



# Physics laboratory course for advanced students

## INFRARED SPECTROSCOPY

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In the infrared spectroscopy experiment, you will become acquainted with the setup and functionality of an FTIR spectrometer as well as its various applications, and you will also learn how to prepare and handle samples in the experiment. In five experiments, you will determine the rotational and distortion constants of CO gas for different states, characterize materials, calculate refractive indices, and investigate phase transitions.

The fundamentals of the experiment include the setup and components of an infrared spectrometer as well as the principle of FTIR spectroscopy. The physical principles of molecular spectroscopy are the harmonic and anharmonic oscillator, the rigid and nonrigid rotator, as well as the corresponding selection rules on which the vibrational, rotational and rotational-vibrational spectra are based.

The written preparation should include the following points:

- IR frequency range, IR sources, IR detectors
- Setup and functionality of an FTIR spectrometer
- Energy levels of the quantum mechanical oscillator, the quantum mechanical rotator and the combination of both
- Prerequisites for IR-active oscillations
- Derivation of equation 2.3 for the calculation of the refractive index from the oscillations in the spectrum

The following books, for example, can be used for preparation:

- Helmut Günzler und Hans-Ulrich Gremlich, IR-Spektroskopie — Eine Einführung (Wiley-VCH, Weinheim, 2003)
- Hermann Haken und Hans Christoph Wolf, Molekülphysik und Quantenchemie — Einführung in die experimentellen und theoretischen Grundlagen (Springer: Berlin, 2006)

# Chapter 1

## Material characterization

### 1.1 Description of the experiment

As the molecular structure of different substances varies, it is possible to distinguish these substances using infrared spectroscopy. In addition to the composition from different atoms, for example, also the change in chain length of alkanes can be measured. This experiment is divided into two parts. In the first part, you select an unknown film from the following available film. Based on the measured spectrum (transmission as a function of the wavenumber  $\bar{\nu} = 1/\lambda$ ), you must identify the material of the selected film.

- Cellulose acetate butyrate
- Cellulose triacetate
- Kapton
- Polycarbonate
- Polystyrene
- Teflon

In the second part, you will measure the spectra of three alkanes with an odd number of C atoms and of two alkanes with an even number and then you have to order these alkanes according to the chain length. The chain lengths of the even alkanes lie between the shortest and longest odd alkane.

If a molecule has a dipole moment, it interacts with the incident infrared beam as shown in Fig. 1.1.

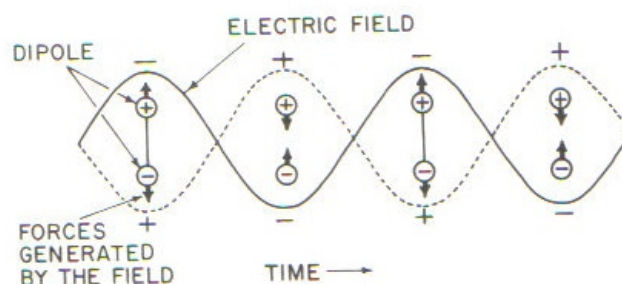


Figure 1.1: Interaction of an electromagnetic wave with a dipole [1].

This means that only molecules are infrared-active that first have a dipole moment and second for which one component of the dipole tensor is parallel to the direction of the E-field.

An n-alkane is a molecule with the molecular formula  $C_nH_{2(n+1)}$ .

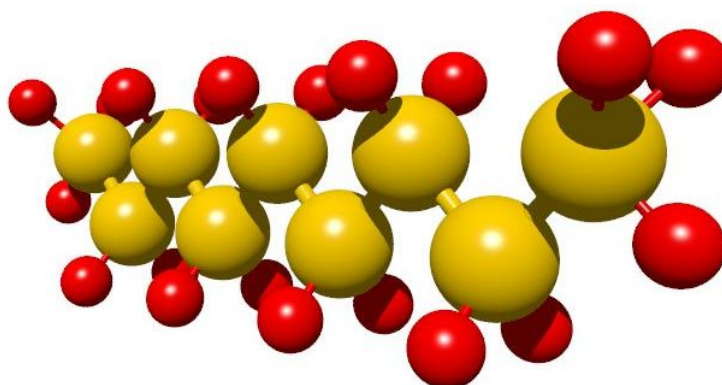


Figure 1.2: Schematic illustration of an alkane (here nonane).

As shown in the figure, an alkane consists of two molecular groups, the methyl groups ( $CH_3$ ) and the methylene groups ( $CH_2$ ). As you can see, there are two methyl groups and  $(n-2)$  methylene groups in every alkane with  $C \geq 2$ . When the chain length increases, then also the IR absorption of the  $CH_2$  vibrations relative to that of the  $CH_3$  vibrations should increase.

## 1.2 Experimental procedure

### Part 1:

In the first part, select one of the films and note the number on the film. Measure a background scan so that you can identify in the final spectrum the vibrations of the studied material. Now place the film in the sample holder (with the aid of the supervisor) and measure the spectrum. The supervisor will explain the experimental settings to you. For preparation you should look up the sum and structural formulas of the substances find characteristic vibrations with which you can easily distinguish the substances (see appendix).

### Part 2:

You will receive five different alkanes (three alkanes with an odd number of carbon atoms and two with an even number). Again, first take a background scan. Make sure that this time you also include the sample cell (with  $CaF_2$  windows) in the beam path, as it belongs to the background. When you fill the alkanes into the cell, it is sufficient to put a drop on the lower window and then carefully place the second window on it (ATTENTION!!! THE IR WINDOWS BREAK VERY EASILY). Make sure that you do not put too much of the liquids on the windows so that the absorption is not too high and you can still see the individual bands clearly. Use a new pipette for each alkane and clean the windows with acetone after each measurement.

## 1.3 Analysis

### Part 1:

Assign the adsorption bands to the corresponding vibrations and thereby determine the corresponding material.

### Part 2:

Fit the  $CH_2$  and  $CH_3$  stretching vibrations (in the wavenumber range of  $3000\text{ cm}^{-1}$ – $2800\text{ cm}^{-1}$ ). When fitting, take into account that there are a total of four peaks in the band of the stretching vibrations, which overlap each other (see Ref. [1]). Sort the alkanes according to their chain length using the ratio  $A = \frac{\text{intensity}(CH_2)}{\text{intensity}(CH_3)}$ . Then plot the ratio  $A$  against the chain length. What do you find?

# Chapter 2

## Determination of the refractive index

### 2.1 Description of the experiment

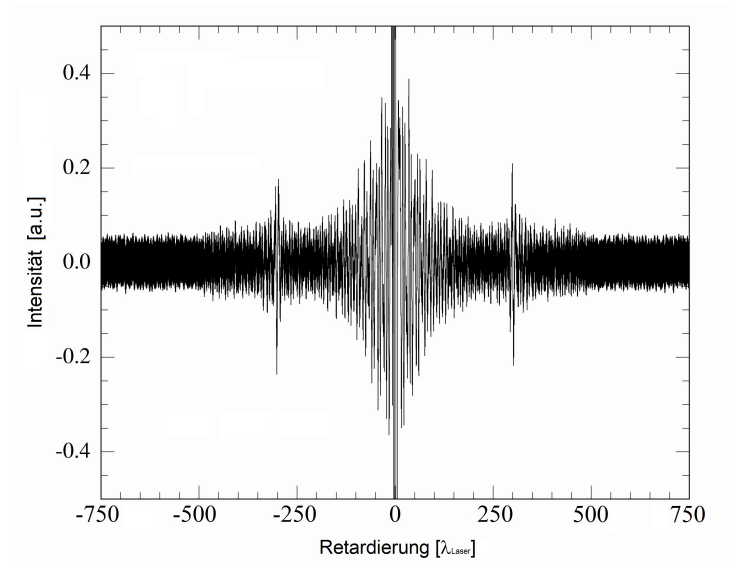


Figure 2.1: Interferogram of porous silicon: The additional peaks at  $\pm 300 \cdot \lambda_{laser}$ , which result from the multiple reflections, are clearly visible.

When an electromagnetic wave passes through an object, multiple reflections occur at the interfaces of this object. These reflections can be recognized both in the interferogram and in the spectrum.

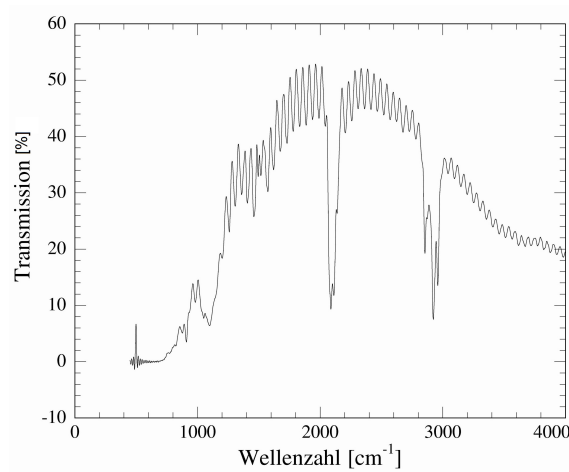


Figure 2.2: Transmission spectrum of porous silicon: Oscillations occur in the spectrum due to multiple reflections at the interfaces.

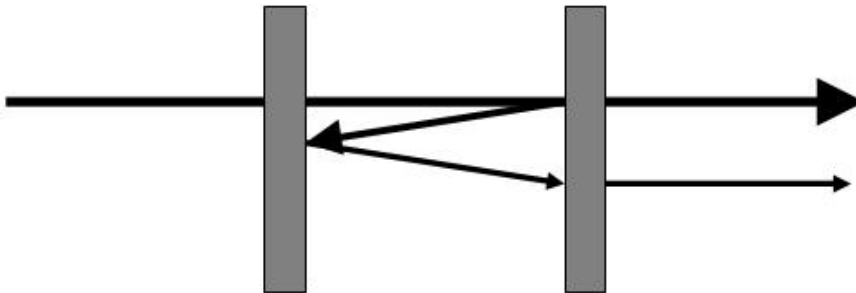


Figure 2.3: Multiple reflections in a medium.

The phase difference between two beams at perpendicular incidence is given by

$$\delta = \frac{4\pi}{\lambda}nd \quad (2.1)$$

where  $n$  is the refractive index of the material under investigation and  $d$  its thickness [2]. For the transmission coefficient  $T$ , i.e., the ratio of the transmitted intensity to the incident intensity, holds [2]:

$$T = \frac{I}{I_0} = \frac{(1 - R)^2}{(1 - R)^2 + 4R \sin^2(\delta/2)} \quad \text{mit} \quad R = \left(\frac{n - 1}{n + 1}\right)^2. \quad (2.2)$$

The absolute value of  $T$  is at a maximum when the argument of the sine is an integer multiple of  $\pi$ , i.e.  $\delta = 2\pi m$  with  $m = 0, 1, 2, \dots$ . This results in oscillations in the spectrum, which can be used to determine the refractive index  $n$ :

$$n = \frac{m}{2d\Delta\bar{\nu}} = \frac{\lambda_{oscill}}{2d}, \quad (2.3)$$

$m$  is the number of oscillations in the spectrum and  $\Delta\bar{\nu}$  is the distance from the first to the  $m$ -th maximum in  $cm^{-1}$  (see Fig. 2.2;  $\lambda_{oscill} = \frac{m}{\Delta\bar{\nu}}$  is the wavelength of the oscillations [cm]).

Alternatively, the refractive index can be determined with the aid of the interference peaks in the interferogram (Fig. 2.1). These are located symmetrically around the main maximum, the center burst (CB). The distance of the interference peaks from the main maximum corresponds to  $\lambda_{oscill}$ . The spectrometer indicates the retardation in points  $x$  that are a multiple of the laser wavelength ( $\lambda_{laser}=850$  nm). Thus, it follows from equation 2.3:

$$n = \frac{x\lambda_{laser}}{2d}, \quad (2.4)$$

## 2.2 Experimental procedure

You will get a known film. Determine its thickness and place the film in the sample holder. Then measure both the spectrum and the interferogram.

## 2.3 Analysis

Calculate the refractive index from both the spectrum and the interferogram and compare it with literature values.



# Chapter 3

## Rotational-vibrational spectrum of CO

### 3.1 Description of the experiment

The energy of molecules is the combination of the translational, rotational and vibrational energy. The rotational energy results in absorption and emission in the microwave and near IR range and the vibrational energy results in absorption and emission in almost the entire IR range. This chapter is based on Ref. [1].

#### 3.1.1 Rotation of a rigid, linear molecule

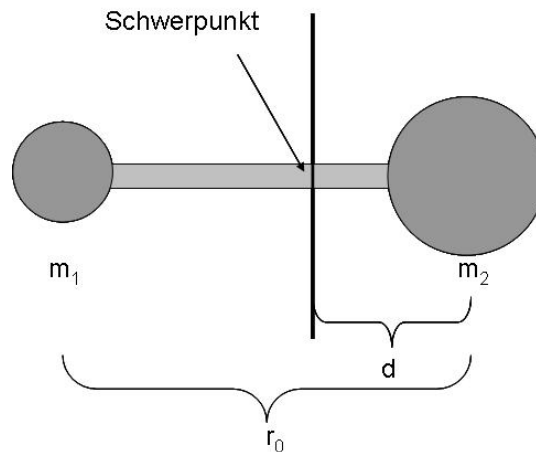


Figure 3.1: Diatomic molecule

A diatomic molecule (as shown in Fig. 3.1) with masses  $m_1$  and  $m_2$  rotates around

its center of mass. The two atoms have an equilibrium distance of  $r_0$  and the distance of the center of mass to atom 2 is  $d$ . Therefore it holds:

$$m_1(r_0 - d) = m_2d \quad \text{and hence} \quad d = \frac{m_1r_0}{m_1 + m_2}$$

Assuming that the molecule rotates as a rigid oscillator around the center of mass, the following holds for the moment of inertia:

$$\begin{aligned} I_b &= m_1(r_0 - d)^2 + m_2d^2 \\ I_b &= ur_0^2 \quad \text{with the reduced mass } u \end{aligned}$$

The rotational energy for molecules is quantized. The following holds for a rigid, diatomic molecule:

$$E_{rot} = \frac{h^2J(J+1)}{8\pi^2I_b} \quad (3.1)$$

or in wave numbers  $\bar{\nu}$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{E_{rot}}{hc} = BJ(J+1), \quad (3.2)$$

where  $J$  is the rotational quantum number and  $B = \frac{h}{8\pi^2I_b c}$  is the rotational constant.

If electromagnetic radiation hits a molecule so that it begins to rotate, quantum mechanics provides the selection rule  $\Delta J = \pm 1$ . This yields for  $J = 1$ :

$$\begin{aligned} \Delta E_{rot} &= Bhc[(J+1)(J+2)] - BhcJ(J+1) \\ \Delta E_{rot} &= 2Bhc(J+1) \\ \rightarrow \bar{\nu}_{rot} &= 2B(J+1) \end{aligned} \quad (3.3)$$

Since the permitted transitions for absorption are only from  $J$  to  $J+1$ , it follows that the distances between two neighboring absorption lines are always equal to  $2B$ .

## 3.2 Rotation of a nonrigid, linear molecule

In a nonrigid, diatomic molecule, the bond length increases with increasing rotational frequency due to the centrifugal distortion. The energy must therefore be corrected by a term:

$$E_{rot} = BhcJ(J+1) - Dhc[J(J+1)]^2, \quad (3.4)$$

where  $D$  is the centrifugal distortion constant. To obtain the appropriate activation energy for a photon, equation (3.3) is subtracted from itself, but with  $J$  substituted

by  $J + 1$ . This yields:

$$\begin{aligned} \frac{\Delta E_{rot}}{hc} &= 2B(J + 1) - 4D(J + 1)^3 \\ \rightarrow \underbrace{\frac{\bar{\nu}_{rot}}{J + 1}}_y &= \underbrace{2B}_a - \underbrace{4D(J + 1)^2}_{bx} \end{aligned} \quad (3.5)$$

Thus, the equation  $y=a+bx$  can be used to determine  $B$  and  $D$ .

### 3.2.1 Rotational-vibrational spectra

#### Rigid molecules

In general, rotation and vibration are superimposed in molecules. Rotational-vibrational bands of gases in the infrared have a complex structure, as a change in vibrational energy is often superimposed by a change in rotational energy. Let us assume that these energies are additive. Then, for a linear molecule, the total energy is given by:

$$E_{v+r} = \left(n + \frac{1}{2}\right)hc\bar{\nu}_0 + BhcJ(J + 1) \quad (3.6)$$

Let  $J''$  be the rotational quantum number in the vibrational ground state  $n = 0$  and  $J'$  that in the first excited state  $n = 1$ . Subtracting equation (3.5) (with  $n = 0$  and  $J = J''$ ) from itself again as above (with  $n = 1$  and  $J = J'$ ), we obtain:

$$\frac{\Delta E_{v+r}}{hc} = \bar{\nu}_0 + B[J'(J' + 1) - J''(J'' + 1)] \quad (3.7)$$

A linear, polyatomic molecule has two vibrational rotation bands, a "parallel band", which results from the fact that the change of the dipole moment is parallel to the molecular axis, and a "perpendicular band", for which the change of the dipole moment is perpendicular to the molecular axis. The selection rules  $\Delta J = \pm 1$  apply to the parallel band and  $\Delta J = 0, \pm 1$  to the perpendicular band. If  $\Delta J = 0$  and  $J' = J''$  holds, equation 1.6 gives:

$$\frac{\Delta E_{v+r}}{hc} = Q(cm^{-1}) = \bar{\nu}_0 \quad (3.8)$$

For  $\Delta J = 1$  and  $J' = J'' + 1$  we get:

$$\frac{\Delta E_{v+r}}{hc} = R(cm^{-1}) = \bar{\nu}_0 + 2B(J'' + 1) \quad J'' = 0, 1, 2, \dots \quad (3.9)$$

and for  $\Delta J = -1$  and  $J' = J'' - 1$

$$\frac{\Delta E_{v+r}}{hc} = P(\text{cm}^{-1}) = \bar{\nu}_0 - 2B(J'') \quad J'' = 1, 2, 3, \dots \quad (3.10)$$

In the case of stretching vibrations, however, the average intermolecular distance and hence the moment of inertia increases if the vibrational quantum number increases. As the so-called rotational constant is proportional to the reciprocal of the moment of inertia, this quantity has a smaller value in an excited state.

Let  $B_0$  be the rotational constant in the ground state and  $B_1$  that in the first excited state, then equation 3.6 must be changed to:

$$\frac{\Delta E_{v+r}}{hc} = \bar{\nu}_0 + B_1[J'(J' + 1)] - B_0[J''(J'' + 1)] \quad (3.11)$$

For the specific branches, this results in:

$$\begin{aligned} Q_J &= \bar{\nu}_0 + (B_1 - B_0)J^2 + (B_1 - B_0)J & J &= 0, 1, 2, 3, \dots \\ R_J &= \bar{\nu}_0 + 2B_1 + (3B_1 - B_0)J + (B_1 - B_0)J^2 & J &= 0, 1, 2, 3, \dots \\ P_J &= \bar{\nu}_0 - (B_1 + B_0)J + (B_1 - B_0)J^2 & J &= 1, 2, 3, \dots \end{aligned} \quad (3.12)$$

With the equations 3.11 we can then calculate  $B_0$  and  $B_1$ :

$$\begin{aligned} R_{J-1} - P_{J+1} &= 2B_0(2J + 1) \\ R_J - P_J &= 2B_1(2J + 1) \end{aligned} \quad (3.13)$$

### Nonrigid molecules

As for rigid molecules, we now also proceed in the same way for nonrigid molecules.  $D$  from equation 3.3 is no longer constant, but has different values for different states. Thus, equation 3.3 must also be rewritten and this results in:

$$\begin{aligned} \frac{\Delta E_{v+r}}{hc} &= \bar{\nu}_0 + B_1[J'(J' + 1)] - D_1[J'(J' + 1)]^2 \\ &\quad - B_0[J''(J'' + 1)] + D_0[J''(J'' + 1)]^2 \end{aligned} \quad (3.14)$$

As in the case of rigid molecules, this results in:

$$\begin{aligned} \frac{R_{J-1} - P_{J+1}}{2J + 1} &= (2B_0 - 3D_0) - D_0(2J + 1)^2 \\ \frac{R_J - P_J}{2J + 1} &= (2B_1 - 3D_1) - D_1(2J + 1)^2 \end{aligned} \quad (3.15)$$

These values can be used to make an extrapolation to the oscillation-free state and to calculate a value  $B_e$  that indicates the rotational constant at the bottom of the potential energy curve:

$$B_n = B_e - \alpha \left( n + \frac{1}{2} \right) \quad (3.16)$$

### 3.2.2 Pure stretching vibrations

The constants can now be used to calculate the frequencies of the pure stretching vibrations for a state  $n$ . For a change to a higher state, the molecule must interact with a photon of the energy

$$\begin{aligned}\Delta E_m &= \left[ (n+z) + \frac{1}{2} \right] h\nu_m - \left( n + \frac{1}{2} \right) h\nu_m \\ &= zh\nu_m.\end{aligned}$$

Using the equations from the previous sections, this gives:

$$\bar{\nu}_n = P(J) + (B_n + B_0)J - (B_n - B_0)J^2 \quad (3.17)$$

### 3.2.3 Morse potential

The potential energy of a molecule depends on the distance of the atoms. This distance depends on the electrical forces and the nuclear repulsion forces. At large nuclear distances, both nuclei attract each other, at small distances they repel each other. This results in an equilibrium position  $r_e$  at which the energy has a minimum.

For a diatomic molecule, the so-called Morse potential supplies a good approximation:

$$V = D_e(1 - e^{-\beta(r-r_e)})^2 \quad (3.18)$$

As it is known that  $e^x \approx 1 + x$  holds for small  $x$ , we get in the vicinity of the equilibrium state:

$$V = D_e\beta^2(r - r_e)^2 \quad (3.19)$$

Thus, the Morse potential near  $r_e$  corresponds to that of a harmonic oscillator and is experimentally accessible as follows: Based on the equation for a pendulum:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{u}} \quad F = \text{spring constant, } u = \text{reduced mass}$$

and the relation  $F = 2D_e\beta^2 = 4\pi^2\nu_e^2u$ , we get for  $\beta$ :

$$\beta = \nu_e \sqrt{\frac{2u\pi^2}{D_e}} \quad (3.20)$$

$\nu_e$  is the vibration frequency for an infinitesimal amplitude and  $D_e$  is the dissociation energy (in  $\text{cm}^{-1}$ ):

$$D_e = \frac{\bar{\nu}_e}{4x_e}, \quad (3.21)$$

$x_e$  is an anharmonicity constant that is related to the wave number as follows:

$$\bar{\nu}_n = \bar{\nu}_e n - x_e \bar{\nu}_e (n + n^2) \quad n = 1, 2, 3, \dots \quad (3.22)$$

### 3.3 Experimental procedure

Measure the spectrum of CO gas in a frequency range from  $4400\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$ . Two absorption regions can be observed. The first contains the peaks of the first excited state (and of isotopes). In the second region you can see the bands of the second excited state. Make sure that the pressure in the sample cell is in a range of 100 – 150 mbar so that you achieve an optimal absorbance (all peak maxima must still be visible).

### 3.4 Analysis

The analysis should contain the following points:

- Calculation of rotation and distortion constants ( $B_n$  and  $D_n$  for  $n = 0, 1, 2$ )
- Calculation of moment of inertia and mean bond length ( $I_n$  and  $r_n$  for  $n = 0, 1, 2$ )
- Extrapolation from first and second excited state to the vibrational-free state and calculation of  $B_e$ ,  $D_e$ ,  $I_e$  and  $r_e$
- Calculation of the pure vibration frequency for the first and second excited state
- Calculation and graphical representation of the Morse potential
- Compare your results with literature values

# Chapter 4

## Phase transition

### 4.1 Description of the experiment

In this part, you will study the liquid-solid phase transition of an alkane using the IR spectrum.

From a thermodynamic point of view, the melting point is given by the intersection of the Gibbs free energy  $G$  of the solid phase with that of the liquid phase [3]. Thus, at the melting temperature  $T_m$  the difference between the Gibbs free energy of the solid and the liquid phase vanishes (see  $G(T)$  diagram in Fig. 4.1) [3]. From the definition of Gibbs free energy:

$$G = H - T \cdot S \quad (4.1)$$

(G: Gibbs free energy, H: enthalpy, T: temperature, S: entropy)

it follows that the lower absolute value of the slope in the solid state in comparison to the liquid state (see Fig. 4.1) can be explained by the lower entropy of the solid phase state [3]:

$$\frac{\partial G}{\partial T} = -S \quad (4.2)$$

In the  $G(T)$  diagram in Fig. 4.1, we have simplifying assumed that the enthalpy  $H$  and the entropy  $S$  are constant in the different phases.

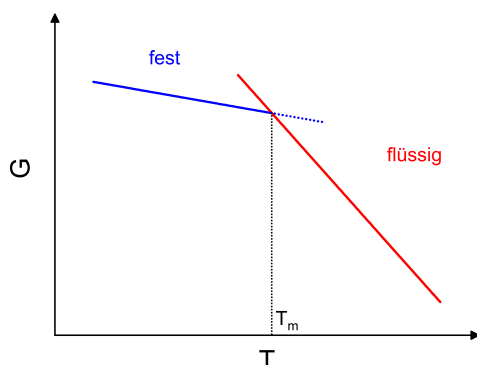


Figure 4.1: Schematic plot of the Gibbs free energy  $G$  as a function of temperature  $T$  (figure based on [3]). For simplification, we have assumed that  $H$  and  $S$  are constant in the different phases.

For adsorbates in nanoporous systems, the melting point  $T_m^{adsorbate}$  and thus the intersection of the Gibbs free energy is shifted to lower temperatures [4]. The curvature of the pore surface (i.e., the pore radius  $r_P$ ) determines the extent of the lowering of the melting temperature [4]:

$$\Delta T_m = T_m - T_m^{adsorbate} \propto \frac{1}{r_P}. \quad (4.3)$$

## 4.2 Experimental procedure

First, you measure the alkane in its bulk state. For this, fill an alkane in the sample cell and seal it with indium (PUT ON GLOVES!). Make sure that the liquid completely fills the sample cell so that the IR radiation actually passes through the alkane. Then switch on the temperature controller and the cold head. The supervisor will help you with this. Measure during cooling and heating in a temperature interval of  $\pm 10$  K above and below the phase transition. Then repeat the measurement with a nanoporous sample. First make a background measurement with the sample cell and the porous sample and then fill the porous sample with the alkane. Then place the sample back into the sample cell. The transition temperature will now be reduced by 5 K - 10 K, take this into account when setting the temperature.



### 4.3 Analysis

In the analysis, you should first describe what differences you notice in the spectra of bulk and pore condensate. Then determine the transition temperature in both states using peak positions, peak widths, peak intensities or splitting of peaks and compare these with each other as well as with literature values.

# Appendix: Frequencies of characteristic vibrations

wavenumber range [ $\text{cm}^{-1}$ ]	oscillation
400 – 1600	CH - vibrations in benzene rings
1600 – 2000	anharmonicities of CH vibration in benzene rings
2850 – 3000	$CH_2$ - and $CH_3$ - stretching vibrations
3000 – 3100	CH - stretching vibrations in benzene rings
680 – 780	$CF_3$ - vibrations
1150 – 1250	$CF_2$ - and $CF_3$ - stretching vibrations
1210 – 1250	O-C-O - stretching vibration
1720 – 1790	C=O - stretching vibration
1265 – 1380	$NC_3$
1035 – 1060	C-O - vibration (alcohol replaced by acetate)
1230 – 1260	C-O - vibration (acetate)
$\approx 1370$	$CH_3$ - vibration (acetate)
1740 – 1765	C-C-O - stretching vibration in ring

# Bibliography

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