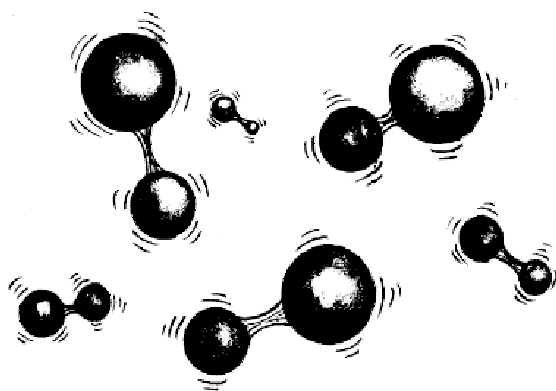


University of Gothenburg
Chalmers University of Technology

A6

INFRARED SPECTROSCOPY

26th October 2017



Name.....

Performed..... Approved.....

Supervisor.....

Aim

Vibrational-rotational transitions in molecules lead to specific branches of absorption lines in IR spectra. From rotational spectra of molecules one can extract information about interatomic forces and dissociation energies as well as binding distances and momenta of inertia.

The main aims of this laboratory work are:

To learn in practice the basic principles of vibrational and rotational spectroscopy from the example of HCl molecules.

To determine the relationship between molecular structural features and absorption bands in the IR spectrum.

To obtain the absorption cross sections for different transitions in HCl by using results from statistical physics and spectroscopy.

Theory

Energies of molecules

A molecule is a stable, electrically neutral group of atoms with a well-defined geometry. Molecules are held together by electrostatic forces which, together with the quantum mechanical behavior of the electron define what is known as a chemical bond. The simplest molecules are diatomic. In order for a bond to form, the (quantum mechanical) energy of the compound must be less than that of the two separated atoms. We are free to choose the zero of energy to be the total energy of the two completely separated atoms. Then the condition becomes

$$E < 0, \tag{1}$$

for at least one quantum state of the molecule. If this is not fulfilled, one does not have a molecule but rather what is called a resonance. We will not deal with those here.

The energy of a molecule is usually calculated with the Born-Oppenheimer separation. In this approximation, the motion of the nuclei is separated from the calculation of the electronic states. The approximation is justified by the large difference in the mass of the electron and the nuclei, $m_e \lesssim m_N/2000$, where the equality holds for the lightest nucleus, which is just a proton. The calculations proceed by fixing the position of the nuclei and calculating the energy of the electrons in this fixed potential. Repeating this procedure for any relevant geometry of the nuclear positions, one gets a curve which is the effective potential in which the nuclei move. For a diatomic molecule there is just one relevant

coordinate, viz. the separation of the two nuclei. The other five coordinates are three translations and two rotations.

Fig. 1 gives a schematic representation of this potential energy. Although the curve

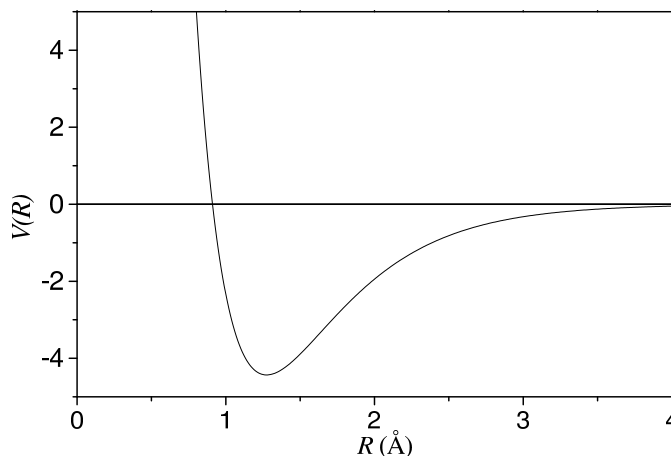


Figure 1: The Morse curve for the electronic and rotational ground state curve of HCl.

applies to HCl, the features are quite general. At large distances, the interaction between atoms is quite weak and the potential energy correspondingly close to zero, but it is always attractive when the separation is sufficiently large, and with general quantum mechanical arguments one can show that the potential varies as $\propto r^{-6}$ (for neutral molecules). The constant of proportionality is related to the electric polarizabilities of the atoms.

We can find the other limit with an equally simple argument. The energy is the sum of electronic energy and the electrostatic repulsion of the nuclei. The electronic energy converges to a constant when the nuclei approach, with a value equal to that of the electronic system of a single atom with the combined charge of the two participating atoms. Adding the electrostatic nuclear repulsion gives that the total potential becomes repulsive, $dV/dr < 0$ and, for small enough distances also positive.

Based on these two limits we can then understand that the potential energy curve must have a minimum at a negative energy for some finite distance. The minimum is the classical ground state. The vibrations and rotations of the molecule are described by quantizing the motion around this classical minimum.

Vibrations

The potential energy curve is often parameterized with a so-called Morse curve;

$$V(R) = D_e \left(1 - e^{-a(R-R_e)}\right)^2 - D_e, \quad (2)$$

where D_e is the (classical) binding energy, R_e is the equilibrium distance (also classically), R is the separation of the atoms, and a is a parameter of dimension inverse length. The Morse curve for HCl, determined by spectroscopic data, is shown in fig. 1

The last term is included to make the energy at infinite separation equal to zero. For $R = 0$ the potential is not infinite but positive and very large. Since the nuclei are never so close that the energy is positive, this is not a problem in the applications here.

For small deviations from equilibrium, $a(R - R_e) \ll 1$, the potential can be expanded to second order to give

$$V(R) \approx -D_e + D_e a^2 (R - R_e)^2. \quad (3)$$

This is the potential energy of a harmonic oscillator. The stationary states of a system with this potential energy are known

$$E_v = \hbar\omega(v + 1/2). \quad (4)$$

There is one state for each of these energies. The degeneracy of an energy level is said to be one in this case.

We can find the frequency in terms of the parameters of the Morse potential if we compare this with the standard expression of the potential energy of a harmonic oscillator with mass μ and the (angular) frequency ω ,

$$V(x) = \frac{1}{2}\mu\omega^2 x^2, \quad (5)$$

we see that

$$\omega = \left(\frac{2D_e a^2}{\mu}\right)^{1/2}. \quad (6)$$

The potential is the effective inter-atomic potential of the two nuclei and the mass μ is therefore the reduced mass of the two atoms,

$$\mu = \frac{M_{^{35}\text{Cl}} M_H}{M_{^{35}\text{Cl}} + M_H}. \quad (7)$$

This gives the energy levels in terms of D_e and a for the Morse potential.

Rotations

The molecules can also rotate. We can find the energy levels starting with the classical expression for the rotational energy of a rigid rotor,

$$E_{rot,cl} = \frac{1}{2}I\omega_{rot}^2 = \frac{\bar{J}^2}{2I}, \quad (8)$$

where ω_{rot} is the angular frequency of the rotation, I is the moment of inertia relative to the center of mass of the molecule, and $\bar{J}$ is the orbital angular momentum (we will disregard the spin in the following). For a rigid diatomic molecule this can be written as

$$I = \mu R_e^2, \quad (9)$$

where μ is the same reduced mass as above and R_e the distance between the atoms. Note the similarity of Eq. (8) with the expression for the translational kinetic energy $\bar{p}^2/2\mu$. Note also that for a given angular momentum, a *larger moment of inertia* gives a *smaller* energy.

Quantum mechanically, angular momentum is quantized. The square of the angular momentum can take the values

$$\bar{J}^2 = \hbar^2 J(J+1), \quad (10)$$

where $J = 0, 1, 2, \dots$. The rotational energies are therefore

$$E_{rot}(J) = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2, \dots \quad (11)$$

The degeneracy of a rotational level is known from the general theory of angular momentum and is $2J+1$. The constant in this expression is called the rotational constant B ,

$$B \equiv \frac{\hbar^2}{2I}. \quad (12)$$

It has unit of energy and is almost always expressed in units of cm^{-1} . We see that knowledge of B is equivalent to knowing the inter-atomic distance.

Note: One cm^{-1} is the energy of a photon that has a wavelength of 1 cm:

$$1 \text{ cm}^{-1} = h\nu(1 \text{ cm}) = hc/1 \text{ cm} \approx 2 \cdot 10^{-23} \text{ J}. \quad (13)$$

(Question: What is the value to five digits?)

Total energies

The molecule may have electronically excited states. This defines a different potential energy curve for each state on which vibrations and rotation can be excited. Figure 2

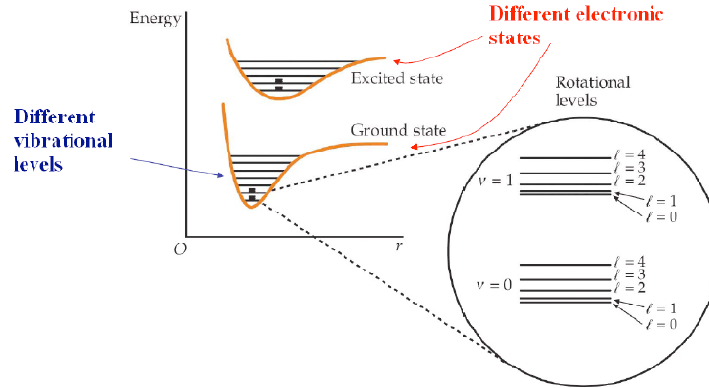


Figure 2: Schematics of electronic, vibrational and rotational states in a diatomic molecule.

shows generically how this may look like for two Born-Oppenheimer curves. The rotational and vibrational excitations are shown in detail in a somewhat schematic representation. The rotational energies depend on the Born-Oppenheimer surface the molecule moving on, because the bond length is different for different surfaces. In other words, B is a function of the electronic quantum number n we use to number the different potential energy surfaces.

As for the rotations, the vibrational energy likewise depends on n , now because the curvature of the potential energy surface does, i.e. the spring constant in the harmonic approximation of the potential energy. It also depends on the angular momentum, for three reasons.

- An angular momentum introduces a term in the potential energy, the one that gives the centrifugal force. This term has a positive curvature (second derivative) as a function of R and will therefore increase the vibrational frequency.
- The second reason is connected to this and is due to the centrifugal stretching of the bond. This increases the moment of inertia and lowers the quantum energy.
- The potential is really asymmetric (see the Morse potential). The asymmetry causes vibrationally excited states to have larger inter-atomic separations and therefore higher moments of inertia.

A numerical evaluation of these effects is beyond the scope of this manual, but the bottom line is that **the rotational and vibrational energies couple** and two higher order terms appear. The total vibrational-rotational energy $E(v, J)$ can be written as:

$$E(v, J) = \hbar\omega(v + 1/2) - \hbar\omega x_e(v + 1/2)^2 + (B_e - \alpha_e(v + 1/2))J(J + 1) - D_e J^2(J + 1)^2. \quad (14)$$

(this D_e has nothing to do with the dissociation energy). We define the rotational constant $B_v \equiv B_e - \alpha_e(v + 1/2)$. We will need only the $v = 0$ case and define $B \equiv B_0 \equiv B_e - \alpha_e/2$. The first two terms on the right hand side of the equation are purely vibrational and tell us that the potential is harmonic but not quite, as shown by the second term with the small parameter x_e . The third and the fourth terms on the right hand side are rotational energies and include the centrifugal stretching. The presence of α_e expresses that the rotational constant diminishes when the vibrational energy increases, due to the asymmetry of the potential. The tabulated values of the parameters that appear in this expression are [1] for the electronic ground state ($n = 0$), with rounded values, $\hbar\omega = 3000 \text{ cm}^{-1}$, $\hbar\omega x_e = 53 \text{ cm}^{-1}$, $B_e = 11 \text{ cm}^{-1}$, $\alpha_e = 0.3 \text{ cm}^{-1}$, $D_e = 5 \cdot 10^{-4} \text{ cm}^{-1}$. These values are not untypical for diatomic molecules. When expressed in eV, typical vibrational energy quanta are in the range of $10^{-1} - 10^{-2} \text{ eV}$. This can be compared to the electronic transitions that are usually located in the UV range of the spectrum, at energies of several eV.

Infrared spectroscopy

Experimentally, these numbers have been measured by detecting the absorption of light. Absorption lines due to transitions between vibrational-rotational levels are located in the infrared light (IR) range of the electromagnetic spectrum, and infrared spectroscopy is one of the most common spectroscopy methods employed today for the investigation of the structure of molecules. Including the rotational transitions, the absorption occurs in the part of the electromagnetic spectrum that lies between the wavelengths of a few μm and 1 mm. For comparison, the red edge of the visible light is around 700 nm, i.e. a few times shorter than the high energy end of the IR spectra. The long wavelength part of the spectrum, in the mm and sub-mm range, involves only rotational transitions. (Questions: When your microwave oven in the kitchen operates at 13 GHz, what is the wavelength of the radiation? What is the photon energy? Give an informed suggestion to what rotations this wavelength are relevant for.)

In practise, the absorption spectra are measured by passing a ray of light through a sample. Some of the light may be absorbed, seen as a reduction in the amount of transmitted light. The frequencies where the light is absorbed fulfill N. Bohr's frequency

condition

$$E_f - E_i = h\nu, \quad (15)$$

where E_f, E_i are the final, initial states of the molecule, and ν is the frequency of the emitted light. Note that **the frequency of the light is determined by the difference in energy of two levels**. In contrast **the thermal population of the initial state is given by the energy of that state** exclusively (in addition to the temperature, of course).

Light that does not obey Eq.(15) for some pair of states will not be absorbed. However, it is not a sufficient condition. Not all combinations of initial and final states will give rise to absorption, even if the energy differences fit perfectly. The so-called selection rules must be obeyed. These rules state that only certain combinations of initial and final state quantum numbers will absorb electromagnetic radiation. A necessary condition for absorption and emission of radiation is, for vibrational transitions, that the electric dipole moment changes during the (classical) vibrational motion. For rotations the condition is that the molecule has a permanent electric dipole moment. HCl qualifies in both respects and has both rotational and vibrational transitions.

This still does not determine what electromagnetic transitions are allowed. It requires a quantum mechanical calculation to determine between which sets of (v', J') and (v, J) a transition can occur. The result of such a calculation is the selection rules for the transition $v = 0 \rightarrow v = 1$

$$J' = J \pm 1, \quad J > 0 \quad (16)$$

and no allowed transition for $J = 0$.

The spectrum can now be calculated with the energy levels in Eq.(14). Let's first for simplicity consider hypothetical transitions that are exclusively vibrational or rotational and do not include higher order corrections. The vibrational absorption spectrum consists of a single line at the photon energy,

$$E_{v+1} - E_v = \hbar\omega, \quad (17)$$

independent of the initial value of v . The purely rotational absorption spectrum for a rigid rotator consists of lines at the energies

$$E_{rot}(J+1) - E_{rot}(J) = B(J+1)(J+2) - BJ(J+1) = 2B(J+1), \quad J = 0, 1, 2, \dots, \quad (18)$$

which is a linear progression in J . The intensities of the lines depend on the population of the initial rotational states.

When all the terms in Eq.(14) are considered, things get a little more complicated looking. However, it will turn out that $D_e J^2(J+1)^2 \ll \alpha_e J(J+1)$ for the relevant values

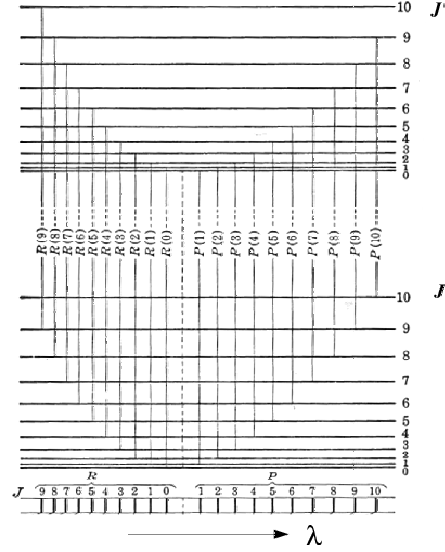


Figure 3: A rot-vib spectrum showing anharmonicity. The vertical lines indicate the transitions between the initial and final quantum state, the energies of which are shown as vertical lines. Note that the photon wavelength, not the energy, is increasing to the right and the high energy is therefore at the left. This is a convention often used by spectroscopists. Figure from Hertzberg (1950).

of J and we can therefore ignore the term with D_e . The transitions with $J' = J - 1$, where the angular momentum goes down by one unit, is called the P-branch of the spectrum and absorbs at the energies

$$\begin{aligned} h\nu = E_{v=1, J-1} - E_{v=0, J} &= \hbar\omega(1 - 2x_e) - B2J - \alpha_e J(J - 1) \\ \Delta J &= -1, \quad J = 1, 2, \dots \text{ P branch.} \end{aligned} \quad (19)$$

The part of the spectrum where $\Delta J = 1$ is called the R-branch and absorbs at

$$\begin{aligned} h\nu = E_{v=1, J+1} - E_{v=0, J} &= \hbar\omega(1 - 2x_e) + B2(J + 1) - \alpha_e (J + 1)(J + 2) \\ \Delta J &= +1, \quad J = 0, 1, 2, \dots \text{ R branch.} \end{aligned} \quad (20)$$

The effect of the anharmonicity is to reduce the spacing between absorption peaks in the R-branch and to increase it in the P-branch, with a value that increases with the initial angular momentum. Fig. 3 shows this.

Extraction of the absorption cross section

The absorption of photons can, for low light intensities, be described as a one-photon absorption process. This has the consequence that the light is attenuated exponentially when it passes through a sample;

$$I = I_0 e^{-\kappa \ell}, \quad (21)$$

where I_0 is the intensity immediately before entry into the sample, I is the transmitted intensity, and ℓ the length of sample the light passes through. The sample is assumed homogeneous, which is a good approximation for a small gas cell. The light intensity is the energy of the light ray passing through a unit area per unit time, in SI units J/m²s. You can also think of it as the flux of photons without changing Eq. (21).

The parameter κ is proportional to the concentration of the absorbing matter c ,

$$\kappa = \sigma c. \quad (22)$$

The constant of proportionality σ is a property of the material. It is called the absorption cross section and has dimension of length squared. Eq. (21) then takes the form

$$I = I_0 e^{-\sigma c \ell}. \quad (23)$$

This is Lambert-Beer's law for the attenuation of light when it passes through a sample. The absorption cross section depends on the wavelength, or equivalently the photon energy.

The spectrometer measures the attenuation of the light, $1 - I/I_0$, as a function of wavelength. The areas of the lines in the spectrum, therefore, need to be converted to I/I_0 . If the lines all have the same shape one may use the peak values instead of the areas to measure the attenuation. The attenuation should be normalised so that an empty cell gives an attenuation of zero. This is often not the case because the cell may contain contamination or the windows of the cell may absorb etc. Therefore the background must be measured in a separate scan and subtracted. This requires some care but you will have guidance in that process.

Assuming now that both of these problems have been taken care of, you have the experimentally determined values I/I_0 for each of the lines you observe in the spectrum. Taking the logarithm of Eq. (23) gives

$$\ln(I/I_0) = -\sigma c \ell. \quad (24)$$

It is important here to understand that the concentration on the right hand side is the concentration of the absorbing species. That is, the molecules that absorb light at the wavelength the sample is exposed to. It needs to have the right quantum numbers, which

in this case is the rotational quantum number. For HCl, only one initial state, i.e. J , contributes to a specific absorption line which simplifies matter, and we just add J as a subscript on c , and express the relation for a specific absorption line as

$$\ln(I/I_0) = -\sigma c_J \ell. \quad (25)$$

The transition is labeled by the initial state because it is the cross section of that state, not the one of the final state, that enters Lambert-Beer's law.

The concentration of the initial state is the Boltzmann factor times the degeneracy of the state, $2J + 1$. The energy of a state with $v = 0$ and rotational quantum number J is $BJ(J + 1)$. For the population we then have

$$c_J = cZ^{-1}(2J + 1) \exp(-BJ(J + 1)/k_B T), \quad (26)$$

where k_B is Boltzmann's constant and T is the temperature and c is the total concentration of HCl. The constant of proportionality Z is the rotational partition function (Sv: Tillståndssumma, German: Zustandssumme) and is given by

$$\begin{aligned} Z &= \sum_{J=0}^{\infty} (2J + 1) \exp(-BJ(J + 1)/k_B T) \\ &\approx \int_0^{\infty} (2J + 1) \exp(-BJ(J + 1)/k_B T) dJ, \end{aligned} \quad (27)$$

where the approximation makes sense because $B \ll k_B T$. The integral can be performed after the substitution $x = \beta BJ(J + 1)$ and gives

$$Z = \frac{k_B T}{B}. \quad (28)$$

Note: Check the units (as always!) when you calculate this quantity. You can use that Boltzmann's constant has the value $k_B = 0.695 \text{ cm}^{-1}/\text{K}$. We now have the equation for the measured intensities

$$-\ln(I/I_0) = \sigma_J c \ell Z^{-1} (2J + 1) e^{-\frac{BJ(J+1)}{k_B T}}. \quad (29)$$

Now we need to measure the length of the cell, estimate the pressure in the cell, and use the ideal gas equation to determine the value of c , assuming the temperature is room temperature. With the value of B determined from the position of the peaks, it is then possible to find the **absolute absorption cross sections** σ_J . These cross sections are different for all the lines and we use the equation for each line separately. Extract the cross sections and compare them to the size of the HCl molecule.

Assignments to be done before the laboratory work

1. Which processes in a molecule are the origin of the absorption of a) visible light?
b) infrared radiation?
2. What model is used to describe vibrations in a molecule?
3. What energy eigenvalues does the harmonic oscillator model have?
4. How do the absorption spectra for a diatomic molecule look like?
5. What are the energies of the stationary states of the rigid rotor model?
6. Give a short description of the transitions in a combined vibrational and rotational spectrum?
7. How does the centrifugal distortion affect the rotational energy and rotational transitions?
8. Does the presence of isotopes effect the rotational energy?

Experimental setup

General instrument description

The experimental setup includes a Perkin Elmer Frontier Fourier Transform Infrared Spectrometer (FTIR) and an arrangement for the sample preparations. The spectrometer uses a Fourier transformation to record and process the spectrum. The instrument has a single beam and the sample spectra are obtained from the ratio of a spectrum with the sample in the beam to a background spectra obtained without the sample.

There are three basic spectrometer components in an FTIR system: radiation source, interferometer and detector. The FTIR is based on the principle of a Michelson interferometer. A temperature stabilized, air cooled ceramic source is kept at a temperature of 1400 K and emits radiation towards the interferometer. An essential component is a system for splitting a beam of radiation and for recombining them. The splitting of the beam is achieved with the beamsplitter, which transmits about 50% and reflects about 50% of light. The most commonly used beamsplitter is a plate of KBr with a germanium coating. This covers a range from about 7200 to 370 cm^{-1} . One part of the beam is directed towards a fixed mirror while the other part of the beam impinges on a movable mirror that can introduce a varying path difference.

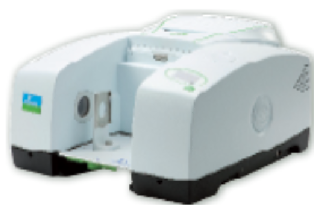


Figure 4: Picture of the Frontier FTIR spectrometer of Perkin Elmer.

The resulting beam then hits a sample cavity and it is eventually focused on the detector. The registered spectrum shows light intensity as a function of frequency and can be obtained from the interferogram by the mathematical process of a Fourier transformation. The interferogram is measured by recording the detector signal as a function of the path difference between the two beams. The signal has to be sampled at precise intervals corresponding to equal steps in path difference. For signal averaging, interferograms have to be measured at exactly the same points. This is achieved by using a helium-neon laser (632.8 nm) as a reference that traverses the same optical path as the infrared beam. A separate detector measures the interferogram produced by the laser, giving a sinusoidal signal with maxima separated by the laser wavelength. This signal is used to trigger the sampling of the infrared signal in a highly reproducible way.

Sample preparation

First the gas cell has to be pumped out to measure the reference background spectrum i.e. the spectrum without HCl gas. For that, the cell must be connected to the water pump through valve 2; valve 1 must be closed. First run the water and then open valve 2 for 1-2 minutes. After that close the valve and disconnect the cell. After the reference spectra are obtained the cell should be connected as in Fig.9 to fill it with HCl gas. Since HCl is of water-soluble, the hydrochloric acid has to go through sulphuric acid and then through the glass wool for drying. The cell has KBr windows transmit a wide spectral range. Remember that KBr windows are hygroscopic, i.e. they have the tendency to absorb water from the atmosphere. Water in any form should be carefully excluded. Sources of water include fingerprints, your breath, and solvents such as alcohols and acetone. The procedure to fill the absorption gas cell with HCl vapor is following:

- Make sure that the set-up looks as presented in Fig. 5.

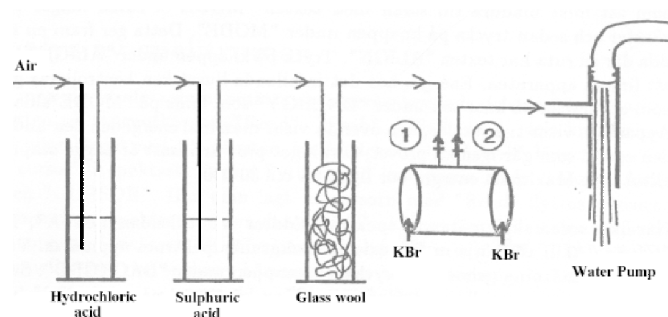


Figure 5: Schematic figure of the filling procedure for the gas cell.

- Open the water tap.
- Open valve 2 and then valve 1.
- After a minute close first valve 2 and then valve 1.

Experiment

1) Measure the background spectra for the empty KBr cell (can be found in the exhaust hood of room F8202). Remember that the resolution for these spectra should be the same as those measured for HCl. **Important: you need to switch in "regional settings" of your computer account the decimal comma "," to a decimal ".".** Otherwise the analysis software will not function properly! Do not forget to change back at the end of the day!

2) Fill the cell with HCl gas using the facilities found in the fumehood and measure a spectrum with a resolution of 4 cm^{-1} .

3) The FTIR will subtract the background spectra from the HCl sample spectra automatically. Observe in the resulting spectrum the peaks corresponding to the rotational transitions (P and R branches).

Calculate the **rotational constants, momenta of inertia and binding distances** for HCl molecules and find the **bandcentre** (i.e. the energy corresponding to the hypothetical transition $J = 0 \rightarrow J = 0$) in the spectra (use the theory presented above). Use

a fit based on equations (19) and (20) to extract the rotational constant B .

4) Perform a second measurement (background and sample) with a resolution of 0.5 cm^{-1} in the region of interest. Note the double peak structure in the spectrum. They appear because of the presence of two chlorine isotopes with natural abundances of 76% ^{35}Cl and 24% ^{37}Cl . Hence, the H^{37}Cl lines have lower intensities than the H^{35}Cl lines. The isotopes cause the vibrational frequencies to differ and also the rotational constant. Calculate these two shifts and compare with the measured shifts. Note: perform the measurement in any case, but work on this task only if time permits it.

5) Calculate the absorption cross sections using the data from the 4 cm^{-1} resolution spectrum for **all** the individual transitions you observed. The length of the cell is 10 cm. Use atmospheric pressure and room temperature for your calculations (i.e. normal conditions). Note: work on this task only if time permits it.

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