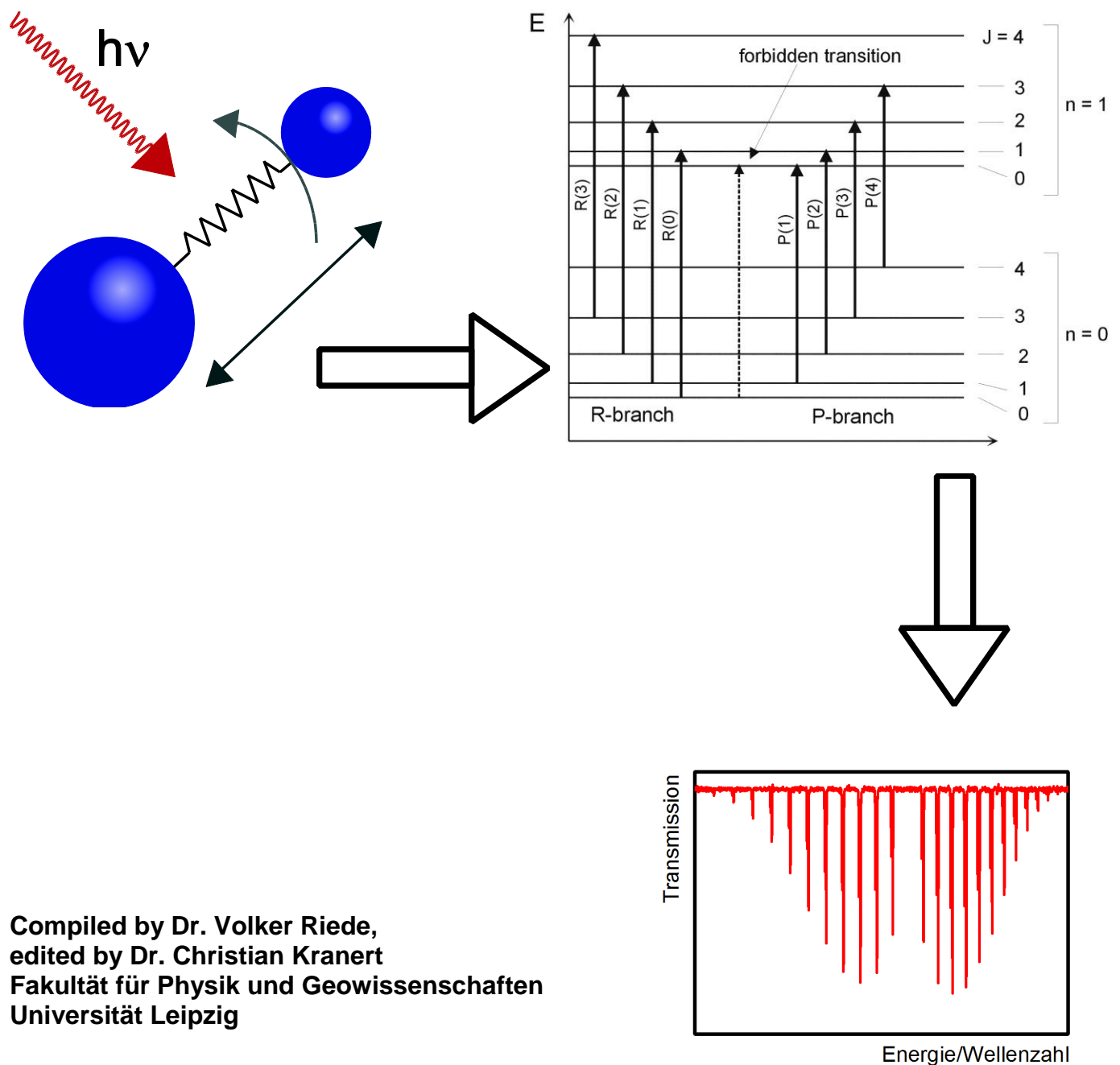


Rotation-Vibration Spectra of Molecules

Experiment for the Advanced Physics Laboratory Course



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1. Tasks

- 1.1 Verify the calibration of the wavenumber scale of the infrared spectrometer Spectrum 100 using water vapor and polystyrene calibration bands. Plot the experimentally determined deviations and discuss them.
- 1.2 Acquire interferograms of the water vapor spectrum using different mirror ranges of the interferometer. Obtain the spectra by applying a Fourier transformation to these interferograms. Calibrate the wavenumber scale of the thereby obtained spectra using the values for the water vapor bands. Determine step size of the optical path from the band width of the spectrum. Discuss the influence of the interferogram length and the applied zerofilling and apodisation on the spectral resolution based on the spectra. Based on the calculated step size, give the theoretical spectral resolution in dependence on the recorded data point count.
- 1.3 Determine the detected signal strength in the blocking range of a glass and a NaCl blocking filter.
- 1.4 Determine the gap width of a cuvette using the interference method. For that, plot of ΔN over $\bar{\nu}_N$ and determine the gap width and its means square error using the method of linear regression [4].
- 1.5 Acquire the rotation vibration spectrum of hydrogen chloride (HCl) gas using an adequate spectral resolution and determine the spectral position of the absorption bands. Calculate the wavenumber of the pure vibration transition, the force constant, the rotation constant, the distance of the two atoms in the molecule and the moment of inertia. Further, determine the vibration-dependent rotation constant B_v , the centrifugal distortion constant D as well as the spectral splitting due to the different isotopes. Determine the relation of abundance of the isotopes using the Lambert Beer law.
- 1.6 Model the intensities of the absorption minima in the P branch using the theoretical absorption coefficient. Obtain the temperature as a free parameter in the model.

2. Remarks on infrared spectroscopy

Infrared spectroscopy is a commonly applied experimental technique for the determination of material properties in all three states of matter. Besides the investigation of lattice vibrations, defects and charge carriers in solids, the determination of the properties of molecules in gases as well as the determination of concentrations of molecular gases belong to the main application fields of this method.

Generally, infrared spectra of gases are measured in transmission. That means that light of a known wavelength λ is guided through a gas volume. The relation between transmitted intensity I and incident intensity I_0 is the transmittance $t(\lambda)$:

$$t(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}$$

The transmission spectrum is obtained by a variation of the wavelength. The following quantities are important:

1. Wavelength for which the transmission is minimal. This is related to the energy of the excited transition.
2. Transmittance at the minimum. This value is a measure for the absorption coefficient of the excited transition.

The transmitted intensity depends on the absorption coefficient $\alpha(\lambda)$ of the material according to Lambert's law:

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)d}$$

Here, d is the thickness of the material. If the material is diluted with the concentration c , then the transmitted intensity is described by the Lambert-Beer-law:

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)cd}$$

The infrared spectral region borders to the visible spectral range, extending towards longer wavelengths. It is further roughly divided into the following regions:

near infrared (NIR)	: 0.76 - 2.5 μm ,
mid infrared (MIR)	: 2.5 - 50.0 μm ,
far infrared (FIR)	: 50.0 - 1000.0 μm .

Thus, measurements using the Spectrum 100 (2.5 - 50 μm) allow to access the MIR range. Various physical quantities are typically used in infrared spectroscopy to characterize the spectral position: the vacuum wavelength λ , the wavenumber $\bar{\nu}$, the frequency ν and the angular frequency ω . These are connected by the following equations:

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\omega}{2\pi c}$$

(c = velocity of light).

Typically, [μm] is used as unit of λ [cm^{-1}] as unit of $\bar{\nu}$. So, a conversion between both can be done using

$$\bar{\nu}[\text{cm}^{-1}] = \frac{10^4}{\lambda[\mu\text{m}]}$$

Within the present lab course experiment, the physical properties of one of the simplest molecules, i.e. the diatomic HCl, is to be investigated using the FTIR spectrometer Spectrum 100. Previous to the conduction of the experiments, the following issues must be prepared:

1. Setup and principle of function of the spectrometer spectrum 100, spectral resolution, accuracy, apodisation, zerofilling, phase correction
2. Theory of rotation vibration spectra of diatomic molecules
3. Transmission of a non-absorbing Fabry-Pérot interferometer, differences between Michelson and Fabry-Pérot interferometers, interference method for the determination of thicknesses.

3. Theory

3.1. General remarks

In this section, the theory on the molecular spectrum of a diatomic molecule is introduced. This description is based on the dumbbell model. The two atoms are considered as point masses, which are connected by binding forces yielding a certain distance between both atoms. The dumbbell can rotate and vibrate with frequencies which depend on the atomic masses, the binding forces and the interaction between rotation and vibration and which are in the infrared spectral range.

For certain molecules, the change of the rotational or vibrational state changes the dipole moment. Such rotations and vibrations interact with infrared light and are thus called infrared active. This is particularly the case for the HCl molecule, for which the periodic oscillation of the positively charged hydrogen atom against the negatively charged chlorine atom results in a periodically alternating electrical field (oscillation of a dipole). The other way round, infrared active rotations and vibrations can also be excited by infrared light. In this process, the light is absorbed in the molecule resulting in absorption lines or bands (group of lines). In the following, the theoretical interpretation of the rotation-vibration-spectrum is described theoretically based on the dumbbell model and it is explained, which physical quantities can be obtained from such a spectrum [1,2,3].

3.2. Rigid rotator with spatially fixed rotational axis

In the simplest form of the model, the eigenstates of a dumbbell with rigid axis rotating around a spatially fixed axis are investigated (see Fig. 1)

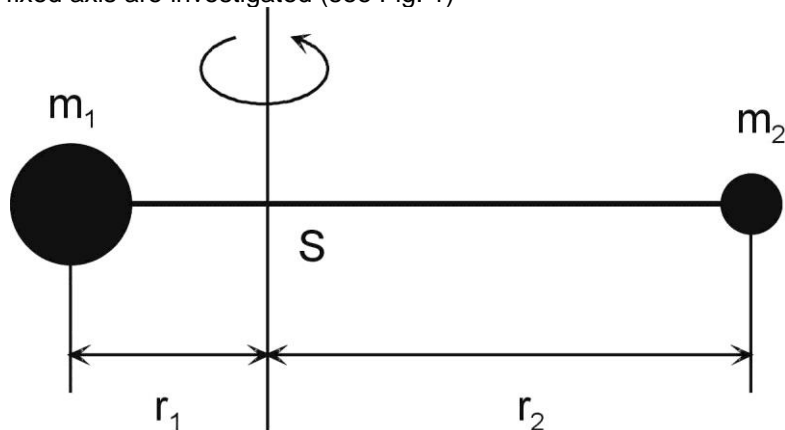


Fig. 1 Dumbbell model of a diatomic molecule.

The rotational axis goes through the center of mass S of the system. The center-of-mass theorem for it reads

$$m_1 \vec{r}_1 + m_2 \vec{r}_2 = 0 \quad (1)$$

Where the point of origin is set in the center of mass. From that follows

$$\vec{r}_1 \frac{m_1}{m_2} = -\vec{r}_2 \quad (2)$$

and for the absolute values $|\vec{r}_1| = r_1$ and $|\vec{r}_2| = r_2$

$$r_1 \frac{m_1}{m_2} = r_2 \quad (3)$$

The distance between both masses is

$$r_0 = r_1 + r_2 \quad (4)$$

From (3) and (4) one can calculate

$$\begin{aligned} r_1 &= \frac{m_2}{m_1 + m_2} r_0 \\ r_2 &= \frac{m_1}{m_1 + m_2} r_0 \end{aligned} \quad (5)$$

The moment of inertia is calculated as

$$I = \sum_{i=1}^2 m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = r_0^2 \frac{m_1 m_2}{m_1 + m_2} \quad (6)$$

Using the reduced mass μ

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

equation (6) can be written as

$$I = \mu r_0^2 \quad (7)$$

Equation (7) shows that the problem is analogue to a rotation of a point mass with the mass μ , which has a distance r_0 from the rotational axis. The energy eigenvalues are calculated using quantum mechanics. The Schrödinger equation

$$\Delta \psi + \frac{8\pi^2 m}{h^2} (E - U) \psi = 0 \quad (8)$$

needs to be solved for the case of the rotating dumbbell. Here, ψ is the wave function, E is the total energy, U is the potential energy, m is the mass and h is the Planck constant

The rotation of the dumbbell does not result in a potential energy, thus (8) can be simplified to:

$$\Delta\psi + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad (9)$$

For the description of the rotational motion, the introduction of polar coordinates is appropriate:

$$\Delta\psi = \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \quad (10)$$

For the rigid rotator, the radial component does not change and thus ψ only depends on the rotational angle ϕ . Using this, (9) and (10) can be combined to

$$\frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad (11)$$

In the special case of a dumbbell, the quantity r needs to be replaced by r_0 and the mass m by the reduced mass μ . For the solution of equation (11), the ansatz

$$\psi = e^{il\phi} \quad (12)$$

is used. Due to the demanded uniqueness of the solution, $\psi(\phi) = \psi(\phi + 2\pi)$ must hold. From that follows

$$e^{il\phi} = e^{il(\phi+2\pi)} = e^{il\phi} e^{2l\pi i}$$

By that follows that $e^{im2\pi} = 1$ and thus $m = 0, \pm 1, \pm 2, \dots$. Inserting (12) in (11) and considering $r = r_0$ and $m = \mu$ yields

$$E_m = m^2 \frac{h^2}{8\pi^2 \mu r_0^2} \quad (13)$$

The energy can only have discrete values E_m .

3.3. Rigid rotator with spatially variable rotational axis

The rotational axis of a real diatomic molecule is not spatially fixed. Thus, the wave function in dependence on the angular coordinate θ needs to be taken into account. By introducing spherical coordinates, (9) becomes

$$\frac{1}{r_0} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right\} + \frac{8\pi^2 \mu E}{h^2} \psi = 0 \quad (14)$$

The solution of this equation is complex. The solution process is described e.g. in [2, S.187 ff]. Also this calculation yields discrete energy eigenvalues:

$$E(J) = \frac{h^2}{8\pi^2 \mu r_0^2} J(J+1) \quad , J = 0, 1, 2, \dots \quad (15)$$

Here, J is the (integer) rotational quantum number.

By introducing the rotational constant

$$B = \frac{h}{8\pi^2 c \mu r_0^2} = \frac{h}{8\pi^2 c I} \quad (16)$$

With the moment of inertia I, (15) becomes

$$E(J) = hcBJ(J+1) \quad (17)$$

The rotational term $F(J) = E/hc$ has the dimension of a wavenumber and is thus well suitable to analyze spectra plotted against the wavenumber. For $F(J)$, equation (17) reads

$$F(J) = BJ(J+1) \quad , J = 0, 1, 2, \dots \quad (18)$$

These equations yield the energy eigenvalues of the system (see Fig. 2). Quantum mechanics also yield the allowed transitions between those states (here without derivation). The allowed transitions are those, for which

$$\Delta J = \pm 1 \quad (19)$$

holds.

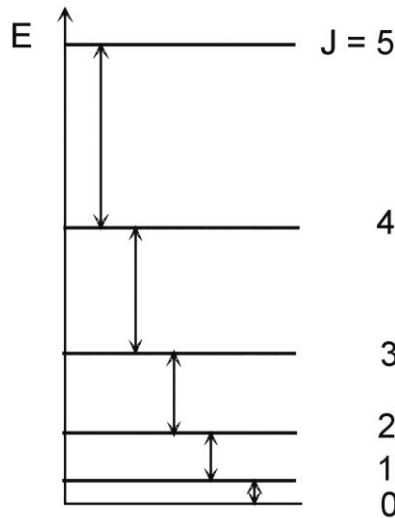


Abb. 2 Energy scheme of a molecular rotator.

If radiation with a wavenumber, which corresponds to the energy difference between two neighboring rotational states, hits the diatomic molecule, the radiation is absorbed and thereby the rotational energy is increased.

In the following, the energy of the individual transitions is calculated. The energy difference is

$$E(J+1) - E(J) = hcB((J+1)(J+2) - J(J+1)) = 2hcB(J+1),$$

$$E(J+1) - E(J) = 2hcB(J+1) \quad (20)$$

Or, in terms of wave numbers:

$$F(J+1) - F(J) = 2hcB(J+1), \quad J = 0, 1, 2, \dots \quad (21)$$

For example, in order to excite the molecule from the state $J=0$ to $J=1$, the molecule must be irradiated with light with the wave number $\bar{\nu}(J=0) = 2B$. The following wave numbers for the individual transitions are obtained:

J	$\bar{\nu}(J)$
0	2B
1	4B
2	6B
3	8B
⋮	⋮

That means that within this model the rotational spectrum consists of equidistant absorption lines with the wave numbers given above. Thus, the distance between these lines is $\bar{\nu} = 2B$.

3.4. Harmonic oscillator

Besides the rotation of the molecule, also the atoms can vibrate against each other. To begin with, the rotation will be neglected in the following as simplification and only the vibration will be considered.

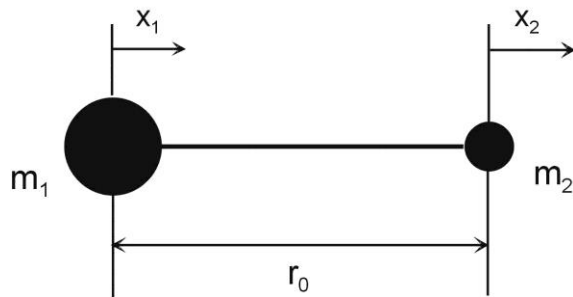


Abb. 3 Vibrating dumbbell.

The displacement from the equilibrium position for the two atoms are x_1 and x_2 (Fig. 3). Within the harmonic approximation, the repulsive force is proportional to the difference of the displacement. One obtains the equations of motion

$$m_1 \ddot{x}_1 = -k(x_1 - x_2) \quad (22)$$

$$m_2 \ddot{x}_2 = -k(x_2 - x_1) \quad (23)$$

By multiplying (22) with m_2 and (23) with m_1 and by subtracting (23) from (22), one obtains

$$\ddot{x}_1 - \ddot{x}_2 = -k(x_1 - x_2) \frac{m_1 + m_2}{m_1 m_2} \quad (24)$$

From $x_1 - x_2 = x$ it follows that

$$\ddot{x} = -\frac{k}{\mu}x \quad (25)$$

This is the equation of motion of a harmonic oscillator with the resonance wave number

$$\bar{\nu}_s = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (26)$$

Here, k is the force constant. It is an important physical quantity as it is a measure of the binding forces in the molecule. Classical mechanics yield

$$x = x_0 \sin(2\pi \bar{\nu}_s t) \quad (27)$$

as solution of (25). In the quantum mechanical treatment, the Schrödinger equation must be solved. For this, the potential energy is required, which can be calculated from

$$-\frac{dU}{dx} = F = -kx$$

One obtains

$$U = 2\pi^2 c^2 \bar{\nu}_s^2 \mu x^2 \quad (28)$$

The Schrödinger equation for the x components then reads

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2} \left(E - 2\pi^2 c^2 \bar{\nu}_s^2 \mu \right) x^2 \psi = 0 \quad (29)$$

The solution procedure for equation (29) is described in [2, p.189]. The resulting energy eigenvalues are

$$E(n) = hc \bar{\nu}_s \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (30)$$

As for the rotator, only discrete energy eigenvalues are allowed. The quantity n is the vibrational quantum number and the energy $E(0) = 1/2 hc \bar{\nu}_s$ is called zero point energy. According to quantum mechanics (again without derivation), only dipole transitions with

$$\Delta n = \pm 1. \quad (31)$$

are allowed. The respective transition energies are

$$E(n+1) - E(n) = hc \bar{\nu}_s \quad (32)$$

This equation (32) is independent of n, i.e. there is only one absorption line in the spectrum. The wave number $\bar{\nu}_s$ of this line is equal to the resonance wave number of the classical harmonic oscillator. One obtains the vibrational term

$$G(n) = \frac{E(n)}{hc} = \bar{\nu}_s \left(n + \frac{1}{2} \right) \quad (33)$$

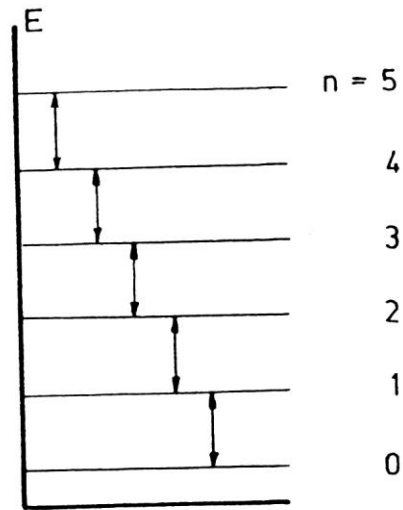


Abb. 4 Energy scheme of the harmonic oscillator

3.5. Rotation-Vibration spectra

a. Molecule with rigid axis

In the upper part, rotation and vibration were treated independent from each other, but in reality they occur simultaneously. The coupling between both shall be ignored for the moment. In order to calculate the wave numbers of the lines in the rotation-vibration spectrum, the total energy of the rotating oscillator is required. Adding equation (17) and (30) yields

$$E(n, J) = hcBJ(J+1) + hc\bar{\nu}_s \left(n + \frac{1}{2} \right) \quad (34)$$

$$J = 0, 1, 2, \dots \quad n = 0, 1, 2, \dots$$

and for the rotational-vibrational term $T(n, J)$

$$\frac{E(n, J)}{hc} = T(n, J) = BJ(J+1) + \tilde{\nu}_s \left(n + \frac{1}{2} \right) \quad (35)$$

The selection rules are

$$\begin{aligned} \Delta J &= \pm 1 \\ \Delta n &= 0, \pm 1 \end{aligned} \quad (36)$$

The transitions $\Delta n = 0$, $\Delta J = \pm 1$ yield the pure rotational spectrum, which can be found in the FIR spectral range.

Considering that the resonance wave number of the vibrational transition $\bar{\nu}_s$ is much larger than the rotational constant B, one obtains an energy scheme from equations (34) and (36) as depicted in Fig. 5.

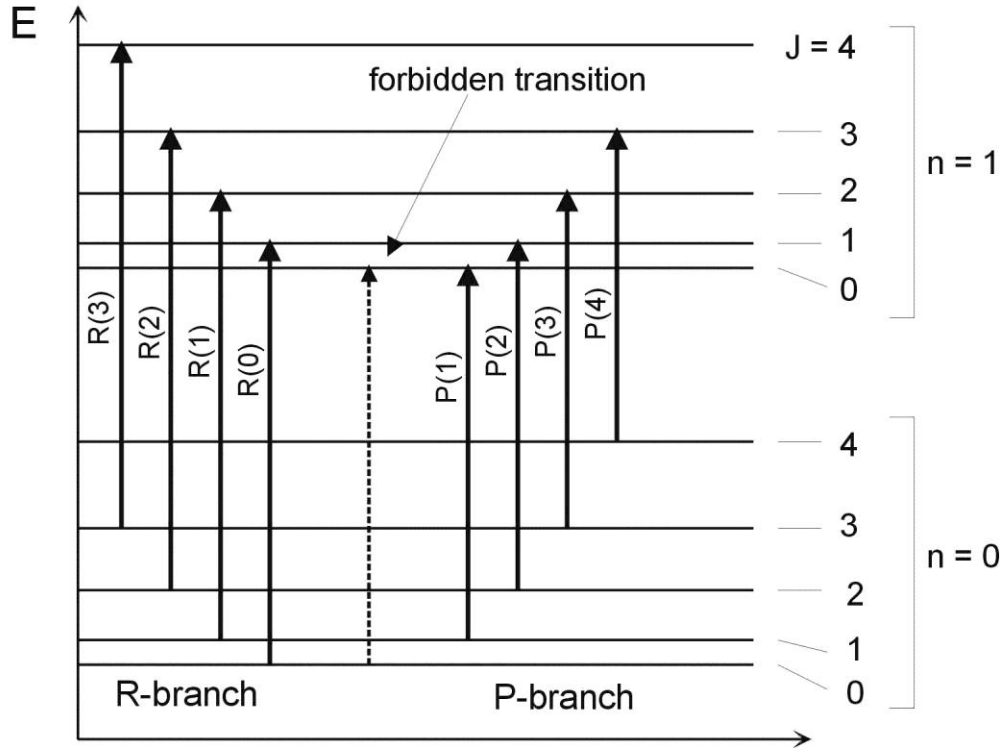


Abb. 5 Energy scheme of a rotating oscillator

The arrow direction shown in Fig. 5 is valid for the case that the molecule is excited from a state of lower into a state of higher energy by the absorption of radiation. Of course, according to equation (36), also the other way, i.e. the emission of radiation, is allowed. The wave number of a certain transition is equal to the difference between the respective rotational-vibrational terms with $\Delta n = 1$ and $\Delta J = \pm 1$. Thus, one distinguishes two cases:

1. $\Delta n = 1, \Delta J = 1$

The difference of the rotational-vibrational terms yields

$$\begin{aligned} T(n+1, J+1) - T(n, J) &= \bar{\nu}_s \left(n+1 + \frac{1}{2} \right) - \bar{\nu}_s \left(n + \frac{1}{2} \right) + B(J+1)(J+2) - BJ(J+1) \\ &= \bar{\nu}_s + 2B(J+1) = \bar{\nu}_R(J) \end{aligned} \quad (37)$$

The respective absorption lines belong to the so-called R-branch. They correspond to the transitions R(0), R(1) ... in Fig. 5.

2. $\Delta n = 1, \Delta J = -1$

$$T(n+1, J-1) - T(n, J) = \bar{\nu}_s - 2BJ = \bar{\nu}_P(J) \quad J = 1, 2, \dots \quad (38)$$

These absorption lines belong to the so-called P-branch. They correspond to the transitions P(1), P(2) ... in Fig. 5. Due to $\Delta J = -1$, there is no P(0) transition and the P-branch starts from J=1.

Because $\Delta J = 0$ is forbidden, no line can be observed for $\bar{\nu} = \bar{\nu}_s$. The wave number of the vibrational transition can be calculated from

$$\bar{\nu}_R(0) + \bar{\nu}_P(1) = 2\bar{\nu}_s \quad (39)$$

The rotational constant can be obtained from the relation

$$\bar{\nu}_R(0) - \bar{\nu}_P(1) = 4B \quad (40)$$

The difference of the wave numbers between two neighboring lines is $2B$ in both the P- and the R-branch.

b. Molecule with non-rigid axis

The very precise measurements with the spectrometer Spectrum 100 allow to study the effects due to the non-rigid axis of the molecule. In the simplified dumbbell model above, the distance of the two atoms was considered as constant. In a real molecule, the centrifugal force of the rotation enlarges the distance between the atoms and thus the moment of inertia. This results in a decrease of the rotational constant, whereby this change depends on J . As a good approximation, the rotational term can be rewritten as

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \quad (41)$$

For which $D \ll B$ holds. D is called centrifugal distortion constant.

Analogously to (37) and (38), one obtains for the lines of the R- and the P-branch:

$$\bar{\nu}_R(J) = \bar{\nu}_s + 2B(J+1) - 4D(J+1)^3 \quad (42)$$

$$\bar{\nu}_P = \bar{\nu}_s - 2BJ + 4DJ^3 \quad (43)$$

Besides the effect of the centrifugal, also anharmonicity effects cause a change of the mean atom distance between the different vibrational states. By that, also the moment of inertia and the constants B and D change and thus become dependent on the vibrational quantum number n . Considering this effect, the rotational term (41) becomes

$$F_n(J) = B_n J(J+1) - D_n J^2(J+1)^2 \quad (44)$$

For the transitions of the P-branch from $n=0$ to $n=1$ ($\Delta J = -1$, $\Delta n = 1$ and $J = 1, 2, 3, \dots$), one obtains

$$\bar{\nu}_P = \bar{\nu}_s + F_1(J-1) - F_0(J) = \bar{\nu}_s + B_1(J-1)J - B_0J(J+1) - D_1(J-1)^2 J^2 + D_0(J+1)^2 J^2$$

From that follows

$$\bar{\nu}_P = \bar{\nu}_s - J(B_1 + B_0) + J^2(B_1 - B_0 - D_1 + D_0) + 2J^3(D_1 + D_0) - J^4(D_1 - D_0) \quad (45)$$

This can be written analogously for the R-branch ($\Delta J = 1$, $\Delta n = 1$ and $J = 0, 1, 2, \dots$) as

$$\bar{\nu}_R = \bar{\nu}_s + B_1(J+1)(J+1) - B_0J(J+1) - D_1(J+1)^2(J+2)^2 + D_0J^2(J+1)^2$$

from which follows

$$\bar{\nu}_R = \bar{\nu}_s + (2B_1 - 4D_1) + J(3B_1 - B_0 - 12D_1) + J^2(B_1 - B_0 - 13D_1 - D_0) - J^3(6D_1 - 2D_0) - J^4(D_1 - D_0) \quad (46)$$

The equations (45) and (46) can be condensed into a single equation using the running index i:

$$\bar{\nu}(i) = \bar{\nu}_s + (B_1 + B_0)i + (B_1 - B_0 - D_1 + D_0)i^2 - 2(D_1 + D_0)i^3 - (D_1 - D_0)i^4 \quad (47)$$

This equation can be further simplified by means of an approximation using the relations $D_n \ll B_n$ and $D_n \approx D_{n+1}$:

$$\bar{\nu}(i) = \bar{\nu}_s + (B_1 + B_0)i + (B_1 - B_0)i^2 - 2(D_1 + D_0)i^3 \quad (48)$$

The running index i is assigned to the quantum numbers J as follows:

	P-Zweig	R-Zweig
J	3 2 1	0 1 2
i	-3 -2 -1	1 2 3

Obviously, $i = 0$ corresponds to the pure vibrational transition ($\Delta n = 1$ and $\Delta J = 0$). In order to determine the quantities B_n and D_n , the following procedure can be used. One calculates the difference between the measured wave numbers $\bar{\nu}(i)$ and then again the difference of these results, that means first

$$\begin{aligned} \Delta \bar{\nu}(i) &= \bar{\nu}(i+1) - \bar{\nu}(i) \\ &= 2B_1 - 2(D_1 + D_0) + 2i(B_1 - B_0 - 3(D_1 + D_0)) - 6i^2(D_1 + D_0) \end{aligned} \quad (49)$$

and then

$$\begin{aligned} \Delta^2 \bar{\nu}(i) &= \Delta \bar{\nu}(i+1) - \Delta \bar{\nu}(i) \\ &= 2(B_1 - B_0) - 12(D_1 + D_0) - 12i(D_1 + D_0) \end{aligned} \quad (50)$$

One obtains $D_1 + D_0$ from the slope of this curve and $B_1 - B_0$ from the intersection with the ordinate axis. Using (49), the individual quantities B_1 and B_0 can be determined.

3.6. Intensity of the rotation-vibration spectrum (Bjerrum's double band)

Only the spectral position of the absorption lines was in the focus in the above elaborations. These allow to determine the physical parameters of a diatomic molecule. In this section, the intensity of these lines is treated.

The envelope of the absorption lines has the shape of a double band, which is also observed for a lower spectral resolution. The transmission passes two minima, i.e. the absorption features two maxima. The maxima belong to the R- and P-branch, respectively, and have a certain spectral distance. From the wave numbers of these maxima, the rotational constant and the wave number of the vibrational transition can

be calculated. For that, the absorption coefficient in dependence on the wavenumber is required, which is calculated in the following.

The transition is depicted in Fig. 5. The lower state (index i) is characterized by the quantum numbers n_i and J_i , the upper state (index j) by the quantum numbers n_j and J_j . The absorption coefficient for the transition between these states is labelled α^{ji} , the energy difference is given as $hc\bar{\nu}_{ji}$.

Let M_{ij} be the number of transitions, which are excited by a given radiation density within a certain volume and time interval. This yields the absorption coefficient

$$\alpha_{abs}^{ji} = M_{ij} h \nu_{ji} = M_{ij} hc \bar{\nu}_{ji} \quad (51)$$

The number of transitions M_{ij} is proportional to the number N_i of molecules in the lower state i per unit volume:

$$M_{ij} = W_{ij} N_i \rho_{ji} \quad (52)$$

Here, W_{ij} is the Einstein coefficient for absorption of light with the wave number $\bar{\nu}_{ji}$. W_{ij} equals the probability of a transition from the state i to the state j. Inserting (52) into (51) yields

$$\alpha^{ji} = W_{ij} N_i hc \bar{\nu}_{ji} \quad (53)$$

Leaving out the indices, the absorption coefficient from Eq. (53) can be written as

$$\alpha = c_1 N W \bar{\nu} \quad (54)$$

where

$$c_1 = hc \quad (55)$$

is a constant.

It is a good approximation that the transition probability for all allowed transitions in Fig. 5 is identical. This makes W a constant, allowing to write (54) as

$$\alpha = c_2 N \bar{\nu} \quad (56)$$

where $c_2 = Wc_1$ is a constant.

Besides the linear dependence on the wave number, the absorption coefficient obviously mainly depends on the number of states in the lower state i. During the measurement, the spectrum is in a thermodynamic equilibrium. Thus, the number of molecules with a particular energy E is given by the Maxwell-Boltzmann distribution:

$$N(E) = \frac{\eta}{Q_r} e^{-\frac{E}{k_B T}} \quad (57)$$

η = total number of molecules,

Q_r = partition function,

k_B = Boltzmann constant,

T = absolute temperature.

In order to obtain the number of molecules $N(n,J)$ in the state with the quantum numbers n and J , the energy from Eq. (34) needs to be inserted into Eq. (57):

$$E(n, J) = hcBJ(J+1) + hc\bar{\nu}_s \left(n + \frac{1}{2} \right) \quad (34)$$

Here, the following must be taken into account:

1. Every state with the total angular momentum \vec{I} is degenerated $2J+1$ times. Thus, the right side of (57) must be multiplied with the factor $2J+1$.
2. At $T = 300$ K, virtually all molecules are in the state $n = 0$, i.e. they are in their vibrational ground state. The thermal energy $k_B T$ at 300 K is approximately 26 meV while the vibrational energy $hc\bar{\nu}_s$ of HCl is approximately 400 meV.

By that, (57) becomes

$$N(J, n=0) = \frac{N}{Q_r} (2J+1) e^{-\frac{hcBJ(J+1)}{k_B T}} e^{-\frac{hc\bar{\nu}_s \left(n + \frac{1}{2} \right)}{k_B T}} \quad (58)$$

The second exponential term in Eq. (58) is constant with respect to J and can thus be incorporated in the constant prefactor. Inserting (58) into (56) then yields

$$\alpha = c_3 \bar{\nu} (2J+1) e^{-\frac{hcBJ(J+1)}{k_B T}} \quad (59)$$

Using this absorption coefficient, the relative intensities of the absorption lines can be calculated using Lambert's law:

$$I(J) = I_0 e^{-\alpha d} = I_0 \exp \left\{ c_4 \bar{\nu} (2J+1) e^{-\frac{hcBJ(J+1)}{k_B T}} \right\} \quad (60)$$

The relation between J and $\bar{\nu}$ already known from equation (48).

3.7. Interference method

If a light beam is guided through an empty cuvette, the light is reflected multiply which results in interference. These interferences depend on the wavelength of the light, the thickness and index of refraction in the cavity, the angle of incidence. In the spectrum, they appear as a periodic modulation of the intensity. In the following, the theoretical principles describing the wavelengths of the transmission maxima and minima are presented.

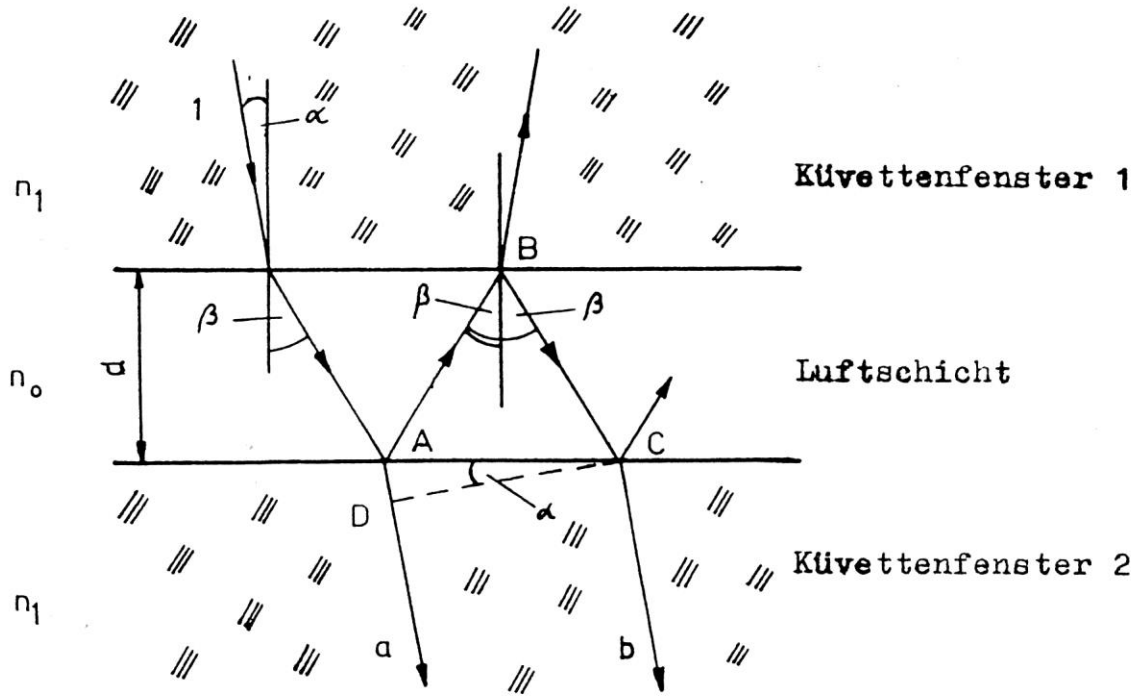


Abb. 6 Beam path through a cuvette. The labels read cuvette window 1, air gap, cuvette window 2 (from top to bottom)

The beam path through a cuvette is depicted in Fig. 6. The beams leaving the cuvette through window 2 are labeled as a and b in the figure. Because all these beams originate from beam 1, they are coherent and can interfere. It depends on the path difference between a and b whether the interference is constructive or destructive. The geometric path difference s , using the labels of Fig. 6, is

$$s = \overline{AB} + \overline{BC} - \overline{AD} \quad (64)$$

The optical path difference Δ also takes the different index of refraction in the different media into account. In our case, this is

$$\Delta = n_0(\overline{AB} + \overline{BC}) - n_1 \overline{AD} \quad (65)$$

Using

$$\overline{AB} = \overline{BC} = \frac{d}{\cos \beta}$$

$$\overline{AD} = \overline{AC} \sin \alpha = 2d \tan \beta \sin \alpha$$

and

$$\frac{n_1}{n_0} = \frac{\sin \beta}{\sin \alpha}$$

it follows that

$$\begin{aligned} \Delta &= n_0 \frac{2d}{\cos \beta} - n_0 \frac{\sin \beta}{\sin \alpha} 2d \tan \beta \sin \alpha \\ &= 2n_0 d \left(\frac{1}{\cos \beta} - \frac{\sin^2 \beta}{\cos \beta} \right) = 2n_0 d \cos \beta \end{aligned}$$

For the transmission measurements with the spectrometer Spectrum 100, an approximately parallel beam is used, thus the calculation can be simplified for the case of normal incidence ($\beta = 0^\circ$), for which the optical path difference is

$$\Delta = 2n_0 d \quad (66)$$

If it is an integer multiple of the vacuum wavelength λ , amplification occurs, i.e. a maximum in the transmission is observed:

$$2n_0 d = N\lambda \quad , \quad N = 0, 1, 2, \dots \quad (67)$$

Transmission minima occur for the wavelength that fulfill

$$2n_0 d = N\lambda + \frac{\lambda}{2} = \left(N + \frac{1}{2} \right) \lambda \quad , \quad N = 0, 1, 2, \dots \quad (68)$$

On the wave number scale with $\bar{\nu} = 1/\lambda$, (67) and (68) become

$$2n_0 d = \frac{N}{\bar{\nu}} \quad , \quad N = 0, 1, 2, \dots \quad (69)$$

$$2n_0 d = \left(N + \frac{1}{2} \right) \frac{1}{\bar{\nu}} \quad , \quad N = 0, 1, 2, \dots \quad (70)$$

N is the order of the extrema. Considering a maximum of order N_1 at $\bar{\nu} = \bar{\nu}_1$ and a maximum of order N_2 at $\bar{\nu} = \bar{\nu}_2$, one obtains the following from equation (69):

$$\begin{aligned} N_1 &= 2n_0 d \bar{\nu}_1 \\ N_2 &= 2n_0 d \bar{\nu}_2 \end{aligned}$$

Subtracting one of the equations from the other yields

$$N_1 - N_2 = 2dn_0(\bar{\nu}_1 - \bar{\nu}_2) \quad (71)$$

Because $n_0 = 1$ for air, one obtains the gap thickness d from equation (71) as

$$d = \frac{N_1 - N_2}{2(\bar{\nu}_1 - \bar{\nu}_2)} \quad (72)$$

Analogously, the same relation is valid for the minima of the transmission. This allows the determination of the gap thickness by the following method: The obtained numbers $N_i - N_0$ are plotted against the wave number difference $\bar{\nu}(N_i) - \bar{\nu}(N_0)$. This yields a straight with the slope

$$2d = \frac{N_i - N_0}{\bar{\nu}(N_i) - \bar{\nu}(N_0)} \quad (73)$$

From this plot, the thickness d can be determined using a linear regression.

4. Experimental procedure

Prerequisite for executing this experiment are the knowledge on the functional principle of a FTIR spectrometer and on the theory of rotational-vibrational excitations. Some additional remarks on the experimental process and the data evaluation are given below.

1. The polystyrene foil and the glass slabs are mounted in a cuvette mount. Particularly the foil must be protected from mechanical stress!
2. The gas cuvette containing the HCl gas must not be opened!
3. All hygroscopic materials (NaCl, KBr) must be kept in the drying containers and must only be handled using the supplied gloves.
4. The sample area must be kept close all the time except for changing the sample.
5. For all measurements, an overview spectrum needs to be recorded at first. After that, resolution and wave number range are to be selected appropriately.

Remarks to task 1.2:

At least 2 measurements with different measurement ranges of the interferometer mirror must be carried out in order to discuss the differences. Because the measurement time is rather short, it is highly recommended to measure further spectra and select from these in the evaluation. For the discussion, the obtained interferogram/spectrum for the maximum mirror range (-8000 to 32000 data points) must be included, a second measurement should use at least a range from -8000 to 8000 data points. Feel free to add further results to the discussion. Measurements with missing data points on one side must be completed by mirroring of the data from the other side around 0. For the comparison of the spectral resolution, different combinations of zerofilling and apodisation shall be compared. The comparison of the measurement with the maximum mirror range, no zerofilling and strong apodisation (Blackman) to measurements with lower mirror range, high zerofilling (factor ≥ 4) and weak (triangle) or no (square) apodisation is of particular interest.

A possible practical procedure for carrying out the zerofilling with factor a for a measurement in the range from $-n$ to $+n$ using the software Origin is described in the following: Create a new worksheet. Set the values in the X-column using the "Set column values"-function of Origin. Enter the range $-a*n$ to $+a*n$ and the function $(i-1)-a*n$ (of course, the product $a*n$ needs to be substituted by the actual value). Similarly, set the values of the Y-column to 0 in the same range. Then you can copy the actually measured values to the appropriate position in the Y-column, i.e. that the X-values match the original ones.

Fourier transformation using Origin:

The interferogram can be converted into the spectrum within Origin using the Fourier transform function. For that, you need to plot the interferogram and subsequently select Analysis->Signal Processing->FFT->FFT... from the menu. The window depicted in Fig. 7 should open.

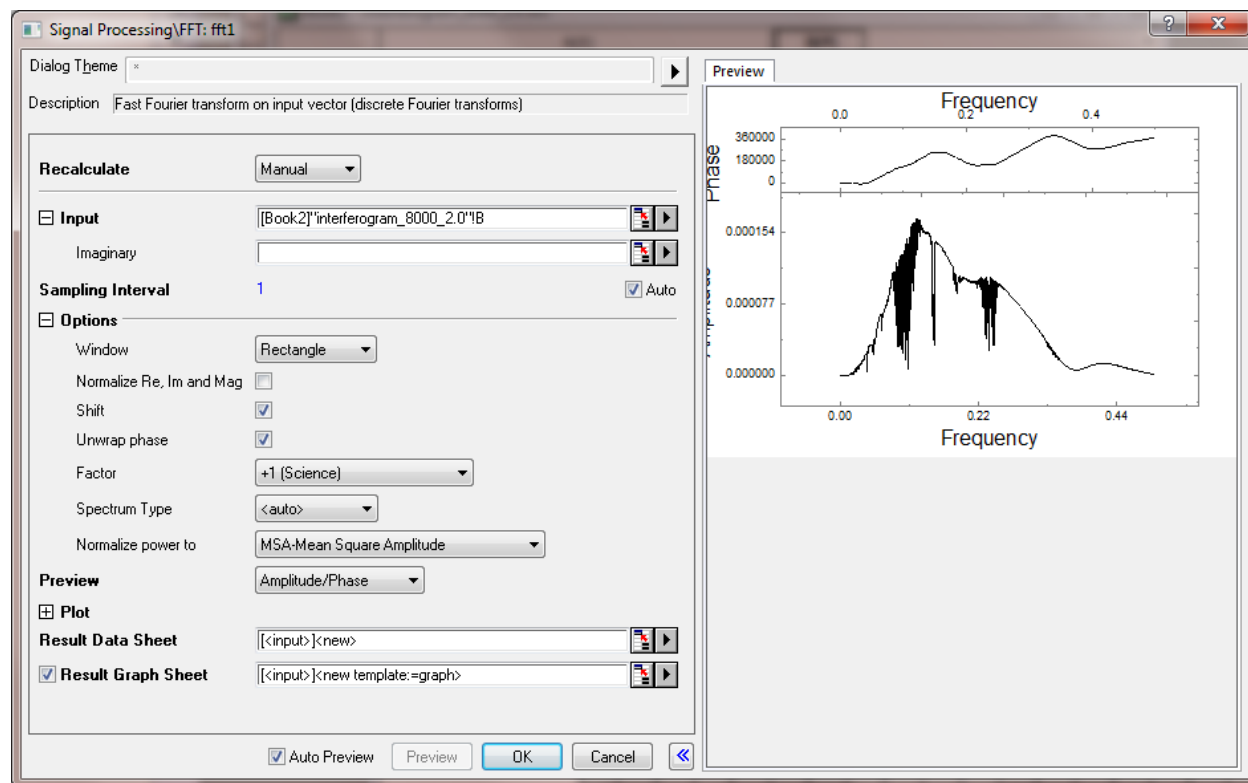


Fig. 7: FFT dialog of Origin 9

The option “Window” allows to select the apodisation function. With the default values, the output spectrum is given in dependency on the frequency in the range from -0.5 to 0.5 and it is mirror symmetric around 0. The region of negative frequencies can be neglected.

The option “Sampling interval” allows to set a value for the distance between two points. For the default value of 1, the obtained frequency corresponds to the reciprocal point distance, i.e. the maximum frequency of 0.5 corresponds to a periodicity of 2 data points. Thus, the step size of the interferometer can be obtained by dividing the frequency of a certain spectral feature in the spectrum transformed using Origin by the actual position of the same feature in the spectra transformed by the measuring software. By entering the obtained point distance (in cm) under the option “Sampling interval”, the frequency scale becomes identical to the wave number scale.

Origin not only gives the real and imaginary part of the Fourier transform, but also other values which can be calculated from that. These include phase and amplitude. The amplitude is equivalent to the phase-corrected spectrum according to the Mertz method and thus should be used to analyze the spectra.

Remarks to task 1.5:

Determine the named parameters for the two isotopes of chlorine individually by investigating the respective absorption lines of one isotope independent from those of the other. Compare the results to the theoretically expectations for the different isotopes.

Remarks to task 1.6:

In order to model the intensity relations of the double band of HCl, the absorption coefficient of equation (59) shall be used. The prefactor c_4 as a free parameter needs to be varied such that the intensities are

reproduced well. As a prerequisite, the spectrum must be corrected for the background, i.e. it must be divided by it. The following procedure is suggested to obtain the background in origin: Plot the spectrum and use the mask function of Origin to mask only the peaks of the double band. Then, apply the interpolation function to the partially masked spectrum. The point density should be identical to the original spectrum. The use of the B-spline method with a smoothing factor of 10 is suggested, but also the linear method yields reasonable results. After unmasking all points, the division of the spectrum by this background yields the corrected spectrum.

Wave numbers of the calibration bands:

Water vapor / ν [cm ⁻¹]	Polystyrene / ν [cm ⁻¹]
1416,08	699,45
1601,20	756,58
1792,65	842,0
1799,61	906,8
1802,47	965,7
1807,70	1028,3
1810,62	1069,1
1807,70	1154,6
1810,62	1368,5
2018,32	1449,7
2041,3	1542,2
	1583,1
	1583,1
	1601,4
	1803,8
	1945,2
	2850,0
	2920,9
	3001,4
	3026,4
	3060,0
	3082,2

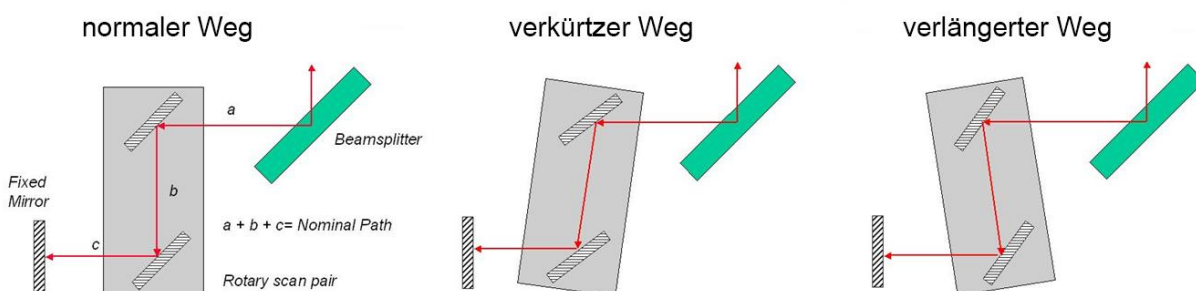
Quelle: D. Gupta, L. Wang, L. M. Hanssen, J. J. Hsia, and R. U. Datla: „Polysterene Films for Calibrating the Wavelength Scale of Infrared Spectrophotometers – SRM 1921”, NIST Special Publication 260-122 (1995)

5. **Literature**

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- [2] W. Brügel: Einführung in die Ultrarotspektroskopie, Dr. Dietrich Steinkopff Verlag, Darmstadt 1969, S. 9-27
- [3] Herzberg, Molecular Spectra and Molecular Structure, Bd. I (Spectra of Diatomic Molecules), D. van Nostrand Comp., Toronto, New York, London 1950
- [4] D. Geschke: Physikalisches Praktikum, B. G. Teubner, Stuttgart, Leipzig 1994
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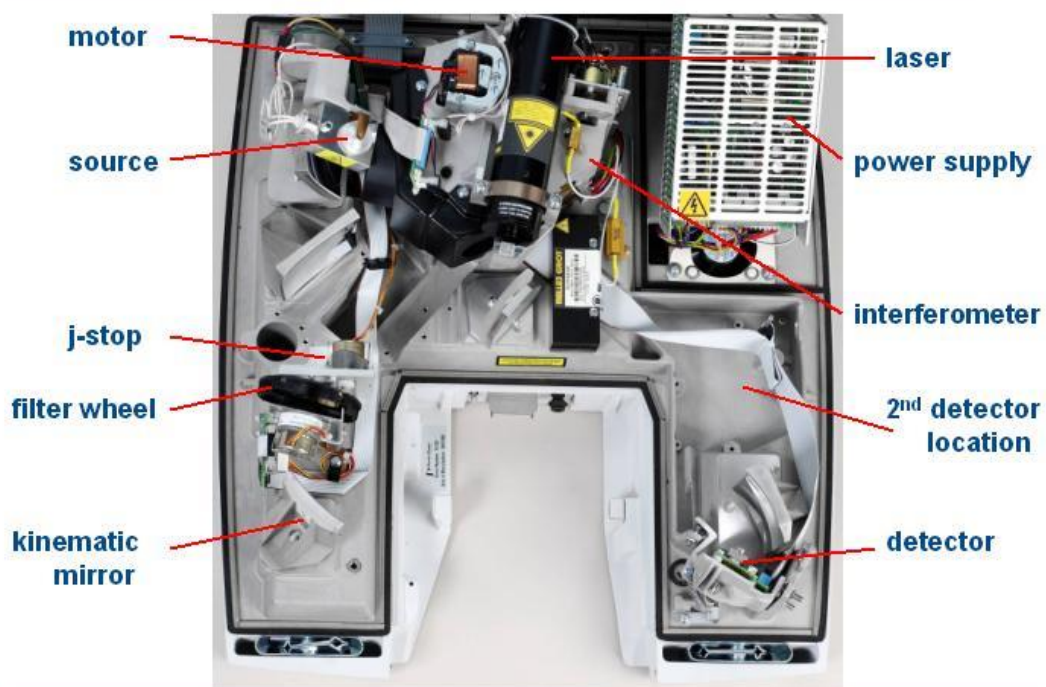
FTIR spectrometer PerkinElmer Spectrum 100

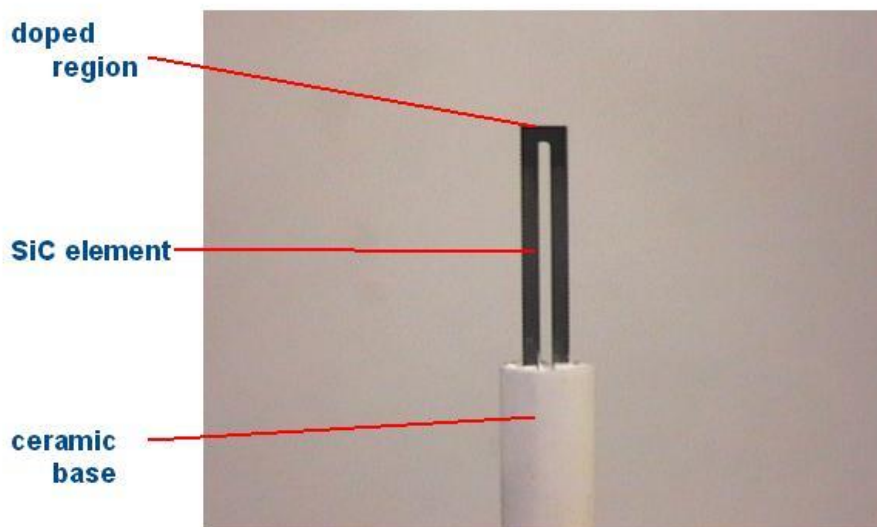
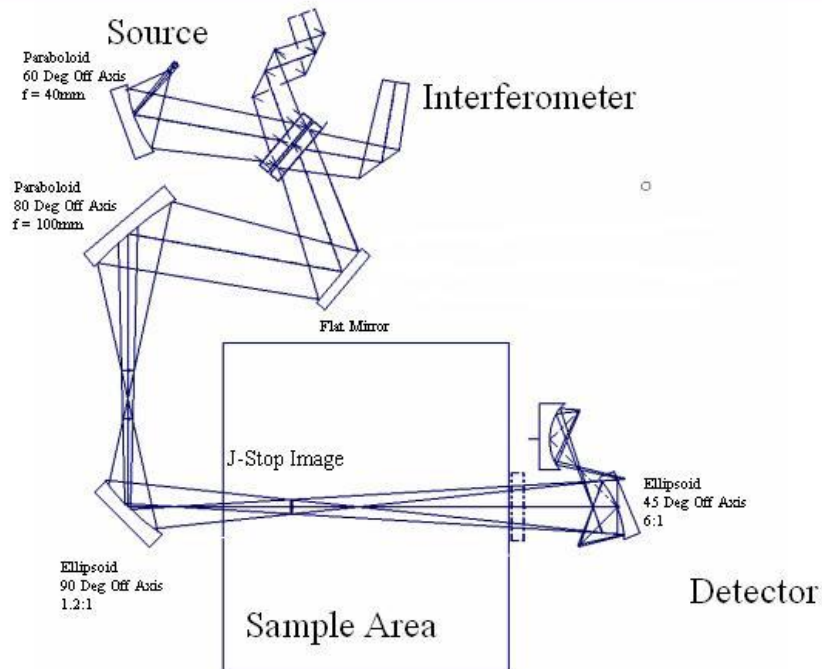
The measurements are carried out using the spectrometer model Spectrum 100 of the manufacturer PerkinElmer. This is based on a modified Michelson interferometer, which is primarily due to the compact design of device. Instead of a translating mirror, a mirror pair is used together with a fixed mirror. By the rotation of the mirror pair around a common axis, the beam path between the beam splitter and the fixed mirror is changed. The path difference is determined based on the interferences of a HeNe laser, which is also coupled into the spectrometer.



A so-called "glowbar" (alternatively "globar" or "Norton source") is used as light source. This is a U-shaped bar made from doped SiC, which is heated by a current flow. It approximately emits a black body spectrum with a maximum in the mid infrared.

Spectrum 100 Interior





A Appendix: Fourier Transform Infrared Spectroscopy

(taken from the script "FTIR Spectroscopy of Solids")

The basic principles of FTIR spectroscopy were found more than 100 years ago. In 1891, A. A. Michelson (1852–1931) developed the Michelson interferometer [3] and at the beginning of the 20th century, Lorg Rayleigh (1842–1919) recognized that the spectrum can be calculated from the interferogram using Fourier transformation[5]. However, it lasted some decades until FTIR spectroscopy was used in practice, particularly due to the necessary extensive calculations. It was not before the 1950s that the FTIR spectroscopy was rediscovered. Since the development of computers, it then has become widely used and is a standard measuring technique nowadays.

A.1 Infrarot-Spektroskopie

The infrared spectral region covers the wavelength range from 0.76 μm to 1000 μm , which can be subdivided into three parts:

- Near infrared (NIR), wavelength range 0.76 μm ... 2.5 μm ,
- Mid infrared (MIR), 2.5 μm ... 50 μm ,
- Far infrared (FIR), 50 μm ... 1000 μm .

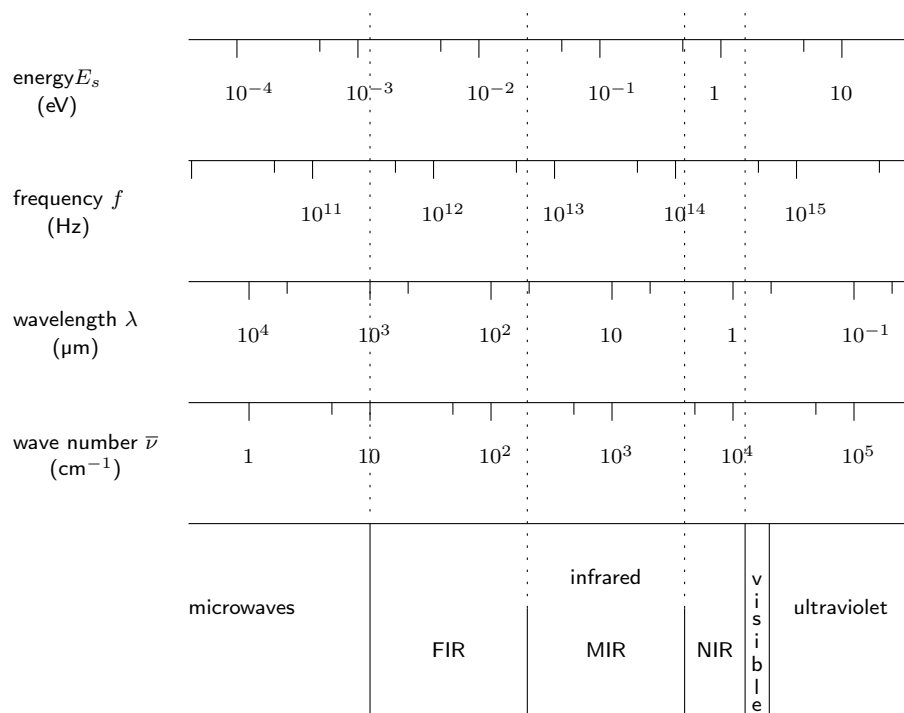


Figure 1: Overview of a part of the electromagnetic spectrum

Figure 1 shows the infrared spectral region within the electromagnetic spectrum. The wavelength λ , the wave number $\bar{\nu}$, the frequency f and the photon energy E_s of the respective photons are given in the figure. These quantities are related to each other by:

$$\bar{\nu} = \frac{1}{\lambda}, \quad c = f \cdot \lambda \quad \text{and} \quad E_s = h \cdot f \quad (1)$$

Here, $c = 299\,792\,458 \text{ m s}^{-1}$ is the speed of light in vacuum and $h = 6.626076 \cdot 10^{-34} \text{ J s}$ is Planck's constant. In the following, the wave number unit is used to characterize the infrared radiation.

A.2 Basics of FTIR spectroscopy

A.2.1 The FTIR spectrometer

An FTIR spectrometer consists of a radiation source, an interferometer unit and a detector. The interferometer unit is typically a Michelson-type interferometer which is drawn schematically in Fig. 2.

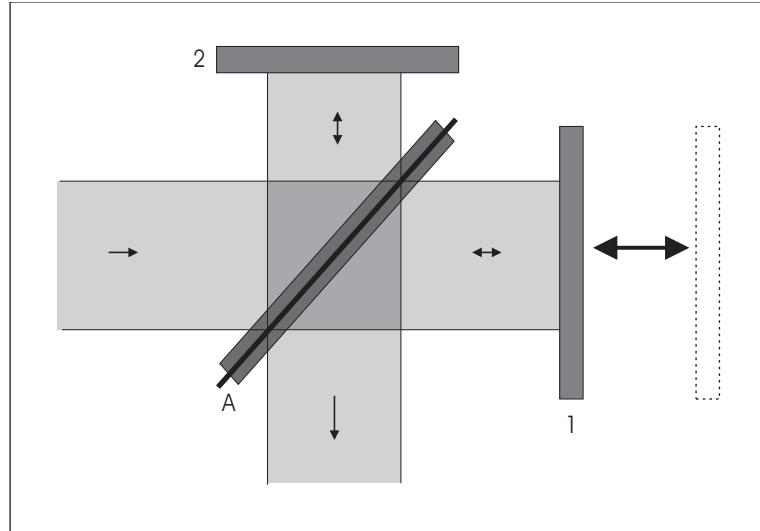


Figure 2: Schematic drawing of the Michelson interferometer.

The radiation, which is emitted by the radiation source, is divided into two beams by a beam splitter (A). These beams are reflected by a movable (1) and a fixed (2) mirror, respectively. After the two beams passed the variable and the fixed optical path x_1 and x_2 , respectively, they are united again by (A), where they interfere. The united beam passes the sample and illuminates the detector, which measures the intensity $I(x)$ of the radiation in dependence on the path difference x :

$$x = x_2 - x_1 \quad (2)$$

The function $I(x)$ is called interferogram. The intensity spectrum $S(\bar{\nu})$ is calculated from the interferogram by Fourier transformation.

In the case of a Michelson interferometer, only the optical path x_1 is varied by the position of the movable mirror (1). Other interferometer setups allow to vary both x_1 and x_2 . The general setup can be represented schematically as in Fig. 3.

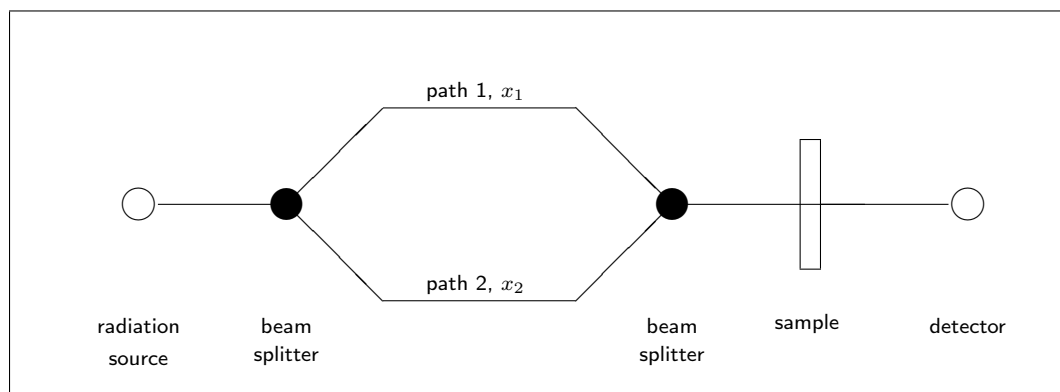


Figure 3: Schematic setup of an FTIR spectrometer.

A.2.2 The Fourier transformation

Das Interferogramm

The IR spectrum can be considered as being composed of an infinite number of monochromatic waves. Thus, for simplicity, the interferogram of a single monochromatic light wave is considered at first. The electric field strength of a plane, linearly polarized, monochromatic light wave, which propagates in z -direction, is given by

$$E(z, t) = E_0 \exp [2\pi(\bar{\nu}z - ft)i] \quad (3)$$

where E_0 is the amplitude, $\bar{\nu}$ the wave number and f the frequency. This wave is split into two partial waves $E_1(z, t)$ and $E_2(z, t)$ at the beam splitter. After passing the optical paths x_1 or x_2 , the two partial waves interfere:

$$E'(z, t) = E_1(z + x, t) + E_2(z, t) \quad (4)$$

Here, x is the optical path difference defined by Eq. (2). The intensity of a wave is proportional to the square of its magnitude:

$$I' = |E'|^2 = |E_1 + E_2|^2 = I_1 + I_2 + 2\sqrt{I_1 I_2} \cdot \cos(2\pi\bar{\nu}x) . \quad (5)$$

The terms I_1 and I_2 are constant and can be neglected in the Fourier transformation because the Fourier transform of a constant yields only contributions with a frequency of zero. The intensity spectrum is thus defined as $S(\bar{\nu}) = \sqrt{I_1 I_2}$, by which the interferogram of a monochromatic wave can be written as

$$I(x) = 2S(\bar{\nu}) \cdot \cos(2\pi\bar{\nu}x) . \quad (6)$$

Such an interferogram of a monochromatic wave is plotted in Fig. 4a. The interferogram of n monochromatic waves is the sum of the interferograms $I_k(x)$ ($k = 0, 1, \dots, n-1$) of the monochromatic waves:

$$I(x) = 2 \sum_{k=0}^{n-1} S(\bar{\nu}_k) \cos(2\pi\bar{\nu}_k x) . \quad (7)$$

Fig. 4b shows an exemplary interferogram of three monochromatic waves.

The interferogram of a continuous spectrum is obtained by replacing the sum in Eq. (7) by an integral:

$$I(x) = 2 \int_0^{\infty} S(\bar{\nu}) \cos(2\pi\bar{\nu}x) d\bar{\nu} . \quad (8)$$

The interferograms of a spectrum with Lorentzian line shape and of an infrared radiation source are shown in Figs. 4c and d, respectively. The calculated interferograms $I(x)$ are plotted for $x \geq 0$ because they are symmetric with respect to $x = 0$.

Fourier transformation

In order to calculate the intensity spectrum from an interferogram, Eq. (8) must be inverted, which is done by Fourier transformation. Before this can be carried out, Eq. (8) has to be generalized first.

1. The region of integration must be extended from $[0, \infty]$ to $[-\infty, \infty]$. This is done by setting $S(-\bar{\nu}) = S(\bar{\nu})$, which changes the form of Eq. (8) to

$$I(x) = \int_{-\infty}^{\infty} S(\bar{\nu}) \cos(2\pi\bar{\nu}x) d\bar{\nu} . \quad (9)$$

2. The cosine terms are generalized by Euler's equation: $\exp(iz) = \cos(z) + i \cdot \sin(z)$. By that, $I(x)$ is written as

$$I(x) = \int_{-\infty}^{\infty} S(\bar{\nu}) \exp(2\pi\bar{\nu}xi) d\bar{\nu} . \quad (10)$$

The additionally introduced sine terms cancel out each other because of the mirror symmetry of $S(\bar{\nu})$ around 0: $\int_{-\infty}^{\infty} \sin(x) dx = \lim_{a \rightarrow \infty} \int_{-a}^a \sin(x) dx = \lim_{a \rightarrow \infty} (\cos(a) - \cos(-a)) = 0$.

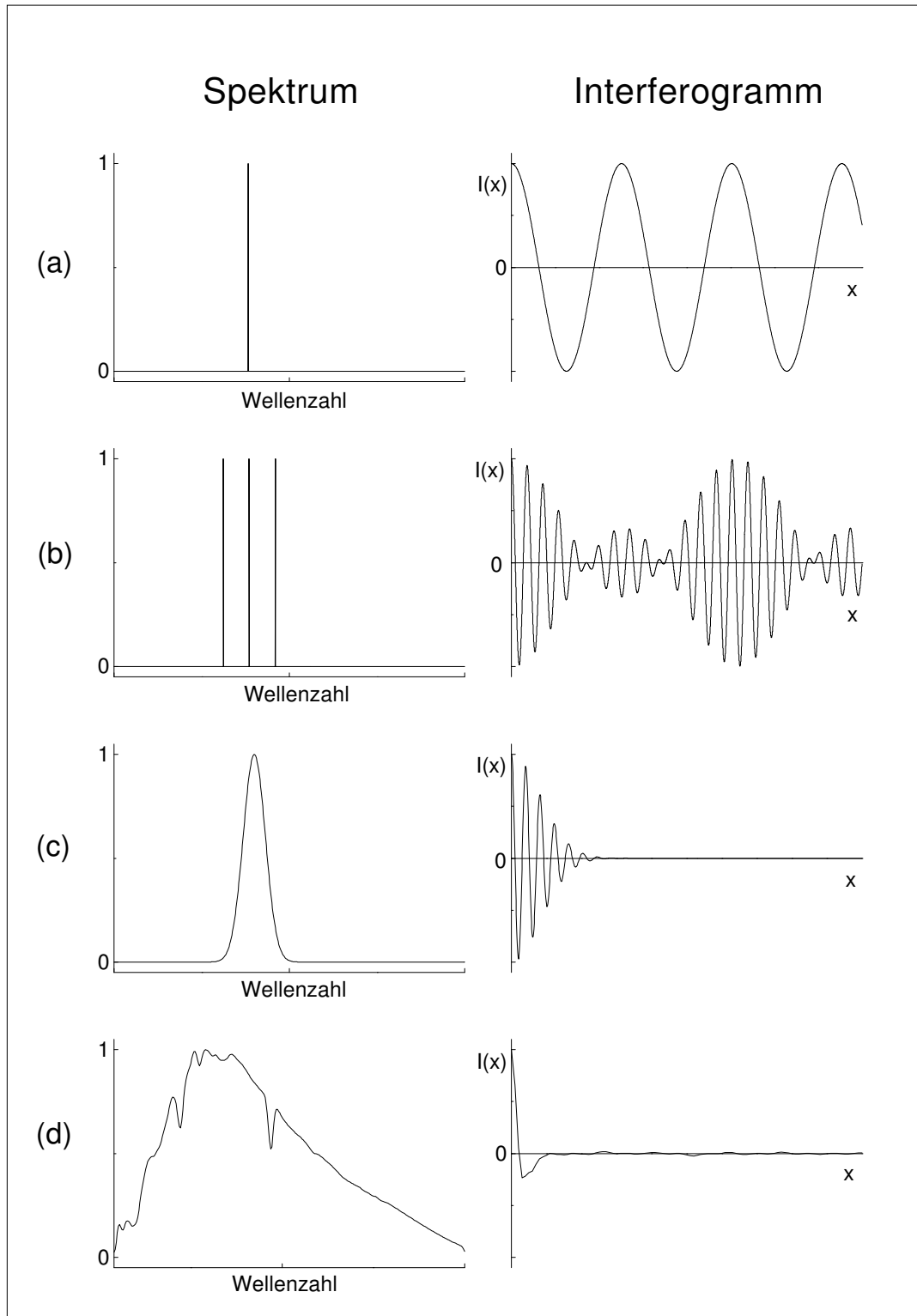


Figure 4: Selected spectra and corresponding interferograms.

The integral in Eq. (10) corresponds to the inverse Fourier transform of the spectrum $S(\bar{\nu})$ [1]. Therefore, $S(\bar{\nu})$ is the Fourier transform of the interferogram $I(x)$:

$$S(\bar{\nu}) = \int_{-\infty}^{\infty} I(x) \exp(-2\pi i \bar{\nu} x) dx . \quad (11)$$

In principle, this equation allows the spectrum calculation from the interferogram. However, it demands that the interferogram covers an infinite range and is continuous. However, the measured interferogram is in general discrete and limited. Therefore, additional steps have to be performed as outlined in the following section.

A.2.3 Practical implementation of the Fourier transformation

Digitalisierte Form der Fouriertransformation

The measured interferogram is digitized and finite with n measuring points in the range $k' \cdot \Delta x$ ($k' = 0, 1, \dots, n-1$) with a fixed spacing Δx . Therefore, the discrete form of the Fourier transformation has to be used instead of Eq. (11) [4]:

$$S(k \cdot \Delta \bar{\nu}) = \sum_{k'=0}^{n-1} I(k' \cdot \Delta x) \exp\left(-2\pi \frac{k'k}{n}\right) \quad k = 0, 1, \dots, n-1. \quad (12)$$

The result of Eq. 12 is a symmetric spectrum with n discrete spectral points with a fixed spacing $\Delta \bar{\nu}$. The maximal wave number $\bar{\nu}_{max}$ is related to Δx by

$$\bar{\nu}_{max} \leq \frac{n \cdot \Delta \bar{\nu}}{2} \quad (13)$$

The spacing between the individual spectral points

$$\Delta x \leq \frac{1}{2\bar{\nu}_{max}}, \quad (14)$$

which can be rewritten using Eq. 13 as follows:

$$\Delta \bar{\nu} = \frac{1}{n \Delta x}. \quad (15)$$

In practice, Eq. 12 is commonly solved with the Fast Fourier Transformation (FFT) approach, which considerably reduces the time needed for the calculation. For further details on the FFT approach, see e.g. [2], [1]

Procedure of calculating a spectrum

The following steps are needed for the calculation of a spectrum from a measured interferogram

1. Apodization (see Sect. A.3.2)
The measured interferogram is finite and breaks off abruptly at its ends. As a result, the line shape of the calculated spectrum is subsumed by interference-like structures. This effect is called leakage effect and can be reduced by apodization, for which the interferogram is multiplied by an appropriate function.
2. Zerofilling (see Sect. A.3.3)
The interferogram is expanded by attaching zeros, which increases the density of data points in the calculated spectrum.
3. Fourier transformation (see Eq. (12))
4. Phase correction (siehe Sect. A.3.4)
In general, the measured interferogram is non-symmetric, i.e. it is not measured with the same range on both sides from the zero point. In consequence of that, the result of the Fourier transformation is a complex-valued spectrum $\underline{S}(\bar{\nu})$. With the help of the phase correction, the real-valued spectrum $S(\bar{\nu})$ is calculated.
5. Division by a reference spectrum
The last step is the division of the spectrum $S(\bar{\nu})$ by a reference spectrum which is obtained from a measurement without a sample and represents the intensity spectrum of the unblocked light beam.

A.3 Advanced aspects of the Fourier transformation

The following section is based on the elaborations in Ref. [4].

A.3.1 Auflösungsvermögen

An important parameter of a spectrometer is its spectral resolution. Typically, the Rayleigh criterion is used for the determination of the resolution. Hereby, two monochromatic spectral lines with wave numbers $\bar{\nu}_1$ and $\bar{\nu}_2$, respectively, are considered. As simplification it is assumed that the intensities of both waves are equal.: $S(\bar{\nu}_1) = S(\bar{\nu}_2)$. Then, from Eq. (7) follows:

$$\begin{aligned} I_1(x) + I_2(x) &= S(\bar{\nu}_1) (\cos(2\pi\bar{\nu}_1 x) + \cos(2\pi\bar{\nu}_2 x)) \\ &= 2 S(\bar{\nu}_1) \cos\left(2\pi \frac{\bar{\nu}_1 + \bar{\nu}_2}{2} x\right) \cos\left(2\pi \frac{\bar{\nu}_1 - \bar{\nu}_2}{2} x\right). \end{aligned}$$

Figure 5 shows the interferogram of two such spectral lines (solid line) and its envelope (dashed line). The period of the envelope curve is $(\bar{\nu}_1 - \bar{\nu}_2)/2 = \Delta\bar{\nu}/2$.

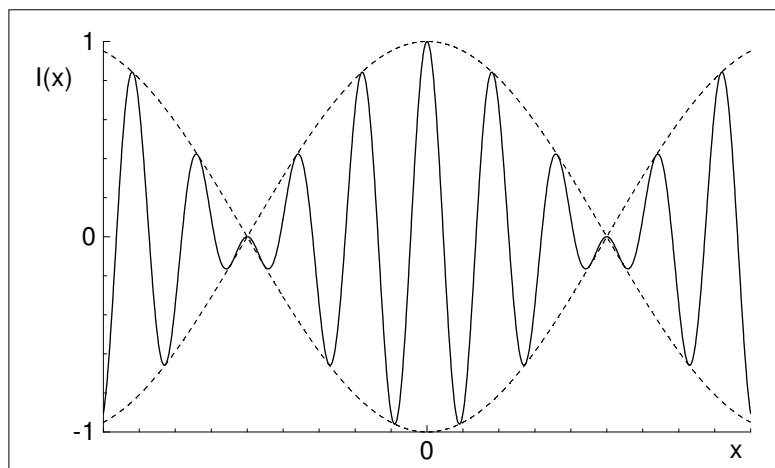


Figure 5: *Interferogram of two monochromatic waves*

In order to resolve two neighboring spectral lines with a wave number difference $\delta\bar{\nu}$, the beating shown in Fig. 5 has to be recorded. Due to the symmetry of the interferogram, it is sufficient to measure the interferogram in the interval $x = 0$ to $x = 1/\Delta\bar{\nu}$.

A high resolution means that a small $\Delta\bar{\nu}$ must be detectable. A smaller $\Delta\bar{\nu}$ corresponds to a wider beating. Consequently, increasing the resolution requires to measure the interferogram over a longer optical path difference x . Because the data points of the interferogram are recorded with a constant spacing Δx , the resolution is increased by increasing the number n of the measured data points. Figure 6 shows an interferogram which corresponds to a spectral resolution of 4 cm^{-1} . Eine höhere Auflösung bedeutet, dass $\Delta\bar{\nu}$ kleiner und die Schwebung breiter wird. Das Interferogramm muss demnach über eine größere optische Wegdifferenz x gemessen werden, um ein höheres Auflösungsvermögen zu erreichen. Bei digitalen Messpunkten mit konstantem Abstand Δx entspricht das einer Erhöhung der Anzahl n der gemessenen Datenpunkte des Interferogramms. Abbildung 6 stellt ein mit dem IFS 48 gemessenes Interferogramm dar, dass einer Auflösung von 4 cm^{-1} entspricht. From this interferogram, spectra with different spectral resolutions were calculated by a reduction of the data points n used in the Fourier transformation. These spectra are shown in Fig. 7.

A.3.2 Leakage effect und apodization

The result of the measurement is an interferogram $I(x)$ of finite length $l = n \cdot \Delta x$. Due to the abrupt cut-off of the measured interferogram, the calculated spectra is subsumed by interference-like structures. This effect is called 'leakage effect',

The leakage effect

The measured interferogram $I(x)$ of finite length may be described as a product of an interferogram of infinite length $I_\infty(x)$ and a rectangle function $A_R(x)$ with the value 1 in the interval $[0, l]$ and the value 0 elsewhere. With that, Eq. 11 reads

$$S(\bar{\nu}) = \int_{-\infty}^{\infty} I_\infty(x) A_R(x) \exp(-i2\pi\bar{\nu}x) dx$$

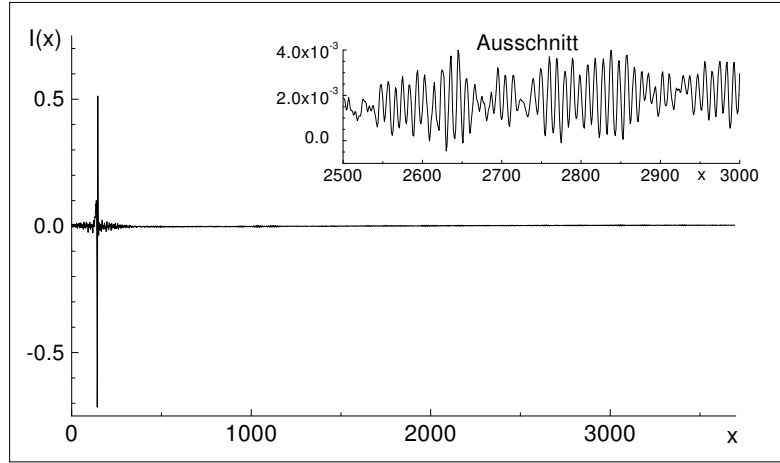


Figure 6: Interferogram corresponding to the spectrum with a resolution of 4 cm^{-1} shown in Fig. 7. The number of data points is $n=3696$.

According to the convolution theorem of the Fourier analysis, the Fourier transform of a product of two functions is equal to the convolution integral of the Fourier transforms of these two functions [1]. This convolution integral is given by:

$$S(\bar{\nu}) = \int_{-\infty}^{\infty} S_{\infty}(y) \tilde{A}_R(\bar{\nu} - y) dy . \quad (16)$$

Here, $S_{\infty}(\bar{\nu})$ and $\tilde{A}_R(\bar{\nu} - y)$ are the Fourier transforms of $I_{\infty}(x)$ and $A_R(x)$, respectively. The Fourier transform of the rectangle function is

$$\tilde{A}_R(\bar{\nu}) = \int_{-\infty}^{\infty} A_R(x) \exp(-i2\pi\bar{\nu}x) dx = l \frac{\sin(2\pi\bar{\nu}l)}{2\pi\bar{\nu}l} . \quad (17)$$

It is plotted in Fig. 8. Besides the principle maximum at $x = 0$, a lot of subsidiary maxima (so-called 'feet') can be seen. Figure 9 illustrates the effect exemplarily for a duplet (due to the Cl isotopes) of the HCl spectrum. The spectrum appears to be superimposed by interference-like structures which are caused by the leakage effect and do not belong to the actual spectrum.

Minimizing the leakage effect by apodization

The leakage effect can be reduced by apodization (from Greek $\alpha\pi\omicron\delta$ (apod): remove feet), which means that the measured, finite interferogram is multiplied by an appropriate function — the apodization function. It has to be chosen such that it yields smaller subsidiary maxima than the Fourier transform of the rectangle function. Consequently, the 'feet' in the calculated spectrum are suppressed.

Selected apodization functions and their Fourier transforms are plotted in Fig. 10. The functions are ordered based on the suppression of the 'feet' from worst (top) to best (bottom). It can also be seen that with increasing suppression of the feet, the height of the principle maximum of the Fourier transforms at $x = 0$ decreases while its FWHM (full width at half maximum) increases. The FWHM values, the height of the principle maximum of the Fourier transforms and the height and depth of the strongest subsidiary maximum and minimum are summarized in Tab. 1 for the different apodization functions.

The above described properties of the Fourier transform of the different apodization functions are transferred to the calculated intensity spectra as shown in Fig. 11 for the example of the HCl spectrum from Fig. 9. From the rectangle to the Blackman-3-term function (from left to right in Fig. 11), the interference structures become smaller. At the same time, the line broadening increases, which corresponds to a reduction of the spectral resolution.

In summary, apodization reduces the interference-like structures caused by the leakage effect, but also reduces the spectral resolution. Thus, the choice of the apodization function is always a trade-off between these two aspects.

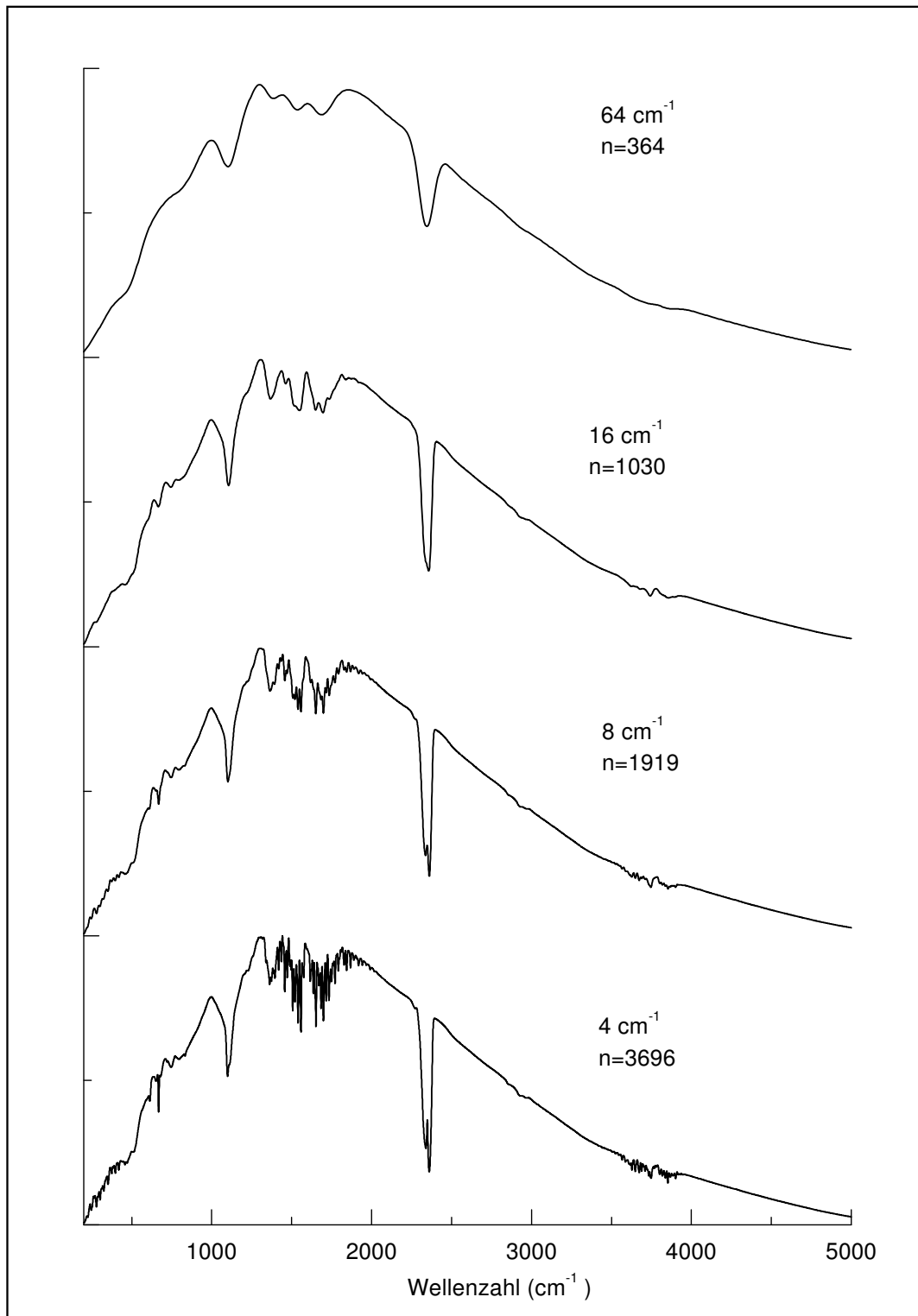


Figure 7: Intensity spectrum of a glowbar light source with different spectral resolutions. The resolution and the number n of data points of the interferogram used for the Fourier transformation are given next to the spectra. The spectra are shifted vertically for clarity.

A.3.3 Picket fence effect and zerofilling

The calculated spectrum is discrete. Therefore, it can happen that a peak in the spectrum is not visible because its maximum is located exactly between two calculated spectral points so the peak will be cut off. This effect

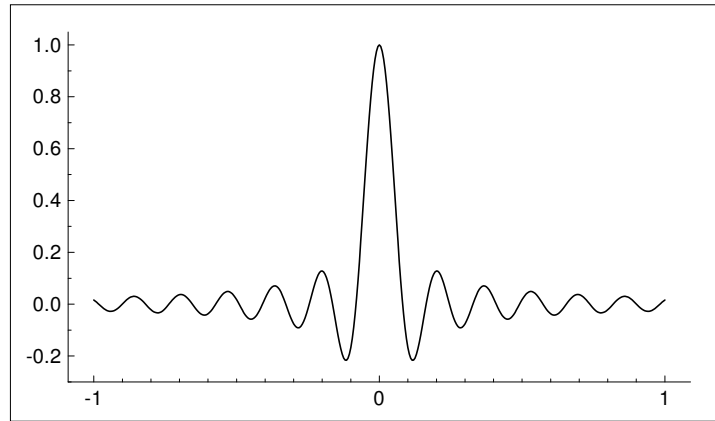


Figure 8: *Fourier transform of the rectangle function*

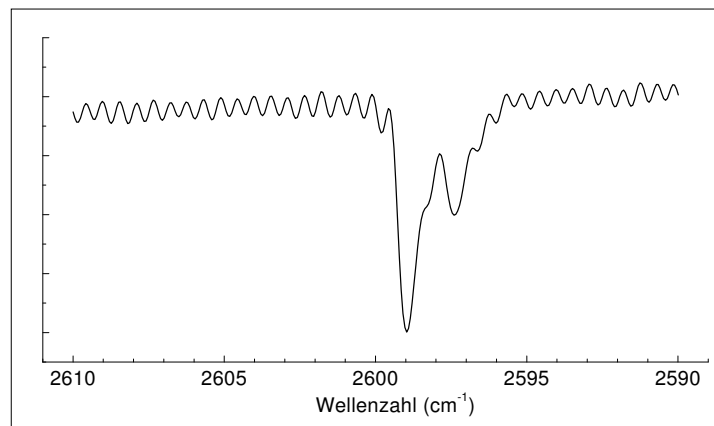


Figure 9: *Illustration of the leakage effect. The interference-like structures subsume the duplet structure in the HCl spectrum.*

apodization function	FWHM	Height of the maximum	Magnitude of the strongest subsidiary maximum	subsidary minimum
rectangle	1	1	0,128	-0,215
trapeze	1,28	0,75	0,023	-0,110
triangle	1,47	0,50	0,024	0,000
Happ-Genzel	1,50	0,54	0,004	-0,004
Blackman 3-Term	1,85	0,43	$1 \cdot 10^{-4}$	$-1 \cdot 10^{-4}$

Table 1: *Characteristic data of the Fourier transforms of selected apodization functions. All data are normalized to the intensity of the principle peak in the interferogram of the rectangle function.*

is called picket fence effect. To avoid this effect, a kind of extrapolation called zerofilling is used. Zerofilling means that the number of data points of the interferogram, which is used for the Fourier transformation, is enlarged by adding zeros. Consequently, the density of calculated data points in the spectrum is increased according to Eq. (15).

Figure 12 shows the effect of zerofilling exemplarily for the duplet in the HCl spectrum from above. The zerofill factor is increased from left to right and with that the density of spectral points is increased as well. The zerofilling factor is the ratio of the length of the interferogram used for the Fourier transformation and the length of the measured interferogram. The first graph in Fig. 12 already indicates the splitting of the duplet structure, but the maxima are cut off and the line shape is distorted. As the zerofill factor increases, the splitting of the double peak becomes more obvious and the spectrum gets smoothed.

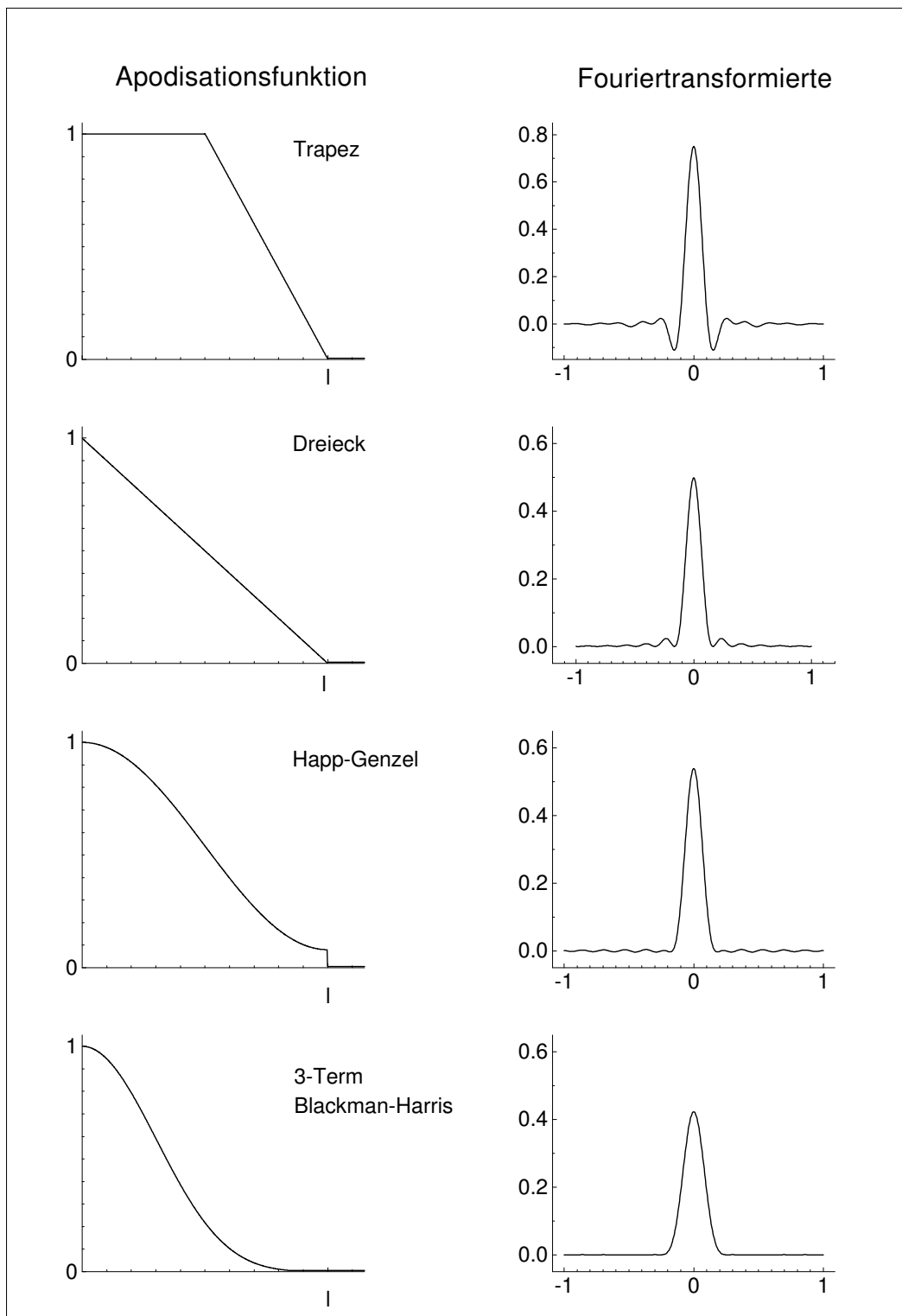


Figure 10: *Selected apodization functions and their Fourier transforms.*

Note that zero-filling does not increase the resolution because the added zeros do not contain any further information. Zero-filling is only used for extrapolation purposes.

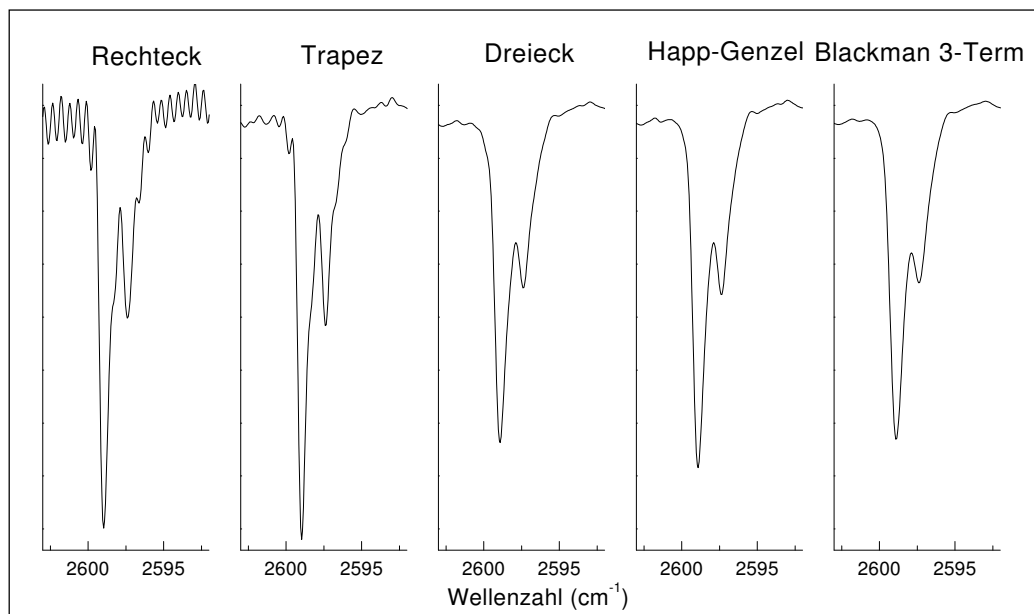


Figure 11: Einfluss der Apodisation auf eine Linie des HCl-Spektrums

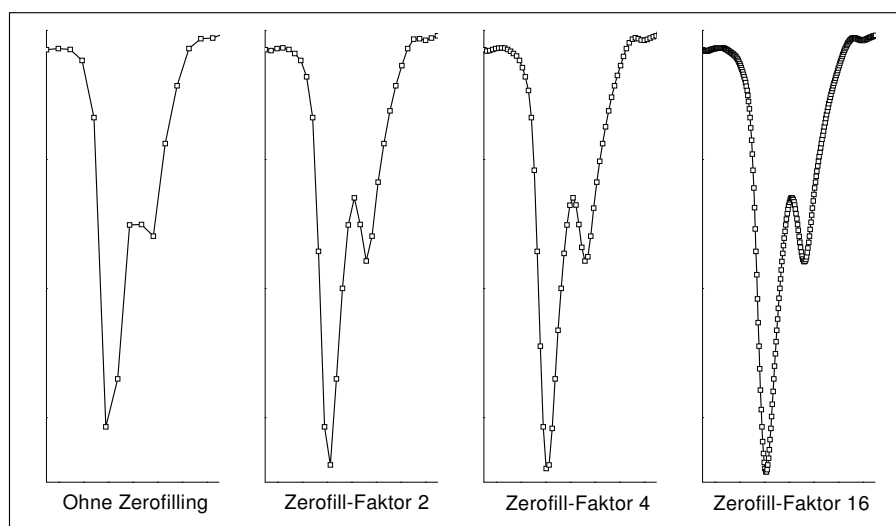


Figure 12: Influence of the zerofill factor on the calculated spectra. By increasing the zerofill factor, the number of data points (indicated by circles) in the spectrum increases.

A.3.4 Phase correction

If the measured interferogram is not symmetric with respect to $x = 0$, the Fourier transformation yields a complex spectrum $\underline{S}(\bar{\nu})$. Thus, the last step for the calculation of the spectrum is the calculation of the real spectrum $S(\bar{\nu})$. This step is called phase correction.

Ursachen des komplexen Spektrums

The measured interferogram is in general not symmetric with respect to $x = 0$ because:

- No measured interferogram point coincides with the central maximum of the interferogram at $x = 0$. The related phase shift may depend also on the wavelength.
- Only one side of the interferogram (with regard to $x = 0$) is measured, or one of the two sides is measured only for a short distance.

Phase correction

The calculated complex-valued spectrum $\underline{S}(\bar{\nu})$ can be written as a sum of a real and an imaginary part

$$\underline{S}(\bar{\nu}) = S_1(\bar{\nu}) + i \cdot S_2(\bar{\nu}) \quad (18)$$

or as a product of the real-valued spectrum and a $S(\bar{\nu})$ and a phase factor $\exp(i\phi(\bar{\nu}))$:

$$\underline{S}(\bar{\nu}) = S(\bar{\nu}) \cdot \exp(i\phi(\bar{\nu})) \quad \text{mit} \quad \tan(\phi(\bar{\nu})) = S_1(\bar{\nu})/S_2(\bar{\nu}) \quad (19)$$

From Eqs. (18) and (19), two methods to calculate $S(\bar{\nu})$ can be derived:

- Power spectrum method

$$S(\bar{\nu}) = |\underline{S}(\bar{\nu})| = \sqrt{S_1(\bar{\nu})^2 + S_2(\bar{\nu})^2}, \quad (20)$$

- Mertz method

$$S(\bar{\nu}) = \underline{S}(\bar{\nu}) \cdot \exp(-i\phi(\bar{\nu})). \quad (21)$$

In the case that the spectrum is positive definite, both methods will give the same result. If the spectrum contains negative values, e.g. due to noise, Eq. 20 disregards the sign. Therefore, the Mertz method should be preferred. This method will be explained in more detail below.

Mertz method

The Mertz method consists of two steps:

1st step: Calculation of the phase spectrum

The measured interferogram $I(x)$ (see e.g. Fig. 6) is shortened in such a way that both sides around the central maximum are equally long. The shortened interferogram $I'(x)$ is multiplied by an appropriate apodization function and is then enlarged by zerofilling. From that, the spectrum $\underline{S}'(\bar{\nu}) = S'_1(\bar{\nu}) + i \cdot S'_2(\bar{\nu})$ and the corresponding phase spectrum $\phi'(\bar{\nu}) = \arctan(S'_2(\bar{\nu})/S'_1(\bar{\nu}))$ are calculated. Because the shortened interferogram $I'(x)$ is used, $\phi'(\bar{\nu})$ has a decreased resolution. The missing data points are interpolated in order to get $\phi(\bar{\nu})$.

2nd step: Calculation of the phase-corrected spectrum

The calculated complex spectrum $\underline{S}(\bar{\nu})$ is multiplied by the complex inverse of the phase factor $\exp(-i\phi(\bar{\nu}))$.

$$\begin{aligned} \underline{S}(\bar{\nu}) \cdot \exp(-i\phi(\bar{\nu})) &= [S_1(\bar{\nu}) + i \cdot S_2(\bar{\nu})] \cdot [\cos(\phi(\bar{\nu})) - i \cdot \sin(\phi(\bar{\nu}))] \\ &= [S_1(\bar{\nu}) \cos(\phi(\bar{\nu})) + S_2(\bar{\nu}) \sin(\phi(\bar{\nu}))] \\ &\quad + i \cdot [S_1(\bar{\nu}) \sin(\phi(\bar{\nu})) - S_2(\bar{\nu}) \cos(\phi(\bar{\nu}))] \end{aligned}$$

In the ideal case, the imaginary part is zero. In practice, the imaginary part cannot be equal to zero because $\phi(\bar{\nu})$ is extrapolated from $\phi'(\bar{\nu})$. However, the imaginary part is so small that it can be neglected. Therefore, the real-valued spectrum is obtained by:

$$S(\bar{\nu}) = S_1(\bar{\nu}) \cos(\phi(\bar{\nu})) + S_2(\bar{\nu}) \sin(\phi(\bar{\nu})). \quad (22)$$

A.4 Pros and cons of FTIR spectroscopy

The FTIR spectroscopy has some essential advantages in comparison to diffraction spectrometers, but the extensive mathematics involved in the calculation of spectra may also lead to problems.

Advantages

- Jaquinot (or throughput) advantage

In an FTIR spectrometer the samples are illuminated by the whole light beam. In contrast to that, diffraction-based spectrometers operate with a slit which cuts off some part of the light beam. As a consequence, the light output ratio is higher for the FTIR spectrometer than for the diffraction-based spectrometer.

- Multiplex (Fellgett) advantage
In FTIR spectroscopy, the entire spectrum of an infrared radiation source is exposed on the sample at the same time. Therefore, fluctuations affect all but not just selected parts of the spectrum.
- Connes advantage (spectral precision)
The position of the moveable mirror is determined using the interferences of a HeNe laser light beam, which travels also through the Michelson interferometer. The wavelength of the laser ($\lambda_{\text{HeNe}} = 632.8 \text{ nm}$) is exactly known and constant. Therefore, the position of the mirror is measured very precisely, resulting in a high precision of the wave numbers in the spectrum.
- Measuring time
The measuring time of an interferogram is so small that it is possible to record dynamical processes such as chemical reactions.
- Spectral resolution
The resolution of a diffraction-based spectrometer is determined, among other factors, by the slit width used. The resolution increases with smaller slits, but at the same time the radiation intensity drops. Consequently, the maximum resolution is limited. The resolution of an FTIR spectrometer is increased by extending the measuring path. Therefore, a higher resolution can be obtained with FTIR spectrometers compared to that of diffraction-based spectrometers.

Disadvantages

- Digitization
The measured interferogram and the spectrum calculated from it are digitized. Therefore, the picket fence effect can occur. This effect can be eliminated by zerofilling (see Sect. A.3.3).
- Finite length of the interferogram
The line shape of the calculated spectrum is disturbed due to the finite length of the interferogram. This effect is called leakage effect and can be reduced by apodization (see Sect. A.3.2).
- Aliasing
The measured spectral range is limited towards large wave numbers by the convolution wave number $\bar{\nu}_f$. $\bar{\nu}_f$ depends on the distance Δx of the data points of the interferogram by $\bar{\nu}_f = 1/(2 \Delta x)$. If the spectrum contains an intensity of above zero for wave numbers above $\bar{\nu}_f$, then they are mirrored back into the region below $\bar{\nu}_f$ by the Fourier transformation. This problem can be avoided by spectral filters which cut off the intensity above $\bar{\nu}_f$.
- Amount of calculation
The Fourier transformation involves a large amount of calculations, which was the main reason for the late success of the FTIR spectroscopy. Modern computers made this disadvantage irrelevant.

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