Physikalische-Chemisches Praktikum für Anfänger

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Infrared Absorption Spectroscopy of CO

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1 Objective

The rotational-vibrational spectrum of carbon monoxide (CO) using a Fourier transform infrared spectrometer (FTIR) is measured. Evaluate and interpret the spectrum and determine the resonant vibrational frequencies, rotational constants, moments of inertia and bond lengths of the CO molecule.

2 The spectroscopic method

Vibrational and rotational states of a molecule can be excited by absorption of infrared radiation. The required energy is a function of the strength of the bond between the participating atoms and of their mass. Consequently, different functional groups absorb light at different know frequencies and the resulting IR spectrum can be seen as the fingerprint of a substance.

Spectroscopic measurements examine the interaction between electromagnetic radiation and matter. The main components of an absorption spectrometer are the light source, the sample cell, the monochromator and the detector. The ratio between irradiated light I_0 and transmitted radiation I is a function of experimental parameters as given by the Lambert-Beer law:

$$E = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon(\lambda)c_J L \tag{1}$$

With: absorbance (or optical density) E, length of sample cell l, concentration of the gaseous sample c_J and the molar decadic extinction coefficient $\varepsilon(\lambda)$. The extinction coefficient is a function of the frequency ν of the irradiated light. Plotting ε vs. wavelength λ (or frequency, or wave number $\tilde{\nu}$) shows the absorption spectrum of the molecule. All following spectra are plotted vs. $\tilde{\nu}$. The general correlation of $\tilde{\nu}$, c, and ν is:
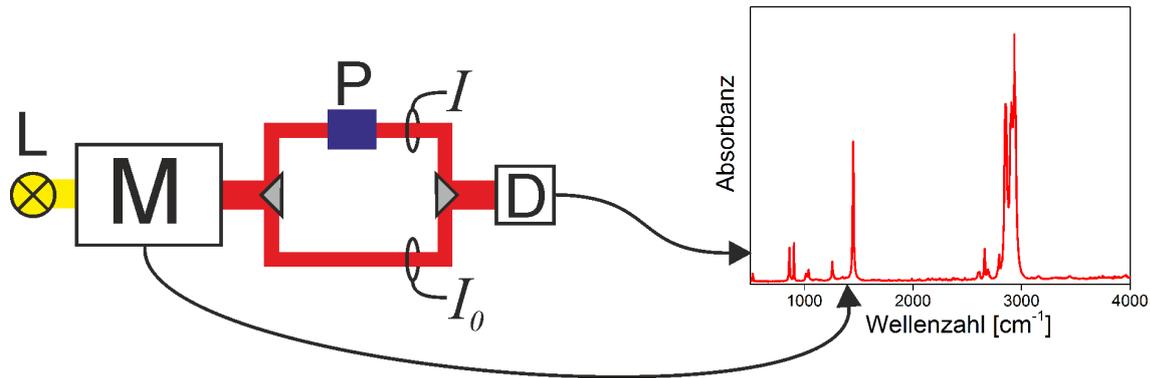
Abbildung 1: Sketch of a classical infrared spectrometer. The monochromator (M) selects the wavelength λ from the broad band light source (L) by rotating a diffraction grating in the monochromator housing. The light is then split into paths: sample beam (intensity I) and reference beam (intensity I_0). I and I_0 are measured by the detector (D). The quotient I/I_0 constitutes the y-axis of the spectrum, the position of the grating is the x-axis

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \tag{2}$$

$\tilde{\nu}$ in units of cm^{-1}.

In a classical spectrometer (not used in this experiment) spectra are recorded using a monochromator, which scans the spectrum step by step from the starting frequency to the maximum frequency. This is realized by a prism or a diffraction grating within the monochromator. The monochromatic light is then split into two beams. One passes through the sample (intensity I), the other is unaltered (intensity I_0) and serves as reference beam (cf. fig. 1). The intensity ratio I/I_0 of the beams or the absorbance $\log_{10} \frac{I_0}{I}$ is recorded by a plotter on the y-axis. The position of the diffracton grating serves as x-axis. This plot is called the *spectrum.*

Fourier-Transform-Spectroscopy

In a Fourier Transform Spectrometer all wavelengths are measured simultaneously. The monochromator is replaced by a Michelson interferometer which generates an interferogram from the light that is transmitted through the sample. In the interferometer, a light beam is split in two arms. One of the arms is reflected by a fixed mirror and one by a movable mirror, which creates a difference in the optical path length of the arms. The interferogram results from the superposition of the two arms of the light beams. All experimental information is therefore contained in the intensity, which is a function of the mirror position. The spectrum is calculated subsequently by a Fourier transformation.

Here we use Fourier transform infrared spectroscopy, which is the most advanced method of infrared spectroscopy and today the standard method. It enables the simul-
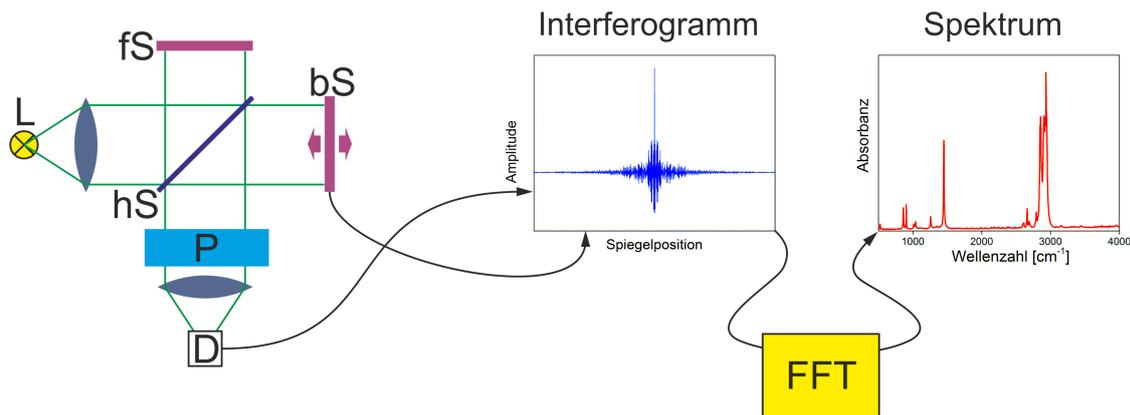
Abbildung 2: Sketch of an FTIR spectrometer used nowadays. Main component is the Michelson interferometer fed by polychromatic light. A beam splitter (hS) reflects light to a fixed mirror (fS) and transmits the other half to a movable mirror (bS). As both light beams are reflected by the fixed and the movable mirror they are superimposed and shine through the sample: an interferogram depending on wave length and mirror position is generated. Finally the interferogram is converted to the spectrum using an FFT-algorithm.

taneous measurement of all frequencies within a wide range of the IR spectrum. The principal optical part of a FTIR spectrometer is the interferometer. Figure 2 shows the diagram of an idealized Michelson interferometer.

Broadband infrared radiation is emitted by a thermal source (L) and arrives at a beam splitter (hS), which ideally reflects half of the incoming radiation while the other half passes through it. The reflected beam hits a fixed mirror (fS) after the distance L, is reflected again and arrives after a total distance of $2L$ a second time at the beam splitter. Similarly the other beam is reflected at mirror (bS), which is however not fixed. This mirror can be moved forward or backward by x along the optical axis with high precision, starting at position L. The total distance is respectively $2(L + x)$. Consequently both beams show an optical path difference of $2x$ when they are recombined at the beam splitter. This leads to interference because the beams are spatially coherent.

The beam, which is modulated by moving the mirror, exits the interferometer, passes the sample Sa and is finally focused on the detector (D). The quantity that is recorded at the detector – the interferogram – is therefore the intensity $I(x)$ of the IR radiation and depends on the deflection x of the movable mirror (bS) from the position L (cf. fig. 2)

The mathematical transformation of the interferogram on the computer – the Fourier transformation – results in the so-called *one channel spectrum*. The ratio between this spectrum and a reference recorded without sample yields a spectrum which is analogous to the conventional spectrum. This spectrum is saved digitally and is available for further analysis on a computer (cf. fig. 2).

Compared to conventional IR spectroscopy the FTIR method has the following fun-

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damental advantages:

- In conventional spectrometers the spectrum is measured directly by measuring the intensity wave number by wave number while continuously changing the monochromator settings. Depending on the spectral resolution only a very small fraction of the radiation arriving at the monochromator gets to the IR detector. In an FTIR spectrometer all emitted frequencies arrive simultaneously at the detector, which is called **multiplex advantage** or **Fellgett advantage**.

- Another advantage results from the larger areas of the circular apertures, which are used in FTIR spectrometers. They allow for an at least 6 times higher radiation throughput in comparison to the linear slits of grating setups. This advantage is called **Jacquinot advantage**.

- The duration of a measurement in FTIR spectroscopy is defined by the time needed by the mirror (bS) to move the distance required for the desired resolution. Because the mirror can be moved very quickly, complete spectra are readily available while, in contrast, measuring a conventional spectrum usually takes minutes. Furthermore, the signal to noise ratio can be improved – as good as the user needs it – by addition and averaging of multiple interferograms.

- The wave number accuracy of an FTIR spectrometer depends on the precision of the moving mirror position in the interferometer. Using a HeNe-Laser assisted interferometer this position can be determined to better than 0,000005 mm (approx. 1% of the laser wavelength). This is the reason for the very good wave number accuracy of FTIR spectrometers, which is better than $0,01\,\mathrm{cm}^{-1}$. This advantage of the FTIR method is called **Connes advantage**. Consequently, FTIR spectroscopy enables to directly compare a measured spectrum with those of a computer stored library of spectra. This ultimately opens up the wide field of computer-aided identification and interpretation under almost real time conditions.

3 Quantum mechanical treatment of vibrations and rotations

3.1 Energy states

The occurrence of discrete lines in high-resolution IR spectra cannot be explained by classical physics. The quantization of energy enables the transition between certain energy levels. As a result high-resolution spectra show no continuous band of adsorption intensity.

Infrared radiation excites the oscillation of the nuclei (but not of the electrons, because the photon energy is not large enough) in the CO molecule and at the same time also the rotation of the molecule (rotational excitation without vibrational excitation is possible, the inverse case is not). The electrons in the chemical bond act like a classic spring

between the nuclei. The plot of the potential energy of the molecule vs. the distance between the nuclei is called potential curve. The oscillation of the nuclei can be described in a first approximation as the oscillation of point masses in a harmonic potential. The following Schrödinger equation has to be solved:

$$\underbrace{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}}_{\substack{\text{operator of}\\\text{kinetic energy}}}\Psi(x) + \underbrace{\frac{1}{2}kx^2}_{\substack{\text{operator of}\\\text{potential energy}}}\Psi(x) = E\,\Psi(x) \tag{3}$$

with the force constant of the chemical bond k, the reduced mass μ (for a diatomic molecule $\frac{1}{\mu} = \frac{1}{m_O} + \frac{1}{m_C}$, m_O and m_C are the mass of the atoms O und C), the deviation from the equilibrium x. As solution of the Schrödinger equation one finds the following energ levels:

$$E_{vib}(\text{v}) = hc\tilde{\nu}_0\left(\text{v} + \frac{1}{2}\right) \quad \text{mit} \quad \text{v} = 0,\ 1,\ 2\ \dots \tag{4}$$

$$\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ ; \quad \left(\tilde{\nu}_0\ \text{in}\ \text{cm}^{-1}\right)$$

The energy levels are equidistant with a spacing of $hc\tilde{\nu}_0$ (cf. fig. 4, potential curve of the harmonic oscillator).

The rotation of a molecule takes place on a much slower timescale than the vibration; hence this motion can be described in good approximation by the rigid rotor. The relevant bond length is the average bond distance r_v of the oscillator state v. In a harmonic oscillator this bond length is independent of the quantum number v! The respective Schrödinger equation yields for the energy states of the rigid rotator:

$$E_{rot}(\text{J}) = hcB\,\text{J}\,(\text{J} + 1) \quad \text{mit} \quad \text{J} = 0,\ 1,\ 2\ \dots \tag{5}$$

$$B = \frac{h}{8\pi^2 cI} = \frac{\hbar}{4\pi cI}\ ; \quad \left(B\ \text{in}\ \text{cm}^{-1}\right)$$

I is the moment of inertia, to be calculated for a two-atomic molecule in the following way: $I = \mu r_\text{v}^2$. B is called the rotational constant. It can be used to derive the bond length r_v of the molecule. The rotational energy states are not equidistant but they grow quadratically with quantum number J. However, the separations of the rotation levels are much smaller than those of the vibrational states.

3.2 Selection rules

A molecule can transform energy from electromagnetic radiation to vibrational or rotational energy only if the global selection rules for each form of motion are satisfied:

- For rotational excitation a molecule must have a permanent electric dipole moment (analog to an antenna as a Hertz dipole). Accordingly rotational excitation of symmetrical molecules like N_2, O_2 and CO_2 with electromagnetic radiation from the microwave band is not possible.

- For vibrational excitation the electrical dipole of the molecule has to change as function of the nucleus-nucleus distance. Hence, diatomic molecules like N_2 and O_2 are IR-inactive but individual vibrational modes of CO_2 can be excited (e. g. antisymmetric stretching vibration).

In addition to the **global** selection rules, which have to be satisfied in any case, there are **specific** selection rules, which limit the possible variations of the quantum numbers (two atomic harmonic oscillator: $\Delta v = \pm 1$, two atomic ridged rotor: $\Delta J = \pm 1$). The selection rules can be derived from the matrix elements of the dipole transition moment for vibrations and rotations.

The combined effect of global and specific selection rules and the quantization of energy levels in heteronuclear diatomic molecules (i. e. equidistant vibrational energy levels, increase of neighboring rotational energy levels by 2B at a time) is a band spectrum with a forbidden Q-branch and a P- and R-branch around the basic vibrational frequency. In spectra with sufficient resolution each peak can be assigned to a rotational transition (cf. fig. 3, rotational-vibrational transitions). From such spectra the rotational constant and the vibration frequency can be determined and from these in turn molecular parameters like the bond length and the spring constant of the harmonic oscillation.

The intensity of a transition depends on two factors. The selection rules can be applied strictly only to the model of a harmonic oscillator or a rigid rotor, respectively. Nonetheless, so called forbidden transitions, for example from v = 0 to v = 2 (harmonic oscillation, abbreviated form: $2 \leftarrow 0$) can be observed. Their intensity is usually much smaller. The intensity pattern of the individual branch – beginning with a linear increase, then a gaußian decay – can be explained with the degree of degeneracy g_J of the rotation states ($g_J = 2J + 1$) and the population of the rotation states according to the Boltzmann distribution.

3.3 Corrections

Corrections to the aforementioned models have to be discussed because we can measure spectra in very high detail with the spectrometer used in this experiment. We can observe that our results do not agree completely with the simple models (harmonic oscillator, rigid rotor). The most fundamental correction is the anharmonic distortion of the potential acting on the nuclei (cf. fig. 4): for high deflections the potential curve becomes shallower and finally reaches a limit at the dissociation energy, for contraction of the oscillator the potential becomes considerably steeper due to the Pauli repulsion (electrostatic repulsion alone cannot explain the effect!).

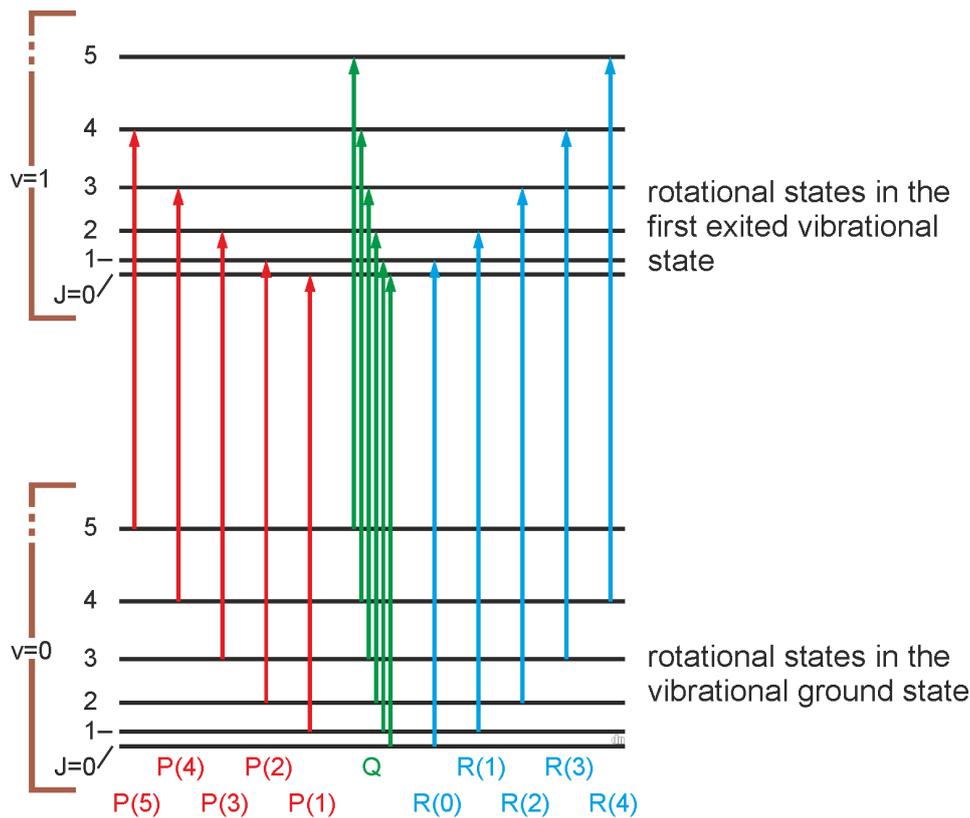The anharmonicity has small but measurable consequences:

Abbildung 3: rotational-vibrational transitions

- The vibrational levels are no longer equidistant. Their distance shrinks as the quantum number v increases. At the dissociation limit the energy levels are close enough to be considered as a continuum.

- Harmonic frequencies, i. e. excitations contradicting the specific selection rules, can be observed as so called *overtones* in the spectrum (with low intensity). Here for example the transition from v = 0 to v = 2 can be detected.

- The average distance of the nuclei is no longer constant and independent of the vibrational quantum number v but increases slightly as a function of v. As a consequence the moment of inertia and the rotational constant of course also depend on v!

To be exact the Schrödinger equation should be solved for the anharmonic potential. This is not done within this experiment. Instead we correct the energy eigenvalues as a Taylor expansion. Terminating the expansion for the vibration after the second term we get:

$$\frac{E_{vib}\mathrm{v}}{hc} = \tilde{\nu}_e \left(\mathrm{v} + \frac{1}{2} \right) - \tilde{\nu}_e x_e \left(\mathrm{v} + \frac{1}{2} \right)^2 \tag{6}$$
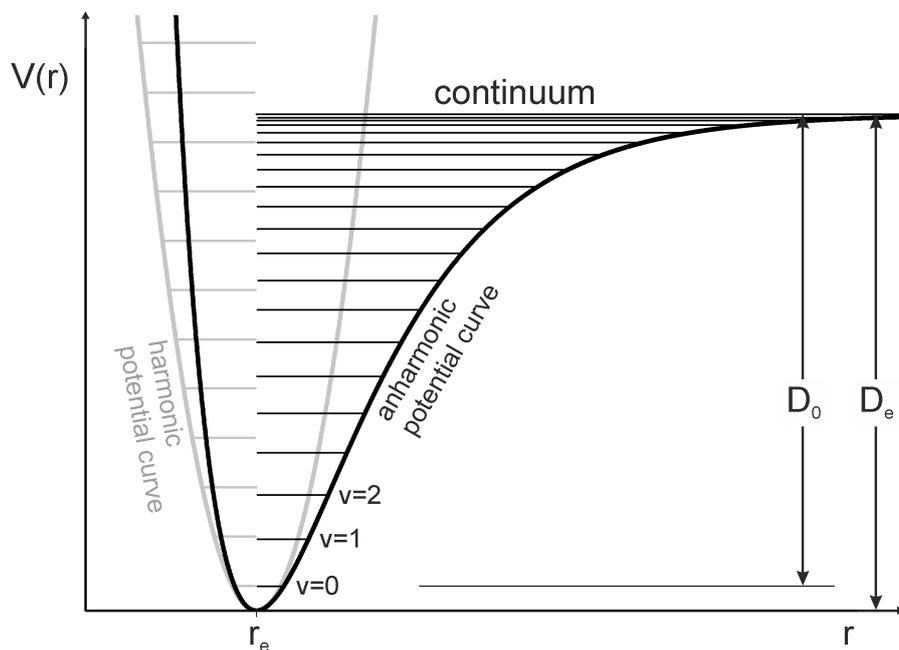
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Abbildung 4: Harmonic and anharmonic oscillator

$\tilde{\nu}_e$ is the hypothetic frequency of the ideal harmonic oscillator from which we derive the experimentally observed real oscillator. The spectroscopic transitions from v = 0 to v = 1 and to v = 2 (written $\tilde{\nu}_{1\leftarrow 0}$ and $\tilde{\nu}_{2\leftarrow 0}$) are therefore not observed at $\tilde{\nu}_e$ and at $2\tilde{\nu}_e$ but at:

$$\tilde{\nu}_{v\leftarrow 0} = v \cdot \tilde{\nu}_e \left[1 - x_e \left(v + 1\right)\right] \quad \tilde{\nu}_e \gg x_e \geq 0 \tag{7}$$

As fundamental correction to the simultaneously excited rotation the stretching of the molecular bond has to be considered. As a consequence we need to differentiate between the rotational constants B_0, B_1 and B_2, which in turn can be derived from the hypothetical rotational constant B_e of the ideal harmonic oscillator:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) \quad B_e \gg \alpha_e \geq 0 \tag{8}$$

B_v varies within the order of a few percent. α_e is the rotational-vibrational coupling constant. Both α_e and x_e are **small** corrections which can be measured nonetheless with our spectrometer!

Strictly speaking another correction should be applied to the rotational constant, which is caused by centrifugal forces stretching the bond for high excitations of rotational states. B therefore becomes a function of the rotational quantum number J:

$$\frac{E_{rot}(\mathrm{J})}{hc} = B\mathrm{J}(\mathrm{J}+1) - D\mathrm{J}^2(\mathrm{J}+1)^2 \, ; \quad \frac{D}{B} \approx 10^{-3} \dots 10^{-4} \tag{9}$$

$$B = \frac{\hbar}{4\pi c I} \, ; \quad D = \frac{\hbar^3}{4\pi c k I^2 r^2} \, ; \quad I = \mu r^2$$

As before I is the moment of inertia, D depends among other things on the force constant k. In the following interpretation of the spectrum we will neglect the centrifugal stretching and focus on the analysis of small rotational quantum numbers ($\mathrm{J} \leq 15$).

4 Experimental procedure

The spectrum is measured in two steps: At first a background spectrum is measured while the beam path is empty. Subsequently the CO cuvette is inserted and the spectrum of the sample is measured. After completing all measurements the cuvette should be stored in the desiccator due to the water sensitivity of the KBr windows. **Also take care not to touch the windows**. A step-by-step manual for the FTIR spectrometer and the software is available at the spectrometer.

For the data analysis the total spectrum should be limited to the wavenumber range where the fundamental excitation and the first overtone is expected (here: $1000\,\mathrm{cm}^{-1}$ to $5000\,\mathrm{cm}^{-1}$). It is possible to automatically label the rotational peaks with the corresponding wave numbers. Print an overview spectrum in the full wavenumber range and then magnified the spectral ranges of the fundamental and the overtone, respectively.

5 Data analysis

- At first the rotational transitions in the P- and R-branch of the fundamental and harmonic oscillation should be identified and explicitly marked on the plotted spectra. Remember that the P-branch begins with P(1) and the R-branch begins with R(0) because peaks are labeled according to their initial quantum numbers! Tabulate the rotational quantum numbers together with their corresponding wave numbers (10 to max. 15 peaks per branch).

- Due to anharmonicity, different rotational constants are expected for the vibrational ground state B_0, for the first excited state B_1 and for the second excited state B_2. By smartly plotting the differences of the peaks within the fundamental oscillation ($\tilde{\nu}_{R(\mathrm{J})} - \tilde{\nu}_{P(\mathrm{J})}$ vs. $4\mathrm{J}+2$) you can determine B_1. B_0 is available plotting ($\tilde{\nu}_{R(\mathrm{J}-1)} - \tilde{\nu}_{P(\mathrm{J}+1)}$ vs. $(4\mathrm{J}+2)$). Similarly, you can obtain B_2 and again B_0 from the peaks within the harmonic oscillation (cf. eq. 10 to 13). Append the corresponding linear regression plots and a determination of errors for the rotational constant. Furthermore calculate the moments of inertia I_v and bond lengths r_v of the vibrational states $\mathrm{v} = 0$, $\mathrm{v} = 1$ and $\mathrm{v} = 2$ from the respective rotational constants.

- Subsequently plot the values for B_v vs. $(v + \frac{1}{2})$. Determine α_e from the slope and B_e from the intercept (cf. eq. 14).

- Determine the basic frequency of the forbidden Q-branch of the CO vibrational transition ($\tilde{\nu}_{1\leftarrow 0}$, and $\tilde{\nu}_{2\leftarrow 0}$ for the overtone) by plotting $\frac{1}{2}\left(\tilde{\nu}_{R(J-1)} + \tilde{\nu}_{P(J)}\right)$ vs. J^2. The vibrational frequency is the intercept of the fit. Additionally determine the rotational-vibrational coupling constant α_e (resp. in the harmonic oscillation $2\alpha_e$?e) from the slope of the plot (cf. eq. 15, 16).

- From the transition frequencies $\tilde{\nu}_{1\leftarrow 0}$ and $\tilde{\nu}_{2\leftarrow 0}$ determine the harmonic frequency $\tilde{\nu}_e$ by plotting $\tilde{\nu}_{v\leftarrow 0}/v$ vs. $(v + 1)$ (cf. eq. 17).

- Discuss the intensity pattern of the rotational peaks within each branch and explain why the intensity of the overtone oscillation is much smaller than the intensity of the fundamental oscillation. Asymmetric behavior (e.g. the distances in the R-branch are smaller than in the P-branch) should also be discussed.

- Finally tabulate all numeric results together with the corresponding error from the regression and compare the values with the corresponding literature values.

Equations for data evaluation

Fundamental

$$\tilde{\nu}_{R(J)} - \tilde{\nu}_{P(J)} = B_1(4J + 2) \tag{10}$$
$$\tilde{\nu}_{R(J-1)} - \tilde{\nu}_{P(J+1)} = B_0(4J + 2) \tag{11}$$

Overtone

$$\tilde{\nu}_{R(J)} - \tilde{\nu}_{P(J)} = B_2(4J + 2) \tag{12}$$
$$\tilde{\nu}_{R(J-1)} - \tilde{\nu}_{P(J+1)} = B_0(4J + 2) \tag{13}$$

Rotational constant

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) \tag{14}$$

Fundamental

$$\frac{1}{2}\left(\tilde{\nu}_{R(J-1)} + \tilde{\nu}_{P(J)}\right) = \tilde{\nu}_{1\leftarrow 0} - \alpha_e J^2 \tag{15}$$

Overtone

$$\frac{1}{2}\left(\tilde{\nu}_{R(J-1)} + \tilde{\nu}_{P(J)}\right) = \tilde{\nu}_{2\leftarrow 0} - 2\alpha_e J^2 \tag{16}$$

Anharmonicity

$$\frac{\tilde{\nu}_{\mathrm{v}\leftarrow 0}}{\mathrm{v}} = \tilde{\nu}_e - \tilde{\nu}_e x_e(\mathrm{v}+1) \tag{17}$$

Final remarks

The protocol to this experiment should focus on the evaluation and interpretation of a physical chemical experiment. The necessary theoretical background should be outlined briefly and the equations required for the evaluation should be listed concisely. Detailed derivations and proofs should be avoided when writing the protocol. The use of computers to plot the data according to specifications given in these instructions and to calculate the subsequent linear regressions is permitted and encouraged. Software like e. g. Origin can be used to simultaneously calculate the linear regression including the errors of slope and intercept. In Excel the option for error calculation has to be manually activated. Of course all plots and linear regressions can be carried out by hand/graphically.

6 What you should know

Fundamentals of quantum mechanics, Schrödinger equation of the harmonic oscillator and its solutions, rigid rotor and its solutions, Born's interpretation of the wave function, Born-Oppenheimer approximation.

Fundamentals of spectroscopy, application of different spectral bands (infrared, microwave, UV-VIS), Lambert-Beer's law, Grotrian diagrams, selection rules, transitional dipole moment, harmonic frequencies, anharmonic corrections.

Fundamentals of Fourier transformation, advantages over classic spectroscopy, signal-to-noise ratio.

7 Literature

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