

FTIR - Spectroscopy

Fourier Transform Infrared - Spectroscopy

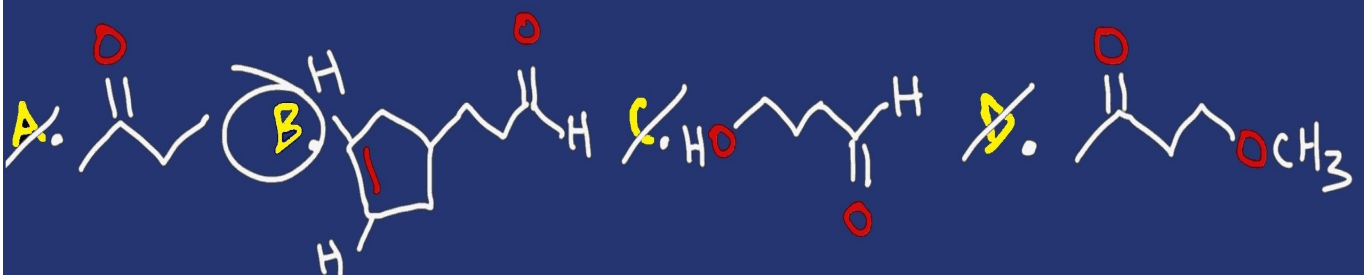
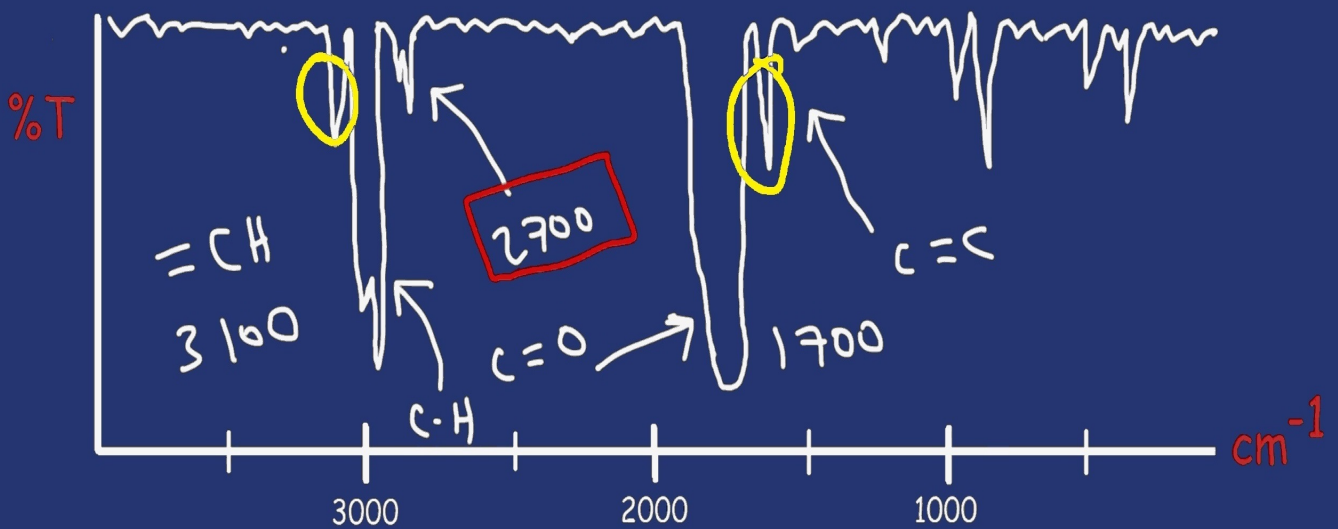
Advanced physical lab exercises

Lab course 1.8, Section B

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1 Introduction

Infrared spectroscopy is a well established and most widely used spectroscopic method. It is based on the absorption of photons from the infrared spectrum. When an electromagnetic wave hits matter, specific interactions can lead to an exchange of energy. When the energy is absorbed, molecules can go through a transition from the ground state to the excited state. The energy difference ΔE is closely related to the structure of the molecules. Depending on the energy, different phenomena are observed in molecular spectroscopy:

- In the far infrared ($\sim 1 - 10 \text{ cm}^{-1}$) one or more sequences of nearly equidistant lines are observed, which cross over between quantum mechanical states of different kinetic energy during the rotation of the molecule around its principal axes of inertia (rotation spectrum).
- In the mid to near infrared range ($\sim 100 - 10^4 \text{ cm}^{-1}$) one observes, one or more groups of lines belonging to transitions, in which, the rotational and vibrational state of the molecule changes simultaneously (rotational vibration spectrum).
- In the near infrared, as well as in the UV/Vis spectral range ($\sim 10^4 - 10^6 \text{ cm}^{-1}$) one finds relatively complicated band spectra. These band spectra are the simultaneous change of the rotational energy, the vibrational energy and the and the electronic excitation energy of the molecular envelope.

In this experiment, among other things, the rotational vibration spectra of different molecules are to be recorded in order to obtain closer information, such as the bond strengths or the geometry of the molecules.

2 Theoretical basics

2.1 Rotational-vibrational spectroscopy

2.1.1 Rotational spectra

If a diatomic molecule is described within the rigid rotator model, its rotation energy is given by the moment of gyration:

$$E = \frac{1}{2}\theta\omega^2; \quad \theta = \mu r_0^2; \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (1)$$

with θ is the moment of inertia about an axis perpendicular to the dumbbell axis, ω is the angular frequency of the rotational motion, the rduced mass μ reduced mass and r_0 is the distance between the mass points m_1 and m_2 .

Quantum mechanically the angular momentum can be quantized with $|\vec{J}| = \sqrt{J(J+1)}\hbar$. Thus, one obtains discrete rotation states with the energy

$$E(J) = \frac{J(J+1)\hbar^2}{2\theta}; \quad J = 0, 1, 2, \dots \quad (2)$$

Expressing this by wave number $\tilde{\nu}$ (dimension cm^{-1}), one can write

$$\tilde{\nu}(J) = BJ(J+1); \quad B = \frac{\hbar}{4\pi\theta c}. \quad (3)$$

The parameter B refereed to the rotational constant. In the model of the rigid rotator, the selection rules $\Delta J = \pm 1$, apply to electric dipole radiation.

2.1.2 Vibrational spectra

Using a harmonic potential to describe the vibration of two atoms against leads to

$$E(n) = \hbar\omega_0 \left(n + \frac{1}{2} \right). \quad (4)$$

With the selection rules for the harmonic oscillator are $\Delta n = \pm 1$. Of course using a harmonic potential is an approximation.

2.1.3 Rotational-vibrational spectra

Both, rotations and vibrations of molecules occur in the mid to near-infrared range and overlap each other:

$$E_{\text{sum}} = E(J, n) = hcBJ(J + 1) + \hbar\omega_0 \left(n + \frac{1}{2} \right). \quad (5)$$

The rotational and vibrational motions of the molecules are not independent of each other. As a result, the rotation constant B depends on the oscillation state n . The simultaneous transitions are only possible through the interaction between rotation and vibration, i.e., the interaction is the actual cause for the existence of rotational-vibrational spectra. In the following case, only vibration transitions from $n = 0 \rightarrow n = 1$ are considered, the selection rule for the rotational transitions remains at $\Delta J = \pm 1$. The lines of the rotational-vibrational transitions can therefore be described by

$$\tilde{\nu} = \tilde{\nu}_0 + B_1 J_1(J_1 + 1) - B_0 J_0(J_0 + 1). \quad (6)$$

Here, $\tilde{\nu}_0$ describes the wave-number of the vibrational transition. For the two cases $\Delta J = +1$; $J_1 = J_0 + 1$ (R-Branch) and $\Delta J = -1$; $J_1 = J_0 - 1$ (P-Branch) we get

$$\begin{aligned} \tilde{\nu}_R &= \tilde{\nu}_0 + 2B_1 + (3B_1 - B_0)J_0 + (B_1 - B_0)J_0^2 & J_0 = 0, 1, 2, \dots \text{ and} \\ \tilde{\nu}_P &= \tilde{\nu}_0 - (B_1 + B_0)J_0 + (B_1 - B_0)J_0^2 & J_0 = 1, 2, 3, \dots \end{aligned} \quad (7)$$

In certain cases, transitions with $\Delta J = 0$ (Q-Branch) are also allowed.

2.1.4 Characteristic group frequencies

Of practical interest in poly-atomic molecules is the fact that the vibrational frequencies of certain organic groups are relatively unaffected by the rest of the molecule. Therefore, characteristic frequencies can be assigned to these groups by which they can be identified even in the case of unknown molecular structures. This is why we speak of characteristic group frequencies. The reason for these quasi-fixed frequencies is that the coupling between different groups within a molecule is suppressed to a small extent or almost completely if:

- The atoms or rigid groups carry very different masses,
- The groups are equipped with very different binding forces,
- The groupings have a strongly deviating geometry (kinks or branches) .

This Fingerprint technique can be used to identify unknown molecules by IR spectroscopy.

2.2 Fourier-Transformations-Infrared spectroscopy (FT-IR)

The decisive advance in modern IR spectroscopy was achieved with the development of FT spectrometers. The FT-IR method is based on the idea of A. Michelson: Two beams are made to interfere. By varying the respective path lengths, the resulting intensity of the interference is shown in an interferogram and the usual IR spectrum is generated by Fourier transformation.

3 Preparation

In addition to the sources given in the literature folder, other sources (e.g. 1 - available in the library) should also be worked on. Various textbooks are available as online resources on the ULB website.

Rotational-vibrational spectroscopy

- First, familiarize yourself with the basics of molecular spectroscopy. How does electromagnetic radiation interact with matter and how can selection rules for rotational and vibrational transitions be defined?
- Rotation and vibration were described by simple models. What deviations can be expected in reality?
- Why can't rotation and vibration be considered independent of each other? Do the selection rules need to be modified?
- Become familiar with the appearance of rotational-vibrational spectra. How can the intensity of individual peaks be estimated, and why is the exclusive consideration of the vibration transition from $n = 0 \rightarrow n = 1$ justified?
- Which condition must be fulfilled to be able to observe a Q-branch?

FT-IR

- Familiarize yourself with the measurement principle of the FT-IR interferometer and state the differences from usual IR spectroscopy. What are the advantages does FT-IR spectroscopy offer?
- What is meant by an apodization function and what is it used for?
- What is the ATR unit (attenuated total reflection), how is it constructed and what is it used for?

4 Execution

Please note: The sample chamber as well as the gas cuvette have NaCl windows, which must be protected from moisture! Touching the windows must be avoided at all costs.

4.1 Air and nitrogen

Interferograms are measured in a range of $-400 - 400$ pts.. Spectra are measured in a range of $7800 - 400$ cm^{-1} with a resolution of 2 cm^{-1} . Perform the following steps:

- Insert the sample chamber for gases into the FT-IR,
- Record an interferogram and spectrum of the empty sample chamber filled with air,
- Flush the chamber with N₂ gas and record an interferogram and spectrum,
- Measure the absorption range of CO₂ with different apodizations.

4.2 Window materials

Install the holder for the window materials and make a blank measurement. Measure the following window materials in the range of $7800 - 400$ cm^{-1} and a resolution of 2 cm^{-1} :

- Quartz glass
- Borosilicate glass
- Sapphire
- Silicon
- Vaporized silicon

4.3 Molecular spectra

Install the glass cuvette and perform a blank measurement. Measure the following gases in the range $4000 - 1000$ cm^{-1} and a resolution of 1 cm^{-1} :

- Methane CH₄
- Carbon-monoxide CO
- Hydrochloric acid HCl
- Methanol CH₃OH
- Acetylene C₂H₂
- Carbon-dioxide CO₂ ($2260 - 2440$ cm^{-1})

4.4 ATR-IR-Spectroscopy

Use the ATR unit to measure the three powder samples provided. Assign the three samples to the molecules - cellulose, glucose and sucrose, respectively.

5 Analysis/Evaluation

- Compare the interferograms of nitrogen and air. How do they differ?
- Discuss the components of the air spectrum. Denote the existing vibrations and assign them to molecules in the air. Compare the obtained values with the literature.
- How do the measured spectra differ at different apodizations? Discuss this with your expectations.
- Discuss the spectra of the measured window materials - especially with respect to their transmittance for different spectral regions.
- From CO₂, CH₄, CO and HCl determine the rotational parameters B_0 , B_1 , B_e and α . For linear, diatomic molecules the moment of gyration θ , the equilibrium distance r_{eq} and the spring constant k . Determine the peculiarity of HCl and compare the obtained values with the literature.
- In the spectrum of CH₃OH determine the characteristic group frequencies and compare them with the literature.
- Discuss the nuclear spin in the spectra of CO₂ and C₂H₂. How do the selection rules change? (To answer this question the sources 1 and 3 are helpful)
- How do the three powder samples differ? Justify the allocation to Cellulose, glucose and sucrose.

6 Protocol

- The protocol should have a small introduction, in which the goal of the experiment is also clearly explained.
- For the evaluation, necessary theories should be discussed in the theoretical principles as well as the topics discussed in the colloquium.
- A common thread should be kept throughout the protocol.
- All information, images and data from external sources should be identified from the references.
- For the evaluation, the procedure should be explained, at least with one example. The results can then be presented in bundles.
- The unprocessed spectra should be included at least in the appendix.
- For the molecular evaluation, the results should be summarized in tabular form and compared with literature data.

7 Literature

Available in the bibliography

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For your own research

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