

Vibration-rotation spectroscopic study of diatomic molecules

Theoretical background: P.W. Atkins: *Physical Chemistry*, Chapters 16.2–3. and 16.7.

Type of experiment: Individual.

Goal of the experiments: Gathering basic knowledge on recording and analyzing vibrational-rotational spectra. Studying the isotope effect.

1 Introduction

1.1 Theoretical background

To interpret the infrared ($7000-200\text{ cm}^{-1}$ range) spectra of gas phase molecules, we have to consider the change in the vibrational and rotation states of the molecule, which is described by the following vibration-rotation term:

$$S(v,J) = \tilde{\nu} \left(v + \frac{1}{2} \right) + BJ(J+1) \quad (1)$$

Here v is the vibration-, J is the rotation quantum number, while $\tilde{\nu}$ is the wavenumber of the vibration:

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}, \quad (2)$$

where k is the vibration force constant, μ is the reduced mass ($\mu = \frac{m_1 m_2}{m_1 + m_2}$ for a diatomic molecule) and c is the speed of light. The B constant is dictated by the geometry of the molecule - for diatomic molecules it is:

$$B = \frac{h}{8\pi^2 \mu r^2 c}, \quad (3)$$

where h is the Planck constant and r is the equilibrium bond length. $I = \mu r^2$ is the moment of inertia. To analyze the spectra, we must consider the selection rules, predicting certain vibrational modes to have zero intensities. In case of vibrational-rotational excitation, the selection rules are $\Delta v = \pm 1$ for the vibrational and $\Delta J = \pm 1$ for the rotational quantum numbers. An exemption is when the molecule possesses angular momentum in the direction of its axis, when the $\Delta J = 0$ is allowed. Furthermore, the equilibrium nuclei distance might change because of the change in the vibrational quantum number, that might alter the value of the rotational constant.

The wavenumber of any vibrational-rotational transition can be given based on the term diagram shown in 1. and described by the following equation:

$$\tilde{\nu}(J_0, J_1) = \tilde{\nu}_0 - B_0 J_0 (J_0 + 1) + B_1 J_1 (J_1 + 1) \quad (4)$$

Here $\tilde{\nu}_0$ is the wavenumber related to the forbidden $J_0 = J_1 = 0$ transition.

The goal of the laboratory practice is to determine $\tilde{\nu}_0$, B_0 és B_1 from the recorded spectra. This can be done in one step based on equation (4), applying two variable linear regression (based on the $z = ax + by + c$ equation) if a suitable number of data points ($\{x,y,z\} = \{J_0(J_0+1), J_1(J_1+1), \tilde{\nu}(J_0, J_1)\}$) are known. The calculations can be also performed in multiple steps based on the following considerations, that always result in simpler data handling (linear regression).

The transitions can be categorized in three groups (keeping in mind that $\Delta J = \pm 1$ in case of allowed transitions):

- Transitions where $J_0 = J_1 + 1$, called the P-branch, and the energy (wavenumber) of the different transitions is expressed as:

$$\tilde{\nu}_P(J_0) = \tilde{\nu}_0 - B_0 J_0 (J_0 + 1) + B_1 J_0 (J_0 - 1) \quad (5)$$

- The forbidden $J_1 - J_0 = \Delta J = 0$ transition is called the Q-branch.
- On the other side of the Q-branch, $J_1 = J_0 + 1$. This region is called the R-branch, and the energy (wavenumber) of these transitions is expressed as:

$$\tilde{\nu}_R(J_1) = \tilde{\nu}_0 - B_0 J_1 (J_1 - 1) + B_1 J_1 (J_1 + 1) \quad (6)$$

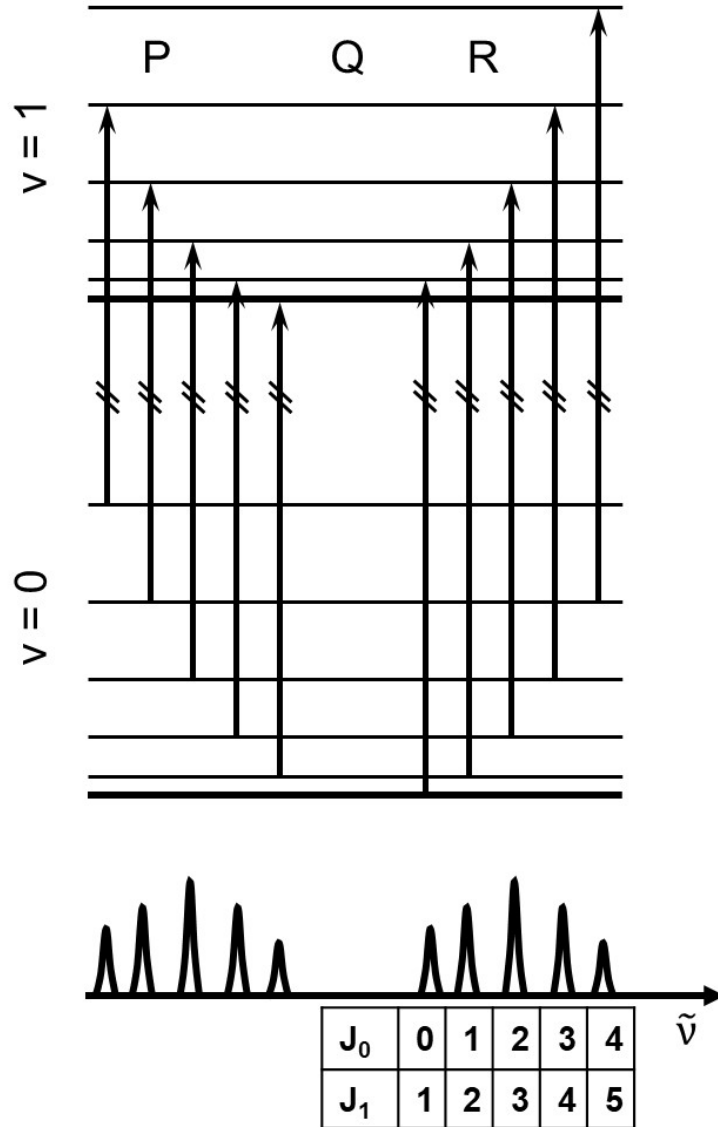


Figure 1: Schematic representation of the vibrational – rotational transitions of a diatomic molecule..

The combination of equations (5) and (6) provides multiple possibilities for data analysis through linear regression. As the independent variables are different in the P- and R-branches, we define a universal variable, J , that denotes $J \equiv J_0$ in the P-branch, while $J \equiv J_1$ in the R-branch. This must be considered during data analysis.

- a) Calculating the $\tilde{\nu}_R(J) - \tilde{\nu}_P(J - 1)$ difference from the wavenumber of the respective absorption line in the R- and P-branches, from equation (5) and (6), we get the following formula:

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J - 1) = B_1(4J - 2) \quad (7)$$

Plotting the wavelength differences in function of $(4J-2)$ a linear with one parameter (slope, B_1) can be fitted on the data set.

- b) Similarly, plotting $\tilde{\nu}_R(J) - \tilde{\nu}_P(J+1)$ in function of $(4J+2)$ also results in a linear correlation, that can also be fitted with a single parameter (slope, B_0)

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J+1) = B_0(4J+2) \quad (8)$$

From these two parameters $\tilde{\nu}_0$ can be calculated from any peak from equation (5) and/or (6).

2. a) Another route is to take the sum of $\tilde{\nu}_R(J) + \tilde{\nu}_P(J)$. From (5) and (6) this results in the following equation:

$$\tilde{\nu}_R(J) + \tilde{\nu}_P(J) = 2\tilde{\nu}_0 - 2(B_0 - B_1)J^2 \quad (9)$$

Plotting this sum in function of J^2 and performing linear regression, the intercept is $2\tilde{\nu}_0$, while the slope is $(B_0 - B_1)$.

- b) In this case the calculation of B_0 and B_1 further necessitates to plot $\tilde{\nu}_R(J) - \tilde{\nu}_P(J)$ in function of J , providing $2B_0 + B_1$ as the slope of the fitted linear:

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 2(B_0 + B_1)J \quad (10)$$

From equations (9) and (10) B_0 and B_1 can be determined. Using these, the force constant and the equilibrium bond lengths can be calculated from (2) and (3).

1.2 Isotope effect

Isotope labelling is a very useful practice for studying the mechanism of different reactions. This is allowed by the differences in the vibrational-rotation spectra of molecules that are formed from the same atoms but from different isotopes. The largest differences can be achieved by exchanging a hydrogen atom to a deuterium (e.g., HCl and DCl). The difference is caused by the different reduced mass of these molecules, as dictated by equation (2). The ratio of the natural vibrational frequencies:

$$\frac{\tilde{\nu}(1)}{\tilde{\nu}(2)} = \frac{\sqrt{\frac{k(1)}{\mu(1)}}}{\sqrt{\frac{k(2)}{\mu(2)}}}, \quad (11)$$

Assuming an unaffected force constant, this can be simplified to:

$$\frac{\tilde{\nu}(1)}{\tilde{\nu}(2)} = \sqrt{\frac{\mu(2)}{\mu(1)}}, \quad (12)$$

Based on equation (3), a similar expression is derived for the vibrational constants:

$$\frac{B_0(1)}{B_0(2)} = \frac{\mu(2)}{\mu(1)}, \quad (13)$$

2 Performing the experiments

If not stated otherwise by the Instructor, the spectra of HCl and DCl will be recorded and analyzed during the experiment. The manual of the currently used FTIR instrument can be found in the laboratory. This must be carefully read prior to the experiment.

Construct the experimental setup shown in Figure 2 under an operating fume hood. Double-check that all the used tools are clean and dry. The last is very important in case of working with D_2SO_4 , hence these

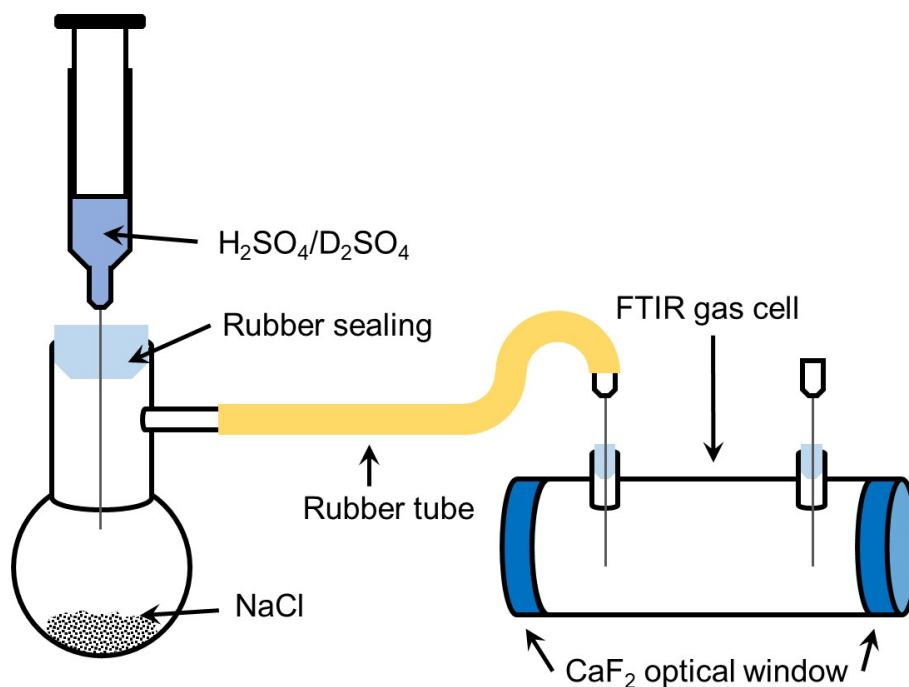


Figure 2: Schematic drawing of the experimental setup used during the laboratory practice for studying vibrational-rotational spectra.

tools must be cleaned and dried between experiments as well. After finishing the last experiment, leave the gas cell in the operating fume hood to remove all the formed HCl/DCl gas from it. Do not wash the gas cell!

Importantly, KBr optical windows are most typically used in such gas cells. In this experiment, however, a humid HCl/DCl gas forms, that would harm the water sensitive KBr, making it misty. This is avoided here by using a CaF₂ optical window.

Put ca. 2 g NaCl in the round-bottom flask and close it with the rubber sealing. Connect the side arm to the gas cell using a rubber tube and a syringe needle, through another rubber septum. Close the other connection of the gas cell with another rubber sealing. To avoid forming overpressure in the setup, put another needle through this sealing. Subsequently, add concentrated D₂SO₄-drop-wise to the NaCl, using a syringe. Be very cautious when working with strong acids! Always wear the protective goggles and rubber gloves, and perform all experiments in the working fume hood. Gas evolution is indicated by vigorous bubble formation. When it is over, remove both needles from the gas cell. Do not remove the rubber septa! Subsequently, transfer the gas cell to the FTIR instrument and record the vibrational-rotational spectrum (the Instructor will demonstrate the use of the software). Clean the equipment (the gas cell must be placed in an operating fume hood, and opened there) and repeat the experiment by using H₂SO₄.

3 Evaluation of the experimental data

Export the spectra (tsv format is preferred, as it can be easily imported in any data analysis software) and transfer it to a PC. Here it can be evaluated by any suitable software including Excel, Origin, QtiPlot etc. Plot each spectrum in three different figures: one showing the full spectrum, in which all observed peaks should be identified. Prepare further two figures showing the analyzed section of the spectrum, where the vibration-rotation transitions of DCl or HCl is found (these wavenumber regions should be identified by the Student). Mark the P-, Q- and R-branches on these figures! Number the peaks in the P- and R-branches, starting from the gap in between (location of the Q-branch), towards smaller or larger wavenumbers, accordingly. Identify the wavenumber position of all peaks (manually or by using peak finder algorithms) and summarize these in a table. When making the table, it must be kept in mind that chlorine has two stable isotopes (³⁵Cl és ³⁷Cl), that are naturally present in approximately 3:1 ratio. Identify their occurrence in the spectra, and evaluate

the two vibrational-rotation transitions of H^{35}Cl and H^{37}Cl separately.

Table 1: Summary of the measured data for performing the evaluation based on equations (7),(8), (9) and (10).

J	$\tilde{\nu}_R(J) (\text{cm}^{-1})$	$\tilde{\nu}_P(J) (\text{cm}^{-1})$	$\tilde{\nu}_0 (\text{cm}^{-1})$ from (5)	$\tilde{\nu}_0 (\text{cm}^{-1})$ from (6)

$\tilde{\nu}_0 = \pm \text{cm}^{-1}$
 $B_0 = \pm \text{cm}^{-1}$
 $B_1 = \pm \text{cm}^{-1}$

Plot the results according to equation (7) and (8) in function of J. Perform a linear regression on the data points and calculate B_0 and B_1 according to equations (7) and (8). Using these, calculate $\tilde{\nu}_0$ from each data point according to equations (5) and (6). Calculate the average and standard deviation of these values!

Similarly, plot the data according equations (9) and (10) in function of J^2 and J, accordingly. Again, fit a linear on the data point and calculate B_0 and B_1 from equations (9) and (10). Using these, calculate $\tilde{\nu}_0$ from each data point according to equations (5) and (6).

To evaluate all the data together, a multi-parameter linear regression should be performed, based on equation (4) ($z = ax + by + c$). First, $\{x,y,z\} = \{J_0(J_0 + 1), J_1(J_1 + 1), \tilde{\nu}(J_0, J_1)\}$ data trios must be performed, and these should be analyzed simultaneously (hint: this fitting can be performed by using the Solver Add-in in MS Excel).

Table 2: Summary of the data for supporting the use of equation (4) .

$J_0(J_0 + 1)$	$J_1(J_1 + 1)$	$\tilde{\nu}(J_0, J_1)$

$\tilde{\nu}_0 = \pm \text{cm}^{-1}$
 $B_0 = \pm \text{cm}^{-1}$
 $B_1 = \pm \text{cm}^{-1}$

Perform this evaluation for each investigated gas (e.g., pl. HCl és DCl). In both cases, the results gathered for different isotopes (i.e., in case of Cl) should be analyzed separately, if the respective vibrational-rotational peaks can be identified separately. Summarize the data and results according to Table 1.

Calculate the k force constant and the equilibrium distances ($r_{v=0}$ and $r_{v=1}$) from equations (2) and (3) (after calculating the B_0 , B_1 és $\tilde{\nu}_0$ values. Summarize the results according to Table 3.

Table 3: Summary of the results.

Method	$B_0 (\text{cm}^{-1})$	$B_1 (\text{cm}^{-1})$	$\tilde{\nu}_0 (\text{cm}^{-1})$	$r_{v=0} (\text{pm})$	$r_{v=1} (\text{pm})$	k (N/m)
(7) and (8)						
(9) and (10)						
(4)						

Calculate the standard deviation of the results! Evaluate, how a given parameter varies with the different methods, and identify which of these provide the most precise results. Justify your choice!

In case of the different isotopes (the respective combinations of ^2D , ^1H , ^{35}Cl , ^{37}Cl), justify the shift of the vibrational-rotational peaks and the differences in the calculated parameters by calculations! Compare the equilibrium bond lengths!

Use the following values for the calculations: $h = 6.626 \times 10^{-34} \text{ J s}$, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$, $c = 2.998 \times 10^8 \text{ m/s}$. The atom masses should be calculated according to the relative isotope masses, using integer numbers.

Control questions

1. Why does the gas and solid phase FTIR spectra of a certain compound differ in the $7000 - 200\text{cm}^{-1}$ wavenumber range?
2. Give the vibrational-rotational term equation!
3. What parameters affect, and how, the vibrational frequency of a certain diatomic molecule according to the classical mechanics model?
4. Give the relation between the B rotational constant and the geometry of the molecule!
5. What are the selection rules that must be kept in mind when analyzing vibrational-rotational spectra?
6. Why is the difference between neighboring vibrational peaks different along the whole wavelength range not constant?
7. What is the pre-requisite of recording an absorption spectrum for a certain compound in case of vibrational-rotational spectroscopy?
8. What does it mean when a molecule is a "spherical top", "linear top", "symmetric top" or "asymmetric top"?
9. How can it be justified from a vibrational-rotational spectrum, that the classical mechanical model (harmonic oscillator model) is not valid for the investigated vibrational transition?
10. How can it be seen from a vibrational-rotational spectrum, that the diatomic molecule is formed of atoms that have multiple stable isotopes (present in comparable amounts)?