forbidden it doesn’t mean that we can’t calculate the energy difference between the ground state and the particular excited state. It does mean that we will find that this excitation has zero intensity.

In reality, forbidden excitations often have nonzero intensity. The idea of an excitation being forbidden arises due to a particular theoretical description of electronic excitations. If we go beyond that description and include things like molecular vibrations and spin-orbit coupling then some intensity can appear. If a forbidden transition does have intensity it is usually rather weak compared to allowed transitions.

The other control that we need to be concerned with is “Number of Excitations” which, unsurprisingly, controls how many excitations we calculate. It should be noted that this is the number of singlet or triplet excitations. So, if Number of Excitations is set to 8 and SingletandTriplet is chosen then you get 16 excitations overall. The other options control technical aspects and more advanced features that we do not cover here.

Note that when we are calculating excitations the *Preset* options *Main Options* should be set as *Single Point* since we are interested in the excitations at a single point on the PES. This assumes that you already have found the minimum on the PES of interest of course.

7.4 Analysis of Results

The most straightforward way to examine the results of a TDDFT calculation is through the SPECTRA program. After a calculation calling for excited states is run the *SCM: Spectra* menu option will open up the graphical spectral analysis tool. We have used this tool in lab 6 for the purpose of looking at simulated IR spectra. Once SPECTRA is open a simulated electronic spectrum built using the calculated data will be displayed (figure 6.2).

The spectrum itself provides a qualitative overview of what the calculation predicts. Quantitative data can be obtained in a few different ways. Moving the mouse over a particular peak will cause a green box to appear. This box will include the following information:

- The symmetry of the transition (singlet-singlet or singlet-triplet and the spatial symmetry).
- The energy (in au) and oscillator strength (intensity) of the transition.
- The composition of the transition (see section 6.5).

Not all excitations will have peaks in the simulated spectrum. They may either be very low in intensity or have zero intensity by symmetry (forbidden). The location of all calculated excitations are indicated by red lines along the x axis of the simulated spectrum. By moving the mouse over a red line the green box for that excitation will appear.

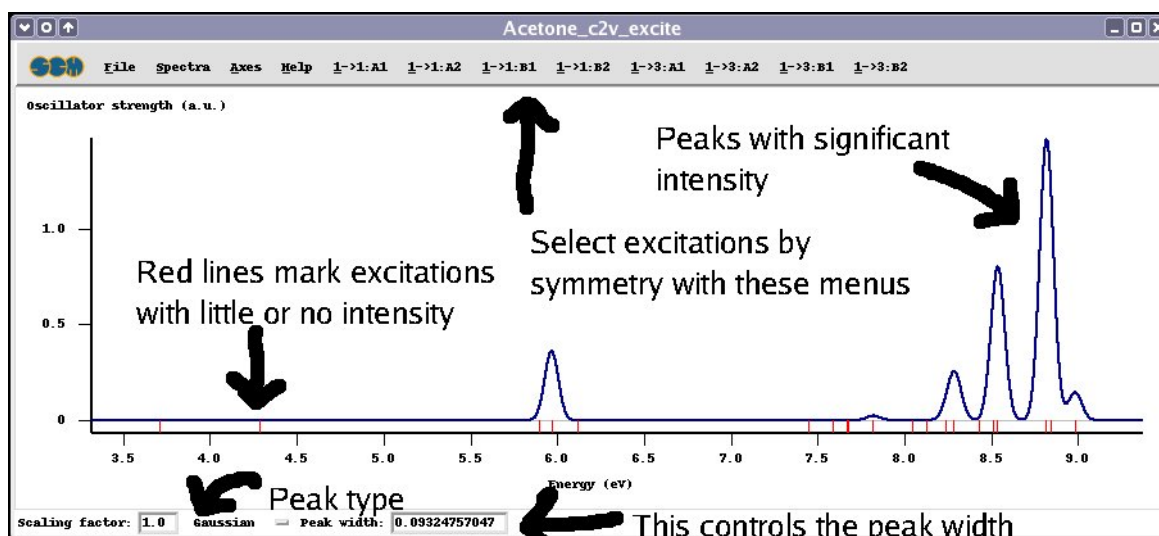


Figure 7.2: The SPECTRA window showing a calculated electronic excitation spectrum. The chosen energy units here are eV.

Alternatively, information on the excitations can be obtained through several of the menu bars. The rightmost menus are labelled with the different excitation symmetries involved in the current calculation. Clicking on one of these menus will produce a list of the excitations of that symmetry along with their energy and oscillator strengths (intensities).

Our calculations give us the energy and intensity of the excitations. They tell us nothing about the band widths. Much like the vibrational spectra we calculated in lab 6, SPECTRA chooses arbitrary but hopefully sensible band shapes for our calculated spectra. You have control over these band shapes through choosing a band width parameter and the functional form of the band shape (Gaussian or Lorentzian).

Exercise 7.1 For these calculations use the LDA functional and a TZ2P basis set. Build a molecule of methanal (formaldehyde). Optimize its geometry. Calculate the first 5 excitations of formaldehyde. Include all singlet and triplet excitations to give a total of 10 excitations. Visualize your calculation with the SPECTRA program. Use eV as your energy axis. Save a picture of your spectrum with the *File: Save Postscript...* command. Change the bandshape function from Gaussian to Lorentzian and the width parameter to 0.2. Save another picture of your spectrum. In the experimental spectrum, weak intensity is found between 3 and 4 eV. What transitions do you calculate to be in this region and what energy do you predict them to have? A more intense absorption is found closer to 7 eV. What excitation or excitations do you predict to be responsible for this intensity? What energy do these excitations appear at?

7.5 Assignment of Excitations in Terms of Orbital Excitations

Electronic excitations are often assigned in terms of excitations from one orbital to another. Examples of such assignments are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ where π and π^* refer to bonding and antibonding π orbitals and n is an orbital describing a nonbonding lone pair of electrons. Orbitals are a theoretical construct growing out of MO theory. They are not real and cannot be directly studied experimentally. Thus assignments like $\pi \rightarrow \pi^*$ are not obtained directly from experimental spectra like the overall state symmetry can. Assignments in terms of orbitals are usually derived from calculations. Although orbitals don't exist in reality they can be used to describe reality well enough and simply enough to be enormously useful in rationalizing and classifying experimental results. Thus being able to assign a given excitation as $\pi \rightarrow \pi^*$ is a very useful thing to be able to do.

The excitations obtained from TDDFT are more complicated than a single orbital excitation such as $\pi \rightarrow \pi^*$. Fortunately, TDDFT does express the excitations as a combination of many orbital excitations and in many cases it is possible to make an orbital assignment like $\pi \rightarrow \pi^*$.

7.5.1 Extracting Orbital Assignments from the SPECTRA Program

As has already been noted, moving the mouse over a band in the SPECTRA window produces a green box with lots of information. The bottom section of this green box is labelled "Composition." Following this label the excitation is broken down into orbital excitations with the most important (in terms of % contribution) first. If one orbital excitation has a far greater % contribution than all others then the calculation suggests this as the assignment. The orbital labels provided by ADF come from the irreducible representations of the point group of the molecule in question. These labels may not be exactly what you are looking for. For instance, if a molecule has D_{2h} symmetry the orbitals will be labelled a_{1g} , a_{1u} , b_{1g} , b_{3u} etc. To decide what orbital you are looking at e.g. in terms of π and π^* you should look at the form of the orbitals in question with the VIEW program as we did in lab 2.

Exercise 7.2 Consider the lowest energy singlet excitation and the intense excitation near 10 eV in the spectrum of methanal. What assignment in terms of orbitals does your calculation predict for these two excitations? Look at the relevant orbitals with the VIEW program. Describe these two excitations in terms of σ , π and n orbitals.

7.6 Rydberg States

One particular type of excited state needs special consideration in order for there to be any hope of treating them correctly: Rydberg States.

A Rydberg state is a state where one electron is very weakly bound to the rest of the molecule. This electron spends most of its time a long way from the molecule. From a distance, a molecule with one electron removed looks a lot like a point charge. Another system we know where an electron sees a point charge is the hydrogen atom. It may not surprise you then that Rydberg states behave a lot like the excited states of the hydrogen atom. They form series that can be indexed by a principle quantum number n and converge

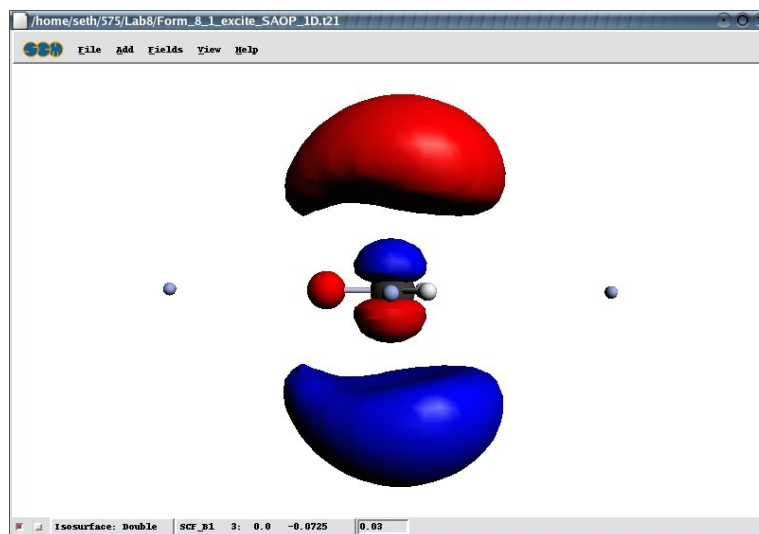


Figure 7.3: A Rydberg p orbital of formaldehyde.

on an ionization potential of the molecule. In terms of orbitals, calculations put the excited electron in an orbital that looks like a very big atomic orbital with s , p , d or higher symmetry. A picture of a Rydberg $3p$ -like orbital can be seen in figure 6.3.

Describing an excitation to a Rydberg state with the normal TDDFT approach often fails to give good results. This is due to two reasons. Firstly, standard basis sets describe the electron density near the nuclei well. They don't have any big functions needed to describe the weakly bound electron. A basis set that includes these big functions (called "diffuse functions") must be used to describe a Rydberg state correctly. Secondly, most standard functionals are very poor at describing the electron density far from the nuclei, ie are very poor at describing Rydberg states. Specially constructed functionals that can describe this region (functionals that are asymptotically correct) must be used to treat a Rydberg state.

7.6.1 ADF and Basis Sets with Diffuse Functions

ADF provides access to more basis sets that just SZ , DZ , DZP , TZP , $TZ2P$ and $QZ3P$. A more precise method of choosing your basis sets is to make use of the *Details: Basis* menu item. The information for each basis set is contained in a file usually in the *atomicdata* directory in your ADF distribution. Once you have selected the *Details: Basis* option you will be able to choose a particular file to use as the basis set for a given atom (see figure 6.4). There are several basis sets with diffuse functions to choose from but we will use the sets in the directory `/home/programs/ADF/adf2006/adf.01/atomicdata/ET/ET-QZ3P-1DIFFUSE`. If you do not specify anything for a given atom type then the basis set for that atom will be whatever is specified in the *Main Options* window.

Technical Point Diffuse functions are rather big and the diffuse functions on different atoms tend to overlap with each other. This overlap means that one functions does the job of

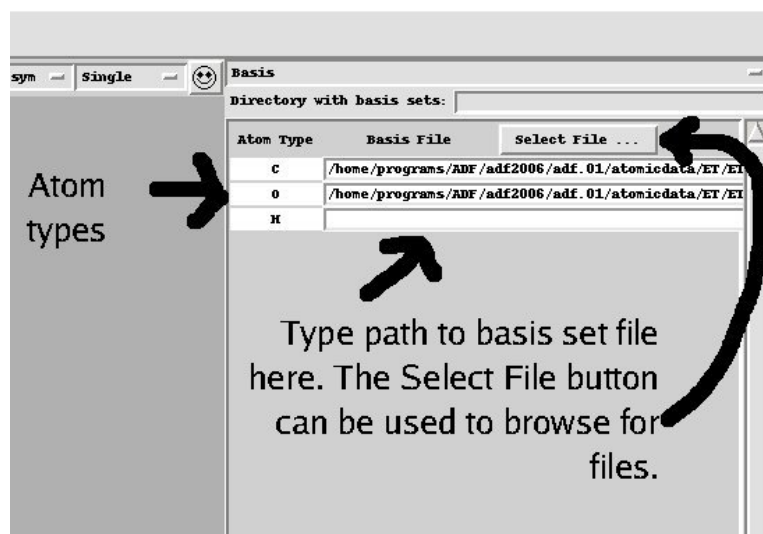


Figure 7.4: Choosing a basis set more precisely.

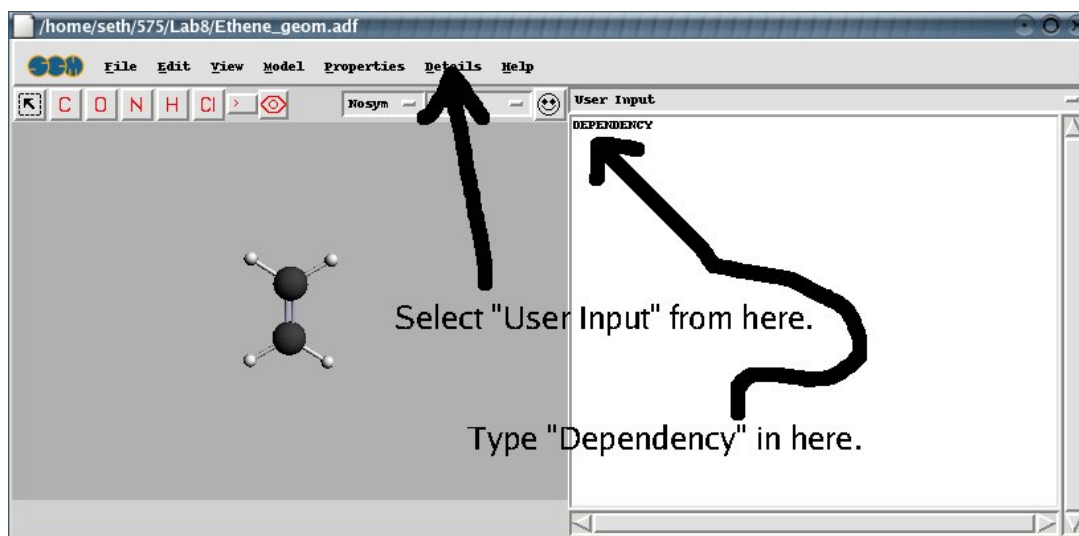


Figure 7.5: Entering the Dependency command through the User Input option.

another because they cover the same space. If you have several diffuse functions it often turns out that one or more of them is redundant because the space covered by them is completely covered by other diffuse functions. This may not seem like a big deal but it leads to situations in the program where 1 divided by 0 or very close to it appears. 1 divided by 0 is undefined mathematically and having it appear in a calculation is very bad.

To avoid this problem the redundant functions must be removed from the basis set. ADF can check to see if any redundant (or, in the mathematical lingo, linearly dependent) functions exist and remove them. There unfortunately is no button or switch in ADFINPUT for this. So, you must add the relevant command by hand. Fortunately, ADFINPUT does provide a way to add commands by hand.

Any particular command can be sent to ADF through the *Details: User Input* menu option. Once this command is selected a blank window opens up and any commands (that ADF understands) can be typed in (figure 6.5). In this case, to avoid problems with linear dependency we type in "DEPENDENCY". It is recommended that this be done whenever diffuse functions are utilized.

7.6.2 ADF and Asymptotically Correct Functionals

ADF has three functionals that are constructed so that they are able to better describe Rydberg states. Of these three, two can be accessed with ADFINPUT. From the list of functionals accessible from the *Model: XC functional* option these two functionals are: *SAOP* and *LB94*. Note that these functionals cannot be used with frozen cores (i.e. you must specify *None* in the Core Type option) or in geometry optimizations. This last limitation is not a big one because the electron density far from the nuclei have little influence on geometry optimizations. There is therefore no advantage to using these special functionals for geometry optimizations.

The SAOP functional is generally believed to be superior to LB94.

Exercise 7.3 Several bands in the electronic spectrum of ethene have been identified as excitations to Rydberg states. Calculate the first three allowed excitations of ethene using the LDA functional and a TZ2P basis set. Repeat the calculation but with a basis set including diffuse functions for the carbon atoms. Repeat the function again ut with the SAOP functional and a basis set including diffuse functions for the carbon atoms. The carbon basis set should be taken from the `/home/programs/ADF/adf2006/adf.01/atomicdata/ET/ET-QZ3P-1DIFFUSE` directory. The standard TZ2P basis should be sufficient for H. Don't forget to include the *DEPENDENCY* command with the diffuse basis sets and also that the SAOP functional can not be used with frozen cores.

Compare the excitation energies obtained in these three calculations.

Consider the first two excitations obtained by these calculations. Assign them as either $\pi \rightarrow \pi^*$ or $\pi \rightarrow \text{Rydberg}$. See if you can identify the Rydberg orbital. For carbon the lowest Rydberg orbitals will be *3s*-like, *3p*-like or *3d*-like. For hydrogen they will be *2s*-like or *2p*-like.

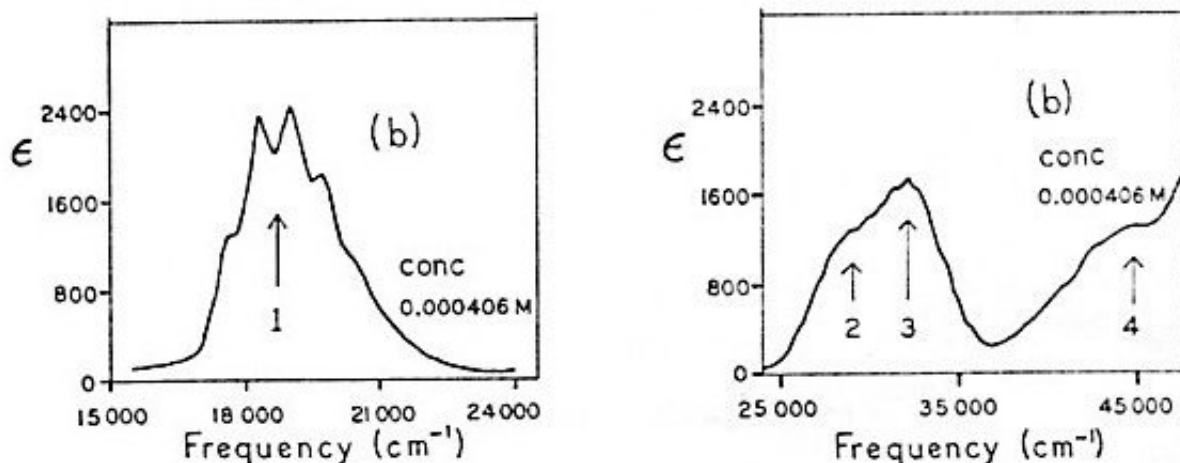


Figure 7.6: The experimental spectrum of MnO_4^- .

Note: In doing this exercise you will find one problem when examining Rydberg orbitals. The VIEW program describes orbitals on a grid. You don't see the parts of the orbitals outside the grid. This leads to orbitals that appear to have their ends cut off. The problem is that Rydberg orbitals are so big that they are usually mostly outside the grid. This makes it difficult to identify Rydberg orbitals with VIEW. Do your best. Use your imagination. The symmetry of the orbital and chemical logic should give you an idea of what an orbital should be.

7.7 Projects

7.7.1 The Absorption Spectrum of MnO_4^-

The absorption spectrum of the permanganate ion (MnO_4^-) is pictured in figure 6.6. The first peak is responsible for the strong purple colour of MnO_4^- . Calculate this spectrum. Save a picture of your calculated spectrum. From your calculations assign the first three peaks of the experimental spectrum in terms of overall state symmetry and in terms of orbital excitations.

The excitations of a metal complex are often described as $d-d$ or charge transfer. A $d-d$ excitation indicates that the excitation essentially takes place between two d orbitals on the metal. These types of excitations are described by ligand and crystal field theory. In a charge transfer excitation an electron is moved from the metal to a ligand (metal to ligand charge transfer), from a ligand to the metal (ligand to metal charge transfer) or from one ligand to another (ligand to ligand charge transfer). Look at the orbitals involved in the three excitations of MnO_4^- and decide if they are $d-d$ or charge transfer. If they are charge transfer, note which kind of charge transfer.

These calculations should be performed with a TZ2P basis set and the BP functional.

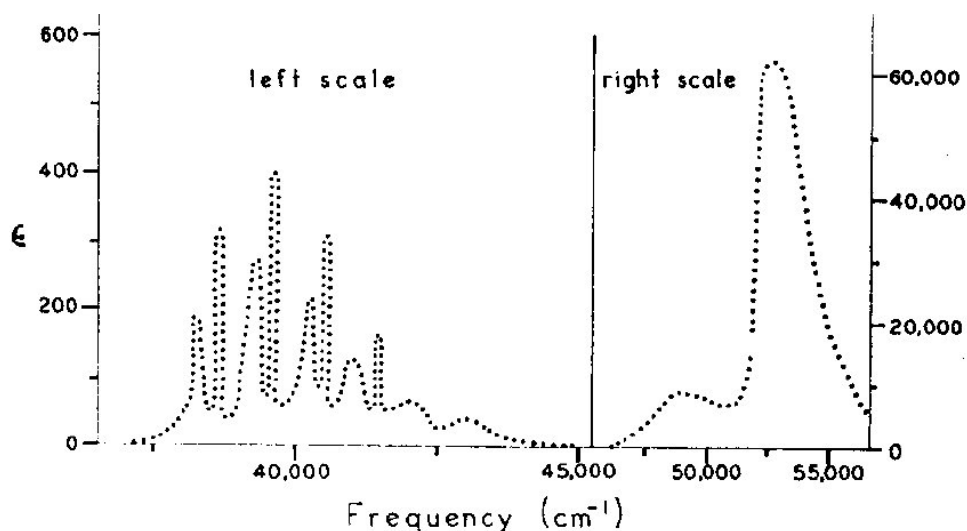


Figure 7.7: The experimental spectrum of benzene.

For the purposes of this project a molecular orbital is classed as a metal d -type MO if it has much metal d character at all.

From you results, provide an estimate of the ligand field splitting of the d orbitals of Mn in the MnO_4^- complex.

You should expect that your calculated excitation energies will be too high by nearly 8000 cm^{-1} . It is still an area of active research to figure out why this large error appears.

7.7.2 The Absorption Spectrum of Benzene

The spectrum of benzene is pictured in figure 6.7.

Three features are apparent in the spectrum: an intense absorption at around $53,000\text{ cm}^{-1}$, a less intense absorption at around $47,000\text{ cm}^{-1}$ and a much weaker and complicated band at around $40,000\text{ cm}^{-1}$. The structure in this last band is due to vibrational states and you can consider it as one band.

Calculate the spectrum of benzene. Use a TZ2P basis set and the BLYP functional in the geometry optimization step and the same combination or something better to calculate the excitations. From your results assign the three bands in the experimental spectrum in terms of state symmetries and in terms of orbital excitations. Note the energy that you get for each of the three bands.