Experiment 5 – Vibrational-Rotational Spectra of HCl and DCl

1. Objectives
1) Review the basic concepts of gas phase vibrational/rotational spectroscopy of diatomic molecules
2) Assign and analyze the experimental spectra to obtain the molecular constants. Investigate the isotopic effects on the molecular spectra.
3) Introduce practical quantum electronic structure calculations and apply them to estimate the bond lengths, rotational constants and vibrational frequencies of HCl and its isotopic variants. Compare the results of the electronic structure theory with experiment.

2. Background
2.1. Rotational-Vibrational Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Molecules possess quantized energy levels, which enables them to absorb and emit the radiation at specific discrete frequencies. These frequencies range from ultraviolet (UV) and visible (VIS) regions for electronic transitions, through infrared (IR) for vibrational transitions, far-infrared (also termed Terahertz – THz) and microwave regions for pure rotational spectra to radio frequencies for nuclear spin transitions (NMR). In this experiment we will study the vibrational spectrum of a simple diatomic molecule, HCl and its isotopic variant DCl. The vibrational spectrum exhibits fine rotational structure, which can be observed in gas phase. As we will see, from analysis of such vibrational-rotational spectrum we can extract information about the molecular structure, such as bond length, the vibrational constant, which is a measure of bond strength and about interactions between vibrational and rotational motions that lead to small corrections of the molecular energy levels. From the opposite end, we will perform ab initio quantum chemical calculations of the rotational and vibrational parameters for a model HCl molecule and the DCl isotope, and see how faithfully the ab initio theory reproduces experimental results.

In the light of Born-Oppenheimer approximation [1], we can treat the molecular vibrations and rotations separately from the motions of electrons. Since the electrons are much lighter than the atomic nuclei, they move much faster and to a good approximation the nuclei can be assumed “frozen” while solving the electronic Schrödinger equation. If the electronic Schrödinger equation is solved for different positions of the “frozen” nuclei, we obtain a molecular potential energy surface. In the case of HCl, it is a 1-dimensional potential energy surface since the only position that matters is the separation between the two nuclei, symbolized as \( r \) (Figure 1). The nuclear motion then can be treated as motion in this effective electronic potential.

The simplest model for a vibrating diatomic molecule is a harmonic oscillator, for which the potential energy depends quadratically on the change in the

![Figure 1](image)

Figure 1. Schematic diagram showing potential energy \( U \) as a function of internuclear separation for a diatomic molecule. The harmonic potential \( U_{\text{harm}} \) is indicated by a dashed curve. The vibrational energy levels are also shown.
Internuclear distance. As Figure 1 shows, quadratic function is a good approximation to the potential energy surface near the equilibrium distance (minimum of the potential). The allowed energy levels of a harmonic oscillator are

\[ E(v) = hv\left(v + \frac{1}{2}\right) \]  

(1)

where \( v \) is the vibrational quantum number \((v = 0, 1, 2, \ldots)\), \( v \) is the vibrational frequency and \( h \) is Planck’s constant.

The simplest model for a rotating molecule is a rigid rotor (“dumb-bell”) in which the two atoms of mass \( m_1 \) and \( m_2 \) are joined by a rigid, weightless rod. The allowed energy levels for a rigid rotor are:

\[ E(J) = \frac{\hbar^2}{8\pi^2 I} J(J + 1) \]  

(2)

where \( J \) is the rotational quantum number \((J = 0, 1, 2, \ldots)\) and \( I \) is the moment of inertia, which is related to the internuclear distance \( r \) and the reduced mass \( \mu = m_1 m_2 / (m_1 + m_2) \):

\[ I = \mu r^2 \]  

(3)

As the real molecule is vibrating and rotating simultaneously, a first approximation to the rotational-vibrational energy levels \( E(v, J) \) would be the sum of equations (1) and (2). A more complete expression is given below in equation (4), with the levels expressed in term values in units of cm\(^{-1}\) (pronounced “wavenumbers”) rather than energy units (\( c \) is the speed of light):

\[ T(v, J) = \frac{E(v, J)}{\hbar c} = v_e \left(v + \frac{1}{2}\right) - v_e x_e \left(v + \frac{1}{2}\right)^2 + B_e J(J + 1) - D_e J^2(J + 1)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J + 1) \]  

(4)

- The first and third terms on the right-hand side are the harmonic oscillator (eqn. 1) and rigid rotor (eqn. 2) terms with \( v = v_e \) harmonic vibrational frequency, \( r = r_e \), the equilibrium distance, and

\[ B_e = \frac{\hbar}{8\pi^2 I_e c} \quad I_e = \mu r_e^2 \]  

(5)

is called the rotational constant (in units of cm\(^{-1}\))

- The second term involving the constant \( x_e \) takes into account the effect of anharmonicity: since the real potential of the molecule differs from the harmonic potential (Fig. 1) the vibrational energy levels are not quite the harmonic ones (eqn. 1) and a correction term is required.

- The fourth term (with the constant \( D_e \)) is the correction for centrifugal distortion. The chemical bond is not rigid, but more like a spring – it stretches when the molecule rotates. But, since \( D_e \) is generally small, this correction is important only for large \( J \) values and we shall neglect this term.

- The last term takes into account the coupling between rotations and vibrations and \( \alpha_e \) is called the vibrational-rotational coupling constant. During a vibration the internuclear distance changes, which changes the moment of inertia and therefore the rotational constant.

2.3. Selection rules

The harmonic oscillator, rigid rotor selection rules are:

\[ \Delta v = \pm 1, \Delta J = \pm 1 \]  

(6)

As a consequence, infrared absorption can occur only when these allowed transitions take place. For an anharmonic diatomic molecule, the \( \Delta J = \pm 1 \) selection rule is still valid, but transitions corresponding to \( \Delta v = \pm 2, \pm 3, \ldots \) can be observed. These are called overtones and are generally much weaker than the
fundamental, $\Delta v = \pm 1$. We are concerned with transitions from various $J''$ levels of the vibrational ground state ($v'' = 0$) to $J'$ levels of the first excited vibrational state ($v' = 1$). By convention the quantum numbers of the lower energy levels are double primed and those of the higher energy level single primed (Figure 2).

From the selection rule, the transition must be from $J''$ to $J' = J'' \pm 1$. Since $\Delta E = h\nu = h\tilde{v}$, the frequency $\tilde{v}$ (in wavenumbers) for this transition will be just $T(v', J') - T(v'', J'')$. When $\Delta J = +1 (J' = J'' + 1)$ and $\Delta J = -1 (J' = J'' - 1)$ we find from eqn. (4) that:

$$
\tilde{v}_R = \tilde{v}_0 + (2B_e - 3\alpha_e) - (2B_e - 3\alpha_e)J'' - \alpha_e J''^2 \quad J' = J'' + 1, \quad J'' = 0, 1, 2, \ldots \quad (7)
$$

$$
\tilde{v}_P = \tilde{v}_0 + (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \quad J' = J'' - 1, \quad J'' = 1, 2, 3, \ldots \quad (8)
$$

where $\tilde{v}_0$ is the frequency of the forbidden transition from $v'' = 0, J'' = 0$ to $v' = 1, J' = 0$:

$$
\tilde{v}_0 = \tilde{v}_e - 2\tilde{v}_e x_e \quad (9)
$$

The two series of lines given in eqns. (7) and (8) are called $R$-branch and $P$-branch, respectively. These allowed transitions are indicated on the energy diagram in Figure 2. If $\alpha_e$ were negligible, eqns. (7) and (8) would predict a series of equally spaced lines with separation $2B_e$ except for a missing line at $\tilde{v}_0$. The effect
of vibrational-rotational coupling (i.e. non-zero $\alpha_e$) is that the lines in R-branch are closer together, while those in the P-branch further apart, as shown in the spectrum in Figure 3.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
 & \multicolumn{5}{|c|}{P-branch} & \multicolumn{5}{|c|}{R-branch} \\
\hline
$m$ & -6 & -5 & -4 & -3 & -2 & -1 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
\hline
$J''$ & 6 & 5 & 4 & 3 & 2 & 1 & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\hline
\end{tabular}
\caption{Rotational-vibrational spectrum for a diatomic molecule}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{Rotational-vibrational spectrum for a diatomic molecule}
\end{figure}

We can simplify the expressions (7) and (8) by introducing a new quantity $m$, where $m = J'' + 1$ for the R-branch (eqn. 7) and $m = -J''$ for the P-branch (eqn. 8) [2]. Using this new quantity $m$ equations (7) and (8) can be combined in a single expression:

$$\tilde{v}_R = \tilde{v}_0 + (2B_e - 3\alpha_e)m - \alpha_e m^2 \quad m = \ldots, -3, -2, -1, 1, 2, 3, \ldots$$

(10)

Note that $m$ takes all integral values except zero! The separation between adjacent spectral lines $\Delta \tilde{v}(m)$ will then be:

$$\Delta \tilde{v}(m) = \tilde{v}(m+1) - \tilde{v}(m) = (2B_e - 3\alpha_e) - 2\alpha_em$$

(11)

Therefore, a plot of $\Delta \tilde{v}(m)$ versus $m$ can be used to determine both $B_e$ and $\alpha_e$. With these known, $\tilde{v}_0$ can be obtained from any of the lines by using eqn. (10).

2.4. Isotopic effects

When an isotopic substitution is made in a diatomic molecule, the equilibrium bond length and the vibrational force constant $k$ are unchanged, since they depend only on the behavior of bonding electrons. In other words, the potential energy (Fig. 1) is independent on the masses of the nuclei. However, the reduced mass does change and this will affect both vibrations and rotations of the molecule. For a harmonic oscillator the vibrational frequency $\nu_{\text{harm}}$ is:

$$\nu_{\text{harm}} = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2}$$

(12)

(just a reminder: $\mu$ is the reduced mass). That means that for a different isotope (denoted by asterisk) we get the relation:
\[ \frac{v_{\text{harm}}^*}{v_{\text{harm}}} = \left( \frac{\mu}{\mu^*} \right)^{1/2} \]  

(13)

For the real molecule, the anharmonicity should be taken into account, but that is not only complicated, but would require information from overtones (\( \Delta v > 1 \)) and we will therefore stick with the harmonic approximation.

For the rotations, the isotope effect follows from eqn. 5 and we see that:

\[ \frac{B_e^*}{B_e} = \frac{\mu}{\mu^*} \]  

(14)

HCl is a mixture of \( ^35\text{Cl} \) and \( ^37\text{Cl} \) molecules and isotopic effect should be present. In addition we will investigate deuterium chloride – DCl, which, on top of containing deuterium instead of hydrogen, will also have both \( ^37\text{Cl} \) and \( ^35\text{Cl} \) isotopes present.

2.4 Quantum chemical calculations

Since spectroscopy probes the transition between quantum energy levels in molecules, it provides information about the molecular quantum states, from which we can extract important molecular properties. However, we can also calculate these quantum molecular states and properties by applying the laws of quantum mechanics. Quantum mechanics states that an object, like a molecule, and all its properties are described by a wavefunction. To find the wavefunction, we have to solve the Schrödinger equation. For all but the most trivial systems, however, exact solutions to the Schrödinger equation are impossible. Various electronic structure methods provide different approximations to its solution.

Ab initio methods (\textit{ab initio} meaning “from the first principles”) use no empirical or experimental information in the computation. Instead, they are based solely on the laws of quantum mechanics and universal physical constants. Ab initio calculations can be performed on several levels. The simplest level and a starting point for all higher level methods is the Hartree-Fock (HF) theory, also termed Self Consistent Field (SCF) according to the computational procedure. An important property of a HF calculations is that they do not include electron correlation. Each electron is treated as if it was moving independently, in an average effective potential of all the other electrons.\(^\dagger\) Electron correlation is a fundamental property – two electrons cannot occupy the same space, rather they have to avoid each other – neglected at the HF level. The higher level methods, also called post-HF methods, use the results of HF calculations as a starting point and try to include electron correlation. These methods include configuration interaction (CI) in its various incarnations, perturbation theory methods (MP\(n\) for Møller-Plesset, who derived it, and \(n = 2, 3, \ldots\) denoting the order of the theory), coupled cluster methods (CC) etc. The correlated, post-HF methods give more accurate solution to the molecular Schrödinger equation, but are typically much more computationally demanding.

Density functional theory (DFT) methods are typically not included among \textit{ab initio} methods, because (some) include one or a few empirical parameters. However, they are very similar to \textit{ab initio} methods. DFT methods are very attractive because they explicitly include electron correlation, while computationally they are comparable, or even more efficient, than the HF! Therefore, DFT provides benefits of the much more expensive, correlated computational methods at no cost as compared to HF.

Both \textit{ab initio} and DFT methods use basis sets. Basis set is used to build the molecular wavefunctions or molecular orbitals (MO). Most commonly, the molecular orbitals are expanded in a linear combination of atomic orbitals (MO-LCAO methods). Basis set is a set of functions that approximate the atomic orbitals.

\(^\dagger\) And nuclei, of course, but in the Born-Oppenheimer approximation the nuclei are “frozen” and not allowed to move during electronic calculations.
By specifying a basis set for a calculation, we specify where the electrons will go. In reality, electrons can be anywhere and thus large basis sets provide better results by imposing less constraints on where the electrons can go. There is, of course, a price to pay: calculations with large basis sets take longer. Generally in quantum mechanical calculations of molecules, Gaussian functions are used as basis functions. While not exactly correct (you know that the H-atom orbitals – also known as Slater-type – are exponential, not Gaussian functions), it turns out that use of Gaussians to approximate the atomic basis functions has tremendous computational advantages, since integrals of Gaussian functions are much easier to calculate. Basis sets can be divided into [3]:

- **Minimal** – contains minimum possible number of basis functions for each atom, for example
  
  H: 1s
  
  C: 1s, 2s, 2pₓ, 2pᵧ, 2pᵣ
  
  An example of minimal basis set is STO-3G (meaning “Slater Type Orbital – 3 Gaussians) where three Gaussian functions are used to approximate an atomic orbital. Each of the atomic orbitals (e.g. 1s for H, 1s, 2s, 2pₓ, 2pᵧ, 2pᵣ) are made of three Gaussian functions.

- **Split valence** – has two or more basis functions for each valence (not core) orbital:
  
  H: 1s, 1s’
  
  C: 1s, 2s, 2s’, 2pₓ, 2pᵧ, 2pᵣ, 2pₓ’, 2pᵧ’, 2pᵣ’
  
  where the primed and unprimed are of different size (e.g. radius for an s orbital). Examples are double zeta basis sets such as 6-31G, which has one basis function made of six Gaussians for core electrons and two basis functions, one made of three and the other of a single Gaussians for valence electrons. Triple zeta basis set like 6-311G uses three basis functions for valence electrons.

- **Polarized** – add functions with higher angular momentum beyond what is required for the ground state of each atom. An example is 6-31G(d) (also denoted as 6-31G*), which is 6-31G basis set (see above) with an added d-type function for heavy atoms (all but hydrogen). A double polarized basis set 6-31G(d,p) (also denoted as 6-31G**) is just like 6-31G(d) but also has a p-type function for hydrogen.

- **Diffuse** – add large size s and p-type functions (as opposed to the standard valence functions). Diffuse functions allow electrons to get farther away from the nuclei. They are important for anions, atoms with lone pairs, excited states and other instances where the electrons are relatively far from the nucleus.

To read more about the *ab initio* calculations, HF, post-HF and DFT methods and basis sets, sign up for CHEM 4560 !

To calculate the vibrational and rotational frequencies for a HCl molecule, in principle we would have to carry out calculations for different H-Cl bond lengths to obtain the potential energy curve (Figure 1). We would find the minimum, which corresponds to the equilibrium length \( r_ₑ \) and using (5) calculate the rotational constant \( Bₑ \). Then we would have to approximate the potential energy near the bottom by a quadratic (harmonic) function (Fig. 1):

\[
U(r) = U(rₑ) + \left. \frac{\partial^2 U(r)}{\partial r^2} \right|_{r=rₑ} (r-rₑ)^2 = U(rₑ) + k(r-rₑ)^2
\]  

(15)
where $k$ is the harmonic force constant, which, as we see from (14) is nothing but a second derivative of the energy $U(r)$ at the minimum ($r = r_0$). Then we would have to find the reduced mass $\mu$ and use (11) to get the frequency. But we will not do all that, the program will do it all for us. The program we will use is called Gaussian 09 (guess where the name comes from). It will find the equilibrium bond length, calculate the rotational constant and the vibrational frequency automatically. In fact, it will go even beyond equation (15) and calculate anharmonic frequencies, which require adding higher terms in the potential energy expansion.

We will input our best guess of what the HCl bond length is and Gaussian will calculate the energy and also the energy gradient, which is nothing but the force on the nuclei. Then it will make a step: it will change the bond length in the direction of the force and recalculate the energy and the forces until it finds the point where the energy is minimum and the forces disappear. That is the equilibrium geometry. Once there, it will calculate the second derivative of the energy and the vibrational frequency. We will see how the calculate values depend on the level of the computation and size of the basis set and how they compare to the experimental data.

4. Experimental

You will measure spectra of both HCl and DCl at the same time using a Fourier Transform Infrared Spectrometer (FTIR).

Review the principles of operation of an FTIR instrument, you should know how the interferometer works, what the interferogram is and how it is related to the spectrum. You should also know what is measured in an absorption spectrum and what absorbance and transmittance are.

1. Ask you instructor or TA to fill the FTIR gas cell for you. You will measure the spectrum of approximately 0.5 atm HCl in the gas cell with path-length of 10 cm.

2. Collect the background spectrum. On the top menu bar go to “Measurement” then “Scan background” Use the whole range (4000-400 cm$^{-1}$), 16 scans, resolution of 1 cm$^{-1}$, interval of 0.1 cm$^{-1}$.

3. Collect the sample spectrum in absorbance mode using the same parameters. In “Measurement” and “Scan sample”, toggle “Ratio”, check that all the parameters are the same as before, and at the bottom switch “Units” to “A”.

4. Zoom in the region of HCl absorption. Use peak-picking tool to display the frequencies of your peaks. Clean it up so that you can read the numbers if necessary. Print the spectrum.

5. Repeat 4. for the DCl region.

6. Call you instructor or TA to empty the cell.

5. Experimental data analysis

1. Spectral assignment: Assign the lines in the P- and R-branches of your HCl spectra with the appropriate values of $J''$ and $m$, as shown in Figure 3. (If you see any $^{35}$Cl/$^{37}$Cl splitting, assign the more intense peaks – the $^{35}$Cl isotope.)

2. Make a table of these values of $J''$ and $m$ and the corresponding frequencies $\tilde{\nu}(m)$ (in cm$^{-1}$). Then list the differences between the frequencies of adjacent lines $\Delta \tilde{\nu}(m)$. Plot $\Delta \tilde{\nu}(m)$ versus $m$ and use eqn. (11) to determine the rotational constant $B_e$ and the vibrational-rotational coupling constant $\alpha_e$.

3. Using the values of $B_e$ and $\alpha_e$ that you just found, pick three lines with low $m$ values in each branch and use eqn. (10) to calculate the fundamental vibrational frequency for $\tilde{\nu}_0$ for HCl.

4. Calculate the moment of inertia $I_e$ and the internuclear distance (bond length) $r_e$ using eqn. (5) make a table of all the molecular constants you found for HCl.
5. Repeat 1.-4. for DCl.

6. Compute the ratios $\tilde{\nu}_0/\tilde{\nu}_0$ and $B_r^*/B_e$ and compare then with values calculated using eqn.’s (13) and (14). The masses (in atomic units) are: $m_H = 1.007825, m_D = 2.014102, m_{^{35}}Cl = 34.968853$.

7. Using (13) and $\tilde{\nu}_0$ for $H^{35}Cl$ and $D^{35}Cl$ estimate $\tilde{\nu}_0^*$ for $H^{37}Cl$ and $D^{37}Cl (m_{^{37}}Cl = 36.965903)$. Based on this estimation, do you see any signs of $H^{37}Cl$ in your HCl spectra? How about in your DCl spectra? Can you estimate the isotopic abundance of $^{37}Cl$?

6. Computations

You will calculate the equilibrium inter-nuclear distance $r_e$, rotational constants $B_e$ and harmonic vibrational frequencies $\tilde{\nu}_0$ for HCl. You will use two different levels of calculation:

- Hartree-Fock (HF) level
- Density Functional Theory (DFT) level. There are several density functionals to choose from, you will use one that is called BPW91 (Becke-Perdew-Wang 91)

In addition, you will use two different basis sets with each level of calculation

- Minimal basis set STO-3G
- Valence double-zeta polarized basis set 6-31G(d)

The calculations will be done using Gaussian 09 quantum chemistry package. To study isotopic effects, instead of running each calculation zillion times, you will use a utility program called “freqchk” to recalculate your parameters for different isotopes.

1. From your PC use the SSH program to connect to the computer. Your instructor or TA will give you the host name, login and password. Do not share it with anyone!

2. Once logged in, you will need some basics of UNIX to get around. Here are some quick tips:

- `cd <directory name>` to change directory
- `pwd` to print name of the working directory
- `ls` to list the contents of the directory
- `mkdir <directory name>` to create a directory
- `cp <file 1 name> <file 2 name>` to copy file 1 to file 2
- `rm <file name>` to remove file (careful: it is irreversible!)

If you mistype something, backspace and arrow keys should work. Delete key probably won’t.

3. Go to directory `spring2015`, there create a new directory for your working group and go to this new directory (hint: `cd spring2015.Dude; mkdir Dude; cd Dude`). In this directory you will run your calculations and keep your results.

4. You will have to generate the Gaussian input file. The easiest way to do it is in Notepad on your Windows desktop and then transfer it to your directory on the UNIX machine through the file transfer program (FTP)

- The input file that you need to type should look like this:
%nproc=1
%mem=500MB
%chk=hcl_hf_sto3g.chk

#HF/STO-3G Opt Freq=Anharm Test 

HCL optimization/frequencies HF STO-3G basis

0 1
C1
H 1 1.29

Here is what it all means:

Each input file starts with so called ‘Link0 commands’ these are the lines with the “%” symbol. Here you define the job resource limits, like number of processors and memory, and specify locations of scratch files:

- %nproc=2 to use one processor (the computer has sixteen)
- %mem=256MB to use 500 MB of memory for the job
- %chk=hcl_hf_sto3g.chk to save the checkpoint file and name it “hcl_hf_sto3g.chk” (this file is very useful and we will always save it and under different name for each job)

The hash sign “#” starts the “Route section” of the input file. Here you specify the job type, i.e. what you want calculated, as well as the calculation method and the basis set. In this case, I requested:

- HF/STO-3G level calculation: HF is the method (Hartree-Fock), and STO-3G is the basis set.
- Geometry optimization (keyword Opt) and vibrational frequency calculation (keyword Freq).
- The additional keyword Test is there to suppress some additional archiving of the output.

Route section must be followed by a blank line!

Next is the title section, where you type a title and some comment about your job, preferably something that will later help you identify what it is, like in this case:

HCL optimization/ frequencies DFT(SVWN) 4-31G basis

The title again must be followed by a blank line!

Molecule specification section starts with a single line with two numbers, in this case

0 1

The first number – 0 – is the charge of the molecule (in our case it is neutral, therefore 0).
The second number – 1 – is the spin multiplicity. In out case the molecule is a spin singlet (closed shell, all spins paired) and therefore it is 1.
After the charge and spin follows the geometry of your molecule. The input

C1
H 1 1.29
is a form of so-called Z-matrix (which is getting little obsolete, but for our purposes will do just fine). What that means is that there is a chlorine atom (Cl) and a hydrogen atom (H) whose distance from the atom 1 (which is Cl) is 1.29 Ångstroms.

The input file must end with the blank line!

You will need to write a couple of files just like the example above. The only difference is that you will have to specify different methods (HF and BPW91) and different basis sets (STO-3G and 6-31G(d)). Your first input file could look like this:

```
%nproc=2
%mem=256MB
%chk=hcl_hf_sto3g.chk
#HF/STO-3G Opt Freq Test

HCL optimization/frequencies HF STO-3G basis

blank line

0 1
Cl
H 1 1.29

blank line
```

5. Transfer the file to your previously created directory on the UNIX box using FTP/SFTP. It should be a part of the SSH program you used to connect to the UNIX computer earlier to create directories etc.

6. Run the Gaussian program. To do that, type

```
g09 <input file name> &
```

You will get a message (a number) that you need not worry about and the program will start running. If you did everything right while setting up your input file, the program will finish in about two minutes. The output is saved to a file, that has the same name as your input file, but the extension “.log”. For example, if my input was “hcl_hf_sto3g.inp” my output will be “hcl_hf_sto3g.log”.

7. Now you will have to open the output file and find what you need. Again the best way it to transfer it to the local machine (Windows) and open it in a text processor, such as WordPad or Word. After you do that, use the Select All button and change the font size to something small (e.g. 9 pt) to keep the formatting.

The output file is pretty long and contains a lot of information you do not need. What you want is the equilibrium geometry for the optimized structure ($r_e$), its energy, its rotational constant ($B_e$) and vibrational frequency ($\tilde{\nu}_0$).

To find your calculated values, scroll down until you find the end of the first part of the job (Geometry optimization) and start of the second one (frequency calculations). It will look something like this:

```
BE NOT THE FIRST BY WHOM THE NEW ARE TRIED,
NOR YET THE THE LAST TO LAY THE OLD ASIDE.
-- ALEXANDER POPE
```

```
Job cpu time: 0 days 0 hours 0 minutes 53.2 seconds.
File lengths (MBytes): RWF=6 Int=0 D2E=0 Chk=4 Scr=1
Normal termination of Gaussian 98.
Link1: Proceeding to internal job step number 2.
#N Geom=AllCheck Guess=TCheck Test RHF/STO-3G Freq
-----------------------------------------------
1/10=4,29=7,30=1,38=1/1,3;
```

this is where the second job starts
Now find the bond length for this structure: it’s right here!

This is your value of the internuclear distance \( r_e \) in Angstroms.

Next you can find your rotational constant. Look for:

It lists two, but you will notice they are the same (HCl as a linear molecule has only one rotational constant, but Gaussian calculates three – in the direction of each principal component of the moment of inertia) – either one of them will do. You will need to convert it to \( \text{cm}^{-1} \) though to get your \( B_e \).

Then find the energy:

The harmonic vibrational frequency appears first like this:

Full mass-weighted force constant matrix:

Low frequencies --- -4.6095 -4.6095 0.0052 0.0065 0.0065 3372.5360

Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
Raman scattering activities (A**4/AMU), Raman depolarization ratios,
Reduced masses (AMU), force constants (mDyne/A) and normal coordinates:

Frequencies -- 3372.5360
Red. masses -- 1.0360
Frc consts -- 6.9427
IR Inten -- 27.8872
Raman Activ -- 58.7253
Depolar -- 0.3478
And then, after lots and lots of other data, including thermodynamics, symmetry analysis, Coriolis couplings, cubic and quartic force constants, there is the vibrational-rotational coupling, called “Vibro-rotational Alpha Matrix”:

```
Vibro-rotational Alpha Matrix

Vibro-Rot alpha Matrix (in cm^-1)
-------------------------------
a(x)           b(y)           c(z)
Q( 1)        0.19110        0.19110        0.00000

Vibro-Rot alpha Matrix (in MHz)
-------------------------------
a              b              c
Q( 1)     5729.12511     5729.12511
```

This is the calculated value of the vibrational-rotational coupling constant \( \alpha \) from eqns. (4), (7), (8), (10) and (11). It looks like there are three, because they are related to three Cartesian axes, but in fact there is only one (a = b and c is zero). Find a record this value.

Finally, after some more other stuff, the harmonic frequency shows up again next to the anharmonic one:

```
Fundamental Bands

Mode (Quanta)       E(harm)   E(anharm)       I(harm)        I(anharm)
1(1)              3372.520   3298.329     27.88680680     28.64008769
```

You want to record both the harmonic and anharmonic frequencies.

After that there is another optimization step, and archive entry and the file ends, just like the first part, by a quote and summary of resources used for the job.

```
HIGGLEDY-PIGGLEDY
NIC`LAUS COPERNICUS
LOOKED AT THE UNIVERSE,
SPOKE TO THE THRONG;
GIVE UP YOUR PTOLOMY,
RISE UP AND FOLLOW ME,
HELIOCENTRICALLY
PTOLEMY'S WRONG.
-- NANCY L. STARK
```

Job cpu time: 0 days 0 hours 0 minutes 30.2 seconds.
File lengths (MBytes): RWF=6 Int=0 D2E=0 Chk=4 Scr=1
Normal termination of Gaussian 09.

The very last line tells you that the job finished OK. If it says something else, the job crashed and something is wrong ....

7. Repeat the calculation using HF/6-31G(d), BPW91/STO-3G and BPW91/6-31G(d) levels. Do not forget to give your input file and checkpoint file a different name.

8. Use the utility program freqchk to calculate the vibrational frequencies for DCl (we will not worry about the \(^{35}\)Cl and \(^{37}\)Cl) for all four calculations.
   - Type `freqchk` and hit enter
   - Give the name of the checkpoint file.
- answer “n” to the question about Hyperchem files
- answer “0” to the temperature question
- answer “0” to the pressure question
- answer “1.0” to the question about the scale factor. We do not want anything scaled.
- answer “N” to the question whether you want to use principal isotope masses. You do not, you want to change isotopes.
- hit enter for atom number 1 (Chlorine) – we do not want to change that
- enter “2” for atom number 2 (Hydrogen). That will change it to Deuterium

Find the new vibrational frequency for your DCl molecule in the output. Repeat for the remaining three calculations.

9. When you are all done, type `exit` to log out.

7. Computational data analysis

1. Make a table summarizing your HCl calculations. List the resulting energy ($E$), equilibrium bond length ($r_e$), rotational constant ($B_e$), harmonic ($\nu_e$) and anharmonic ($\tilde{\nu}_0$) vibrational frequencies, the anharmonicity constant $x_e$ and the rotationa-vibrational coupling constant ($\alpha_e$) he anharmonicity constant $x_e$ can be calculated from the computed harmonic and anharmonic frequencies using eqn. (9). Construct the table with the methods grouped together in such a way that the effects of the calculation method (HF versus DFT) and basis set effects can be easily seen.

2. Compare calculated energies. What is the effect of increasing the size of the basis set on the energy? What is the effect of including electron correlation (by the DFT)? It that want you expect based on what you know about the electron correlation and basis set size? Discuss your results.

4. Compare the experimentally determined and computed (from Gaussian 09) vibrational and rotational parameters Can you find any trends in the dependence of $r_e$, $B_e$, $\nu_e$, $\tilde{\nu}_0$, $x_e$ and $\alpha_e$ on the basis set? On including the electron correlation? How do these trends compare to those you found for the quantum mechanical energy? Which of the calculations would you expect to give most accurate results? Why?

8. Putting together experiment and theory

When you complete both part of this experiment, combine the results of your experimental measurements with your computations.

1. Make a table (or tables) that compare your calculated values of $r_e$, $B_e$, $\nu_e$, $\tilde{\nu}_0$ and $\alpha_e$ for HCl at the different levels of theory and with different basis sets to the experimental data. Can you compare the calculated anharmonicity constant $x_e$ to experiment? If not, why? Calculate differences between theoretical and experimental values and list them in your tables.

2. Make the same table for DCl.

3. Based on comparison between theory and experiment: which method and basis set gives the best result? Does it agree with what you would expect? (point 3, previous section) If not, can you think about some possible reasons? Discuss your results and conclusions about the effects of the basis set and electron correlation on the computed molecular properties.
References

Prelab quiz questions
1. What is *Born-Oppenheimer approximation*?
2. Why do we need to solve the electronic *Schrödinger equation* when we are interested in nuclear motions such as rotations and vibrations?
3. True or false:
   a) For a harmonic oscillator, the potential energy depends quadratically on the internuclear distance and the energy levels are equally spaced
   b) For a harmonic oscillator, the potential energy depends linearly on the internuclear distance and the energy levels are equally spaced
   c) For a harmonic oscillator, the potential energy depends quadratically on the internuclear distance and the energy levels are not equally spaced, but get closer together as the vibrational quantum number increases
   d) For a harmonic oscillator, the potential energy depends quadratically on the internuclear distance and the energy levels are not equally spaced, but get further apart as the vibrational quantum number increases
4. True or false:
   a) Real molecules are harmonic oscillators.
   b) Real molecules are anharmonic oscillators, but the harmonic oscillator approximation is valid for small displacements of the nuclei from the equilibrium positions
   c) Real molecules are harmonic oscillators, but to describe their vibrations we use an anharmonic oscillator approximation
5. What is the *reduced mass* for a diatomic molecule?
6. Pick all true statements
   a) If the reduced mass of a diatomic molecule *increases*, its rotational energy will *increase*, because its moment of inertia will *increase*.
   b) If the reduced mass of a diatomic molecule *increases*, its rotational energy will *decrease*, because its moment of inertia will *increase*.
   c) If the reduced mass of a diatomic molecule *increases*, its rotational energy will *decrease*, because its moment of inertia will *decrease*.
   d) If the internuclear distance in a diatomic molecule *increases*, its rotational energy will *decrease*, because its moment of inertia will *increase*. 

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e) If the internuclear distance in a diatomic molecule increases, its rotational energy will increase, because its moment of inertia will increase.

f) If the internuclear distance in a diatomic molecule increases, its rotational energy will increase, because its moment of inertia will decrease.

7. True or false
   a) Rotational energy levels for a rigid rotor are equally spaced
   b) Rotational energy levels for a rigid rotor are not equally spaced, but their separation decreases as the rotational quantum number increases
   c) Rotational energy levels for a rigid rotor are not equally spaced, but their separation increases as the rotational quantum number increases

8. What are the selection rules for transitions between the energy levels of a harmonic oscillator? What are the selection rules for transitions between the energy levels of a rigid rotor?

10. What is an overtone, and what is its origin?

11. What is the origin of the coupling between molecular vibrations and rotations?

12. True or false:
   a) Energy levels of the ground vibrational state are labeled by quantum numbers with a double prime (”) while those of the excited state by quantum numbers with a single prime (’)
   b) Energy levels of the ground vibrational state are labeled by quantum numbers with a single prime (’) while those of the excited state by quantum numbers with a double prime (”)
   c) Energy levels of the ground vibrational state are labeled by quantum numbers with a single prime (’) while those of the excited state by quantum numbers with a tilde (˘)

13. What is referred to as R-branch and as P-branch in the rotational-vibrational spectrum of a diatomic molecule?

14. True or false:
   a) Due to the rotational-vibrational coupling, the spectral lines in the P-branch are higher in frequency, but more widely spaced than those of the R-branch.
   b) Due to the anharmonicity of the molecular oscillator, the spectral lines in the P-branch are lower in frequency, but more widely spaced than those of the R-branch.
   c) Due to the rotational-vibrational coupling, the spectral lines in the P-branch are lower in frequency, but more closely spaced than those of the R-branch.
   d) Due to the rotational-vibrational coupling, the spectral lines in the P-branch are lower in frequency, but more widely spaced than those of the R-branch.

15. In equations (9) and (10) what is the relationship between \( m \) and the rotational quantum numbers for the P-branch and for the R-branch?

16. Pick all true statements:
   a) When an isotopic substitution is made in a diatomic molecule, its equilibrium bond length changes.
b) When an isotopic substitution is made in a diatomic molecule, its equilibrium bond length does not change, but its reduced mass does.

c) When an isotopic substitution is made in a diatomic molecule, both the rotational constant and the vibrational frequency will change.

d) When an isotopic substitution is made in a diatomic molecule, the rotational constant will remain the same, but its vibrational frequency will change.

17. True or false:

a) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its vibrational frequency will increase by a factor of two.

b) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its vibrational frequency will decrease by a factor of square root of two.

c) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its vibrational frequency will increase by a factor of square root of two.

d) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its vibrational frequency will decrease by a factor of two.

18. True or false:

a) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its rotational constant will increase by a factor of two.

b) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its rotational constant will decrease by a factor of square root of two.

c) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its rotational constant will increase by a factor of square root of two.

d) When an isotopic substitution is made in a diatomic molecule so that its reduced mass is doubled, its rotational constant will decrease by a factor of two.

19. What does *ab initio* mean and what are *ab initio* calculations based on?

20. What is electron correlation?

21. True or false:

a) In Hartree-Fock (HF) theory, the electron correlation is approximated by empirical parameters and therefore HF is very accurate and computationally efficient, but it is not an *ab initio* method.

b) In Hartree-Fock theory, the electron correlation is calculated from the first principles, and therefore HF is very accurate *ab initio* method, but is computationally very expensive.

c) In Hartree-Forck theory the electron correlation is neglected, therefore HF is computationally efficient *ab initio* method, but is not very accurate.

22. True or false:

a) In Density Functional Theory (DFT) the electron correlation is sometimes approximated using empirical parameters and therefore DFT is very accurate and computationally efficient, but it is not rigorously an *ab initio* method.

b) In Density Functional Theory (DFT), the electron correlation is calculated from the first principles, and therefore DFT is very accurate *ab initio* method, but is computationally very expensive.
c) In Density Functional Theory (DFT) the electron correlation is neglected, therefore DFT is computationally efficient ab initio method, but is not very accurate.

23. What is a basis set and what types of basis sets can you name?

24. True or false:
   a) Molecular basis sets use Gaussian functions, because atomic orbitals are correctly described by Gaussian functions.
   b) Molecular basis sets use Gaussian functions, even though atomic orbitals are not correctly described by Gaussian functions, but can be approximated by Gaussian functions and Gaussians tremendously simplify the calculations.
   c) Molecular basis sets use Gaussian functions because the wavefunction is related to probability, and the most common probability distribution is Gaussian distribution.

25. Why does Fourier Transform Infrared Spectrometer have “Fourier Transform” in its name? What does it use the Fourier Transform for?

26. How are you going to fill the IR cell with HCl/DCl gas for your experiment?

27. Based on your answers to question 15: is HCl spectrum going to be at higher vibrational frequency than the DCl or vice versa?

28. Which equation and what procedure are you going to use to determine the HCl molecular constants from your spectra?

29. What methods will you use for your quantum chemical calculations of HCl and what basis sets?

30. When using the UNIX operating system:
   a) How will you change directory?
   b) How will you create a new directory?
   c) How will you check to contents of a directory?

31. One you are logged in:
   a) What directory will you go to?
   b) How are you going to create a new directory for your workgroup and go to that directory?

32. Pick all true statements:
   a) Gaussian input file must have blank line between the “Link0 command section” (starting with “%”) and “route section” (starting with “#”).
   b) Gaussian input file must have blank line between the “route section” (starting with “#”) and the title section.
   c) Gaussian input file can have blank lines, but they are not necessary because they are ignored by the program.
   d) Gaussian input file must have blank line between the title section and the molecule specification section.
   e) Blank line must terminate the Gaussian input file.

33. True or false:
a) When running calculations at different levels and with different basis sets, you will specify
different file name for each checkpoint file, so that you can use it later for calculating the effects of
isotopic substitutions.

b) When running calculations at different levels and with different basis sets, you will leave the same
file name the checkpoint file, so that it gets overwritten and you lose all the information and will
have to redo the calculation

35. When running the Gaussian calculation:
   a) How will you start the job?
   b) What will your output file be named?
   c) Where in the output file will you start looking for the data of interest?
   d) Where in the output file will you find the equilibrium bond length, the rotational constant, energy
       and vibrational frequency?

36. What program are you going to use to do recalculate the molecular parameters for DCl? What do you
    need to run it and how are you going to do it?

37. How are you going to compare the results of your calculations at different levels and with different
    basis sets? How are you going to compare your calculations with your experimental results?

38. How can you determine the anharmonicity constant $x_e$ if you know both the harmonic and anharmonic
    vibrational frequencies?