Rotation-Vibrational Spectrum

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1 Introduction

Molecules are composed of atomic nuclei and electrons. The Born-Oppenheimer approximation states that the motion of electrons is much faster than that of the nuclei - due to their smaller inertia. The nuclei are effected by the electrostatic potential of their electrons which holds them in a bound state.

In such a state, the quantum mechanical system has discrete energy eigenvalues, between which the system can change. In the process of such a transition, light is emitted or absorbed in quanta which carry the energetic difference of initial and final state. By observation of those quanta’s spectral distribution, information about the molecule can be obtained. The conservation of the total angular momentum leads to selection rules for the change in vibrational and rotational quantum numbers.

In order to induce a change of the motional state by infrared radiation, the molecule must have a dipole moment (either a permanent one as in HCl or a fluctuating one as in certain vibrations of CO$_2$). These modes are called "IR active". IR inactive modes can also be excited by Raman spectroscopy which is based on inelastic scattering of photons.

2 Theoretical background

The detailed theoretical quantum mechanical description is quite complex which is why only diatomic molecules will be considered thoroughly.

2.1 Quantum mechanical description

The stationary Schrödinger equation for a diatomic molecule with only one electron (a three body problem),

$$\begin{bmatrix}
-\frac{\hbar^2}{2m_e} \Delta_e - \frac{\hbar^2}{2m_1} \Delta R_1 - \frac{\hbar^2}{2m_2} \Delta R_2 - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_1|} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_2|} + \frac{e^2}{4\pi\varepsilon_0 |\vec{R}_1 - \vec{R}_2|}
\end{bmatrix} \times
\Psi(\vec{r}, \vec{R}_1, \vec{R}_2) = E \Psi(\vec{r}, \vec{R}_1, \vec{R}_2),$$

is already relatively complicated. For simplicity, a separation of the electronic and nuclear motions is done according to Born-Oppenheimer. This leads to an approach

$$\Psi(\vec{r}, \vec{R}_1, \vec{R}_2) = \psi(\vec{r}, \vec{R}_1, \vec{R}_2) \Phi(\vec{R}_1, \vec{R}_2),$$

where the total wave function is split into an electronic component $\psi$ and a nuclear part $\Phi$. Each partial wave function is now determined by its own Schrödinger equation. The eigenvalues $W$ of the electronic equation,

$$\begin{bmatrix}
-\frac{\hbar^2}{2m_e} \Delta_e - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_1|} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_2|}
\end{bmatrix} \psi = W(R_{12}) \psi, \quad (1)
$$

depend only on the distance $R_{12}$ of the nuclei and contribute to the potential of the nuclear equation

$$\begin{bmatrix}
-\frac{\hbar^2}{2m_1} \Delta R_1 - \frac{\hbar^2}{2m_2} \Delta R_2 + \frac{e^2}{4\pi\varepsilon_0 |\vec{R}_1 - \vec{R}_1|} + W(R_{12})
\end{bmatrix} \Phi = E \Phi.$$

In order to solve this equation, a transformation into new coordinates (center of mass $\vec{R}_S$ and relative coordinate $\vec{R}$) is necessary.

$$\Phi(\vec{R}_1, \vec{R}_2) = \tilde{\Phi}(\vec{R}_S, \vec{R})$$
We will not discuss the mathematical details here, suffice it to say that the nuclear wave function is split again into angular and radial parts.

\[
\tilde{\Phi}(\vec{R}_S, \vec{R}) = e^{i\vec{K}_{\Sigma} \cdot \vec{R}} f(R) F(\theta, \phi)
\]

\(f\) is the radial function, \(F\) the angular part. The motion of the center of mass is simply that of a free particle (a plane wave). After the mentioned transformation of coordinates, the Schrödinger equation becomes [1]

\[
\left[ -\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{L^2}{2\mu R^2} + V(R) \right] fF = \mathcal{E} fF. \tag{2}
\]

The only angular dependency is the angular momentum operator \(L\) whose eigenfunctions are the spherical harmonics.

\[
L^2 Y_J(\theta, \phi) = \hbar^2 J(J + 1) Y_J(\theta, \phi)
\]

After inserting this into eq. (2), the radial equation takes the form of a harmonic oscillator with eigenvalues \(\hbar \omega(v + \frac{1}{2})\).

Eventually, the total energy is

\[
E = \frac{\hbar^2 K^2}{2M} + V(R) + \hbar \omega(v + \frac{1}{2}) + \frac{\hbar^2}{2\mu R^2} J(J + 1),
\]

where \(V(R)\) hosts the electronic as well as the repulsive potential of the nuclei and the first term is just the translational energy of the whole molecule.

Of course, this has only been a brief sketch of the quantum mechanical description. Nevertheless, under the respective approximations involved in this calculation, the rotational and vibrational energies are the same as those we will derive below - which justifies the semi classical picture used in the following sections.

![Figure 1: General structure of the energetic levels of a diatomic molecule. The nuclear eigenstates are determined by the Morse-shaped potentials of the electronic movement. The discrete structure is composed of vibrational states (indicated by \(v\)) and rotational levels (indicated by \(J\)). [1]](image-url)
2.2 Rotation I - The rigid rotator

The classical energy of a rigid rotator as shown in fig. 2 is

$$E_{\text{rot}} = \frac{1}{2} \theta \omega^2 = \frac{L^2}{2 \theta},$$

where $\theta$ is the moment of inertia and $L$ is the angular momentum. In a semi-classical approach, we replace $L^2$ by its quantum mechanical eigenvalue $\hbar^2 J(J+1)$ with the rotational quantum number $J$. The moment of inertia is $\theta = \mu r^2$ with the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and $r$ is the distance of the nuclei.

$$E_{\text{rot}} = \frac{\hbar^2}{2 \mu r^2} J(J+1)$$

In IR spectroscopy, the energy is expressed in terms which are more convenient, since they have the same unit as the measured frequencies. $F(J) = \frac{E_{\text{rot}}(J)}{\hbar c}$ is the rotational term and has the unit cm$^{-1}$. Defining the rotational constant as $B = \frac{\hbar^2}{2 \mu r^2} \frac{1}{h c} = \frac{h}{8 \pi^2 c \mu r^2}$, the rotational terms are simply

$$F(J) = BJ(J+1).$$

In a transition from a rotational level $J''$ (lower level) to $J'$ (higher level), the selection rule $\Delta J = \pm 1$ applies. It can be calculated by Fermi’s rule for transition probabilities but it becomes clear considering that a photon has spin one, i.e. $J_{\text{photon}} = \pm 1 \cdot \hbar$. Conservation of angular momentum now requires the system to compensate the lost or gained angular momentum quantum by changing into a state with one quantum $\hbar$ lower or higher.

The spectrum therefore consists of transition energies corresponding to the distances of neighboring levels, as shown in fig. 3. The wave numbers of those spectral lines can be calculated from a difference in terms.

$$\bar{\nu} = F(J') - F(J'') = BJ'(J' + 1) - BJ''(J'' + 1) = 2B(J'' + 1)$$

The spectrum is made up of equidistant lines with a gap of $2B$ in between.
2.3 Vibration - The harmonic oscillator

The electronic potential \( W(R_{12}) \) introduced in eq. (1) and shown schematically in fig. 1 is usually approximated by a harmonic (i.e. parabolic) potential having a minimum at the equilibrium distance \( r_e \).

\[
V = \frac{1}{2} k (r_e - r)^2
\]

\( r \) is the distance of the nuclei and therefore a relative coordinate. The harmonic oscillator is well understood in quantum mechanics. It has equidistant energy levels

\[
E_{vib} = \hbar \omega \left( v + \frac{1}{2} \right),
\]

wherein \( \omega = \sqrt{\frac{k}{\mu}} \). For this system, there is a selection rule \( \Delta v = 1 \) and in our experiment, we consider a transition from \( v'' = 0 \) to \( v' = 1 \). At room temperature, usually only the lowest vibrational state is thermally occupied.
As for the rotational energies, the vibrational terms are the relevant quantity in spectroscopy. They are denoted by
\[ G(v) = \frac{\hbar \omega}{\hbar c} (v + \frac{1}{2}) = \omega_{osc}(v + \frac{1}{2}) \]

(3)

Therein, \( \omega_{osc} = \frac{\nu_c}{c} = \frac{1}{2\pi\sqrt{\frac{k}{\mu}}} \). The wave number of the transition \( v'' \rightarrow v' \) is
\[ \tilde{\nu} = G(v') - G(v'') = \omega_{osc}(v' - v'') \]

In our case, we have \( v' = v'' + 1 \), so
\[ \tilde{\nu} = \omega_{osc} \]

In a more precise treatment of the vibration in molecules, a Morse potential replaces the parabolic one. In effect, the equidistant levels become closer with increasing \( J \), converging to the dissociation threshold, above which there is a continuum.

\[ FK.5: \text{The energy levels in the Morse potential.} \ [1] \]

Since we are only interested in the first two vibrational levels, the harmonic oscillator is a good approximation.

2.4 Rotation II - The non-rigid rotator

Since the molecule is stretched due to centrifugal forces, the model of a rigid rotator is no longer appropriate. Independent of the vibrational state, the distance increases, when the molecule is rotating. This effect is taken into account by a correction, so the rotational terms become
\[ F(J) = BJ(J + 1) - DJ^2(J + 1)^2 \]

with the extension constant \( D = \frac{4b^3}{\omega_{osc}^2} \). With increasing rotational excitation, the energetic levels are more and more lowered. Consequently, the spectrum is no longer equidistant, as shown in fig. 6.
When the molecule is in a high vibrational state, the internuclear distance increases, which can be observed in fig. 4. To compensate for this effect, altered constants are inserted for $B$ and $D$.

$$B_v = B - \alpha \left( v + \frac{1}{2} \right)$$

$$D_v = D - \beta \left( v + \frac{1}{2} \right)$$

This results in $v$-dependent rotational terms.

$$F(v, J) = B_v J(J + 1) - D_v J^2 (J + 1)^2$$

(4)
2.5 Rotational-vibrational spectrum

From the previous sections, we have learned that the energetic terms of a diatomic molecule are described by eqs. (3,4).

\[
T(v,J) = G(v) + F(v,J) = \omega_{osc} \left( v + \frac{1}{2} \right) + B_v J(J+1) - D_v J^2 (J+1)^2
\]

In a rotational-vibrational spectrum, we have to consider the selection rules \( \Delta v = 1 \) and \( \Delta J = \pm 1 \). Specifically, in this experiment we have \( v'' = 0 \) and \( v' = 1 \), as mentioned before. The case \( \Delta J = J' - J'' = -1 \) is called “P branch” while \( \Delta J = +1 \) is called the “R branch” (see fig. 7). With those selection rules, we can determine the visible wave numbers of our spectrum.

\[
\tilde{\nu} = T(1,J') - T(0,J'') = \omega_{osc} + F(1,J') - F(0,J'')
\]
In case of the two branches, we explicitly get $P(J) = \tilde{\nu}$ and $R(J) = \tilde{\nu}$, respectively.

\[
\begin{align*}
P(J) &= \omega_{osc} + F(1, J - 1) - F(0, J) \\
R(J) &= \omega_{osc} + F(1, J + 1) - F(0, J) \\
\tilde{\nu}_{P/R} &= \omega_{osc} + (B'_v + B''_v) m + (B'_v - B''_v - D'_v + D''_v) m^2 \\
&- 2 (D'_v + D''_v) m^3 - (D'_v - D''_v) m^4
\end{align*}
\]

Therein, $m = J + 1$ for the R branch and $m = -J$ for the P branch ($J = J''$). This last formula gives the peaks of the spectrum. We will now discuss the respective intensities.

The partition function of the rotation is

\[
q_{rot} = \sum_{J=0}^{\infty} g(J) e^{-\beta E_{rot}(J)}.
\]

$g(J)$ is the degeneracy, which is $2J + 1$ according to the degeneracy of the spherical harmonics. Then we just have to insert the rotational terms. For simplicity, we will use the formula obtained from the model of a rigid rotator, $E_{rot}(J) = \hbar c B J (J + 1)$.

\[
q_{rot} = \sum_{J=0}^{\infty} (2J + 1) e^{-\beta \hbar c B J (J + 1)}
\]

Regarding the rotational spectrum as almost continuous, the summation can be approximated by an integration over $J$ which we (exactly) solve by a computer algebra system.

\[
q_{rot} = \int_{0}^{\infty} (2J + 1) e^{-\beta \hbar c B J (J + 1)} dJ = \frac{k_B T}{\hbar c B}
\]

Now, Boltzmann statistics suggest that the number of molecules in the state characterized by $J$ is given by

\[
\frac{N_J}{N} = \frac{e^{-\beta E_{rot}(J)}}{q_{rot}} = \frac{\hbar c B}{k_B T} (2J + 1) e^{-\frac{\hbar c B J (J + 1)}{k_B T}}.
\]

The intensity of a peak is proportional to the occupation number $N_J$ of the initial state.
3 Questions

1. How many degrees of freedom of movement does an n-atomic linear/non-linear molecule have?
   A non-linear molecule has 3 degrees of translation and 3 of rotation. A linear molecule has 3
degrees of translation and 2 of rotation. In a linear molecule, the rotation around the internuclear
axis is “frozen”. The total number of degrees of freedom is 3n.

2. How many vibrational degrees of freedom does an n-atomic linear/non-linear molecule have?
   A non-linear molecule has 3n – 6 degrees of freedom of vibration. A linear one has 3n – 5. The
frozen rotational degree transforms into a vibrational one, because the total number of degrees
is conserved.

3. How many vibrational degrees of freedom does a CO₂ molecule have and what do the normal
   vibrations look like? What is their energetic order?
   CO₂ is a linear molecule and has 3n – 5 = 4 vibrational degrees of freedom.

   ![Figure 8: Normal vibrations of CO₂.][1]

   There are two stretching vibrations (symmetric and antisymmetric) and two degenerate deformation vibrations (in the two spacial dimensions perpendicular to the internuclear axis). The energetic order can be found in section 4.

4. Give the selection rules for pure IR transitions!
   For the vibrational levels, it is Δv = 1 in a harmonic oscillator (this rule is invalid in the
anharmonic Morse potential), for the rotation we have to consider ΔJ = ±1(under certain
circumstances ΔJ = 0, the Q branch, is also possible).

5. What are the selection rules for rovibrational transitions in the case of CO₂ and HCl?
   In these molecules, there is no Q branch.

6. What kind of enveloping band shapes are to be expected for CO₂ and for the IR-active modes?
   Which modes are IR active?
   First of all, the symmetric stretching vibration is IR-inactive since the dipole moment remains
zero at all times. In the three other cases, a fluctuating, temporary dipole moment is present
and those three modes are IR-active.
   In fig. 7, you can see the enveloping shape which is due to the linearly increasing degeneracy
and the exponentially decreasing thermal occupation of the rotational levels.

7. Explain the terms “parallel” and “perpendicular band”!
   Unfortunately, we couldn’t find anything about this distinction or we only know it under a
different name.

8. What can you say about the rotational constants B′_v and B′′_v of HCl, are they different? Give
   arguments.
$B'_v$ denotes the rotational term constant of the state $v = 1$, while $B''_v$ means $v = 0$. In the excited state, the radius is larger (as discussed in section 2.4), so because of $B \propto r^{-2}$, $B'_v$ is smaller than $B''_v$. This is in accordance with the formula

$$B_v = B - \alpha \left( v + \frac{1}{2} \right),$$

which means

$$B'_v = B - \frac{3}{2} \alpha,$$
$$B''_v = B - \frac{1}{2} \alpha.$$
4 Preparation for the evaluation

The tasks not mentioned here will be attended in the evaluation.

Task 1

See table 4 in the evaluation.

Task 2

The Hamiltonian for a triatomic linear molecule separates in three terms. The coordinates $x_i$ are the displacement from the equilibrium point, and $m_i$ are the masses of the particles. We also use the harmonic approximation with the same force constant and $m_1 = m_3$:

$$
\begin{align*}
    m_1 \ddot{x}_1 &= -k(x_1 - x_2), \\
    m_2 \ddot{x}_1 &= -k(2x_2 - x_1 - x_3), \\
    m_1 \ddot{x}_1 &= -k(x_3 - x_2).
\end{align*}
$$

We use the oscillation ansatz $x_i(t) = x'_i e^{i\omega t}$, which leads to

$$
\begin{align*}
    0 &= -k(x'_1 - x'_2) + m_1 \omega^2 x'_1, \\
    0 &= -k(2x'_2 - x'_1 - x'_3) + m_3 \omega^2 x'_2, \\
    0 &= -k(x'_3 - x'_2) + m_1 \omega^2 x'_3.
\end{align*}
$$

In matrix notation this is just

$$
\begin{pmatrix}
    m_1 \omega^2 - k & k & 0 \\
    k & m_2 \omega^2 - 2k & k \\
    0 & k & m_1 \omega^2 - k
\end{pmatrix}
\begin{pmatrix}
    x'_1 \\
    x'_2 \\
    x'_3
\end{pmatrix} = \vec{0}.
$$

The characteristic polynomial must vanish if we want to get a solution which is different from the trivial one. So we get

$$
(m_1 \omega^2 - k)^2 (m_2 \omega^2 - 2k) - 2k^2 (m_1 \omega^2 - k) = 0.
$$

One root is $m_1 \omega^2 + k = 0$, which leads to the first eigenvalue,

$$
\omega_1 = \sqrt{\frac{k}{m_1}},
$$

and the other one is (the first one has been canceled out)

$$
0 = (m_1 \omega^2 - k) (m_2 \omega^2 - 2k) - 2k^2
= 2\omega^4 m_1 m_2 - \omega^2 k (m_1 + 2m_2) = \omega^4 - \omega^2 \frac{k(m_1 + 2m_2)}{2m_1 m_2}
= \omega^2 - \frac{k(m_1 + 2m_2)}{2m_1 m_2}.
$$

So we have found our second eigenvalue,

$$
\omega_2 = \sqrt{\frac{k(m_1 + 2m_2)}{2m_1 m_2}} = \sqrt{\frac{k}{m_1} + \frac{k}{2m_2}} > \omega_1.
$$

The asymmetric vibration needs more energy because the tongues are compressed harder. So $\omega_2$ is the asymmetric and $\omega_1$ is the symmetric vibration.
For the deformation vibration the force, which wants to bring back the atom in its equilibrium point, depends on the angular displacement $\delta$ and the distance $L_0$ of the molecules in equilibrium. So we get

$$F = -L_0 \kappa \delta,$$

where $\kappa$ is the angle deformation constant. Because of the $L_0$ in the force it has the same dimension, as the normal force constant. The frequency is given by:

$$\omega_3 = \sqrt{\frac{\kappa (m_1 + 2m_2)}{m_1 m_2}}.$$

**Task 3**

For the vibration frequencies of CO$_2$, we found the following values in [1].

\[
\begin{align*}
\nu_{\text{sym}} &= 1337 \text{ cm}^{-1} \\
\nu_{\text{asym}} &= 2349 \text{ cm}^{-1} \\
\nu_{\text{def}} &= 667 \text{ cm}^{-1}
\end{align*}
\]

**Task 4**

We want to get $k$ and $\kappa$ out of the measured frequencies, so we just solve the expressions found in section 4.

$$k = \frac{2m_1 m_2 \omega_3^2}{(m_1 + 2m_2)} \quad \text{and} \quad \kappa = \frac{m_1 m_2 \omega_3^2}{(m_1 + 2m_2)}$$

(6)

The results from the experiment are presented in table 4 in the evaluation.

**Task 5**

In order to determinate the constants $B'_v, B''_v, D'_v, D''_v$, we need proper equations. We remember the energy term for the two relevant vibrational levels 1 and 0. The higher energy level is always labeled '$ (v = 1)$ and the lower energy is labeled $'' (v = 0)$. In the following we leave the index $v$ away, for simplicity.

$$T(v = 1, J) = T'(J) = G(1) + F'(J) = \omega_{\text{osc}}(1 + \frac{1}{2}) + B'J(J + 1) - D'J^2(J + 1)^2$$

$$T(v = 0, J) = T''(J) = G(0) + F''(J) = \omega_{\text{osc}}(0 + \frac{1}{2}) + B''J(J + 1) - D''J^2(J + 1)^2.$$  

For the $R$ branch, with $\Delta v = 1$ and $J' - J'' = +1$ we get

$$R(J) = T'(\underbrace{J + 1}_{J' = J''+1}) - T''(\underbrace{J}_{J''}) = \omega_{\text{osc}} + F'(J + 1) - F''(J).$$

For the $P$ branch $J' - J'' = -1$ we get

$$P(J) = T'(\underbrace{J + 1}_{J' = J''-1}) - T''(\underbrace{J}_{J''}) = \omega_{\text{osc}} + F'(J - 1) - F''(J).$$

From this definition, it is clear that in our formulas $J = J''$. By combining these two bands, we get equations, in which we have only rotational constants of one vibrational level. The two variants are:

$$R(J - 1) - P(J + 1) = F''(J + 1) - F''(J - 1) = \Delta F''$$

$$R(J) - P(J) = F'(J + 1) - F'(J - 1) = \Delta F'.$$

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Now we insert the precise expressions for $F(J)$ and get
\[
\Delta F''(J) = B''(J + 1)(J + 2) - D''(J + 1)^2(J + 2)^2 - B''(J - 1)J - D''(J - 1)^2J^2
\]
\[
= B''(3J + 1)J + 2B'' - D'' \left(8J^3 + 12J^2 + 12J + \frac{1}{2}\right)
\]
\[
= 4B'' \left(J + \frac{1}{2}\right) - 8D'' \left(J^3 + \frac{3}{2}J^2 + \frac{3}{2}J + \frac{1}{2}\right)
\]
\[
= (4B'' - 6D'') \left(J + \frac{1}{2}\right) - 8D'' \left(J^3 + \frac{3}{2}J^2 + \frac{3}{4}J + \frac{1}{8}\right)
\]
\[
= (4B'' - 6D'') \left(J + \frac{1}{2}\right) - 8D'' \left(J + \frac{1}{2}\right)^3.
\]

The $J$ dependence is the same for $F'$ and $F''$, only the prefactors are different. From eqs. (7,8) we can immediately write down the equation for $\Delta F'$:
\[
\Delta F'(J) = (4B' - 6D') \left(J + \frac{1}{2}\right) - 8D' \left(J + \frac{1}{2}\right)^3
\]
\[
= 4B' \left(J + \frac{1}{2}\right)^2 - 8D' \left(J + \frac{1}{2}\right)^3.
\]

Now we have found our two equations and will plot $\frac{\Delta F''(J)}{J + \frac{1}{2}}$ over $(J + \frac{1}{2})^2$ to get a linear dependence.

The relation between the fit parameters $a$ and $b$ and the constants $B'$, $B''$, $D'$ and $D''$ are
\[
D'' = -\frac{a''}{8},
\]
\[
B'' = \frac{1}{2} \left(b'' - \frac{3}{4}a''\right),
\]
\[
D' = -\frac{a}{8},
\]
\[
B' = \frac{1}{2} \left(b' - \frac{3}{4}a'\right).
\]

If we use the definition of $B_v = B_e - \alpha(v + \frac{1}{2})$ and $D_v = D_e - \beta(v + \frac{1}{2})$, we get:
\[
\alpha = B'' - B',
\]
\[
\beta = D'' - D'.
\]

And by reinserting in the definition:
\[
B_e = B' + \frac{\alpha}{2},
\]
\[
D_e = D' + \frac{\beta}{2}.
\]

The equilibrium distance $r_e$ can be calculated from $B_e$.
\[
r_e = \sqrt{\frac{h}{8\pi^2 c\mu B}}
\]

The distances $r'$ and $r''$ are corresponding to the $B'$ and $B''$.
\[
r' = \sqrt{\frac{h}{8\pi^2 c\mu B'}} \quad \text{and} \quad r'' = \sqrt{\frac{h}{8\pi^2 c\mu B''}}.
\]

\[\text{We fit the measured values with } f(x) = ax + b.\]
Task 6
See the evaluation, especially tab. 7.

Task 7
See tab. 7.

Task 8
We want to get the maximum of the function \( n(J) \), which is the number of molecules in state \( J \), divided by the total number of molecules \( N \).

\[
n(J) = \frac{N(J)}{N} = \beta \hbar c B (2J + 1) e^{-\beta \hbar c B(J+1)\frac{1}{2}}
\]

\[
\frac{\partial n(J)}{\partial J} = \beta \hbar v B \left\{ 2 e^{-\beta \hbar c B(J+1)\frac{1}{2}} - \hbar c B (2J + 1) e^{-\beta \hbar c B(J+1)\frac{1}{2}} (2J + 1) \right\} = 0
\]

\[
0 = 2 - \hbar c B (2J + 1) \Rightarrow \sqrt{2} = \sqrt{\hbar c B (2J + 1)}
\]

\[
J_{\text{max}} = \sqrt{\frac{k_B T}{\hbar c B} - \frac{1}{2}}.
\]

We will later insert \( T = 298 \text{ K} \) and \( B = B'' \) in order to get \( J_{\text{max}} \) and compare it with the experimental result.

Task 9
Some literature values for the HCl molecule [2]:

\[
\begin{align*}
\omega_{\text{osc}} &= 2989.74 \text{ cm}^{-1} \\
B &= 10.5909 \text{ cm}^{-1} \\
\alpha &= 0.3019 \text{ cm}^{-1} \\
r_c &= 1.27460 \cdot 10^{-10} \text{ m}
\end{align*}
\]

Task 10
c)
The partition function is defined as

\[
z = \text{Tr} \left[ e^{-\beta H} \right].
\]

For the vibrational and rotational energies we can introduce quantum numbers \( v \) and \( J \). We will also make the approximation, that the energy values only depend on the corresponding quantum number. No coupling between \( E_{\text{rot}} = E_{\text{rot}}(J, v) \) or \( E_{\text{vib}} = E_{\text{vib}}(J, v) \). With this approximation we get

\[
z = \sum_{J,m_J,v} e^{-\beta (E_{\text{rot}} + E_{\text{vib}})} = \left( \sum_{J} \sum_{m_J=-J}^{J} e^{-BJ(J+1)} \right) \left( \sum_{v} e^{-\beta \hbar \omega_{\text{osc}}(v+\frac{1}{2})} \right) = z_{\text{rot}} z_{\text{vib}}.
\]

The energy level for the rotation are very close, so we just integrate.

\[
z_{\text{rot}} = \int_{0}^{\infty} dJ (2J + 1) e^{-\hbar c BJ(J+1)} = \frac{k_B T}{\hbar c B}
\]
The vibrational partition function is

\[ z_{\text{vib}} = \sum_{v=0}^{\infty} e^{-\beta \hbar \omega_{\text{osc}} (v + \frac{1}{2})} = e^{-\frac{\beta \hbar \omega_{\text{osc}}}{2}} \frac{1}{1 - e^{-\beta \hbar \omega_{\text{osc}}}} = \frac{1}{2 \sinh \frac{\hbar \omega_{\text{osc}}}{2k_B T}}. \]

With the literature values from the previous section and \( T = 293.15 \text{K} \), we can calculate these values.

\[ z_{\text{rot}} = 19.24 \]
\[ z_{\text{vib}} = 383.9 \]
5 Measurement

5.1 Infrared spectrometer

We used a commercial infrared spectrometer “IMR 16” by Zeiss. So everything was calibrated already.

![Picture of the spectrometer.](image)

The possible range was $625\text{cm}^{-1}$ to $4000\text{cm}^{-1}$. Five possible programs were available, which had an influence on the relation between wave numbers and resolution on the printout. The best resolution was obtained in program 5, which we used for the detailed measurement. The properties of this program are presented in the table below.

<table>
<thead>
<tr>
<th>Wave number range</th>
<th>Resolution with maximal aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4000 \text{cm}^{-1}$ - $2000 \text{cm}^{-1}$</td>
<td>$2 \text{cm}^{-1}$ per mm</td>
</tr>
<tr>
<td>$2000 \text{cm}^{-1}$ - $625 \text{cm}^{-1}$</td>
<td>$1 \text{cm}^{-1}$ per mm</td>
</tr>
</tbody>
</table>

Table 1: Resolution of the spectrometer.

For the overview we used program 1, which gives a fast overview ($\approx 2$ min) over the spectrum. Before we started the first measurement we filled the chamber (see fig. 10) with $\text{N}_2$. This gas gives no contribution to the spectrum and brings out rests of $\text{H}_2\text{O}$. Then we filled in a small amount of the test gas.

Too much test gas lead to wide peaks. At the beginning of the experiment we were also informed, that we will work with $\text{CH}_4$ instead of $\text{HCl}$, but fortunately we can use a lot of the formalism of the diatomic gas. We will come to this point later in the protocol.
5.2 The CO$_2$ molecule

At the beginning we measured the whole spectrum and got three main peaks.

One was the asymmetric stretching vibration, the second the deformation vibration and the last peak was a linear combination of eigenvibrations. The peaks were identified by their energetic order. The smallest one was the deformation energy, the next one must be the asymmetric vibration and the one with the highest energy was a linear combination.

The values for these peaks were obtained from three detailed measurements. We set the full width of the peak at half maximum (FWHM) as the error.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>$\nu$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{def}}$</td>
<td>666 ± 3</td>
</tr>
<tr>
<td>$\nu_{\text{sym}}$</td>
<td>2346 ± 6</td>
</tr>
<tr>
<td>$\nu_{\text{linear}{\text{comb}},1}$</td>
<td>3702 ± 6</td>
</tr>
<tr>
<td>$\nu_{\text{linear}{\text{comb}},2}$</td>
<td>3598 ± 6</td>
</tr>
</tbody>
</table>

Table 2: The three measured frequencies for the CO$_2$ molecule.
5.3 The CH₄ molecule

For the CH₄ molecule we got two bands in the spectrum, which we call high and low energy band.
In each band we see a $Q$, $R$ and $P$ branch. For the two bands we also made a measurement with high resolution. This will be used in the evaluation to get the $B$ and $D$ values. Because of the tetrahedral symmetry we can treat the CH$_4$ molecule as linear rotator in good approximation.

Figure 16: The high energy band of the CH$_4$ molecule.

Figure 17: The low energy band of the CH$_4$ molecule.
From the $Q$ branches we get the wave numbers of these two vibrations.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>$\bar{\nu}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{low}}$</td>
<td>1308 ± 3</td>
</tr>
<tr>
<td>$\nu_{\text{high}}$</td>
<td>3014 ± 6</td>
</tr>
</tbody>
</table>

Table 3: The two vibrations of the CH$_4$ molecule.

Later we will try to identify these two vibrations with one of the eigenvibrations of the molecule by comparison with literature values.
6 Evaluation

For all calculated quantities \( g = g(x_1, ..., x_N) \), which depend on variables with an error \( \Delta x_i \) we use the Gauss formula

\[
\Delta g = \sqrt{\sum_{i=1}^{N} \left( \frac{\partial g}{\partial x_i} \Delta x_i \right)^2}.
\]

We did the linear fits with 'gnuplot', which is a standard open source program. It uses just the least square algorithm.

6.1 The CO\(_2\) molecule

For this triatomic linear molecule we can calculate from the asymmetric stretching vibration the force constant with eq. (6) and \( \omega_{\text{asym}} = E_{\text{asym}}/h = \hbar \nu_{\text{asym}}/h \). For the error we use the Gaussian formula and insert the mass values for oxygen \( m_1 = 16 \text{ u} \) and carbon \( m_2 = 12 \text{ u} \). We treat these values as accurate.\(^2\)

\[
k = \frac{2 \cdot 16 \cdot 12}{(16 + 2 \cdot 12)} \text{ u} \cdot \omega_1^2 = \frac{9 \cdot 1,66 \cdot 10^{-27} \cdot E_{\text{asym}}^2}{h^2} \frac{N}{m} = (3115 \pm 8) \frac{N}{m}.
\]

\[
\kappa = \frac{16 \cdot 12}{(16 + 2 \cdot 12)} \text{ u} \cdot \omega_3^2 = \frac{4 \cdot 1,66 \cdot 10^{-27} \cdot E_{\text{def}}^2}{h^2} \frac{N}{m} = (126 \pm 2) \frac{N}{m}.
\]

The two high energy frequencies are a combination of the symmetric stretching vibration and the asymmetric one. This leads to a wave number of \( \nu_{\text{asym}+\text{sym}} = 3686 \text{ cm}^{-1} \).

<table>
<thead>
<tr>
<th>Constant</th>
<th>Experiment</th>
<th>Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{\text{def}} )</td>
<td>(666 ± 3) cm(^{-1})</td>
<td>667 cm(^{-1})</td>
</tr>
<tr>
<td>( \nu_{\text{asym}} )</td>
<td>(2346 ± 6) cm(^{-1})</td>
<td>2349 cm(^{-1})</td>
</tr>
<tr>
<td>( k )</td>
<td>(3115 ± 8) ( \frac{N}{m} )</td>
<td></td>
</tr>
<tr>
<td>( \kappa )</td>
<td>(126 ± 2) ( \frac{N}{m} )</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Overview for the CO\(_2\) molecule.

6.2 The CH\(_4\) molecule

As mentioned in section 5.3, we treat the CH\(_4\) molecule like a diatomic molecule and want to use eqs. (7,8) to get the constants. So the first step is to identify the \( P \) and \( R \) peaks and get the wave numbers (tab. 5). We do this procedure for the high energy band, because this spectrum looks better (see fig. 15 in comparison to fig. 16). By combining these \( P \) and \( R \) branches we can calculate \( \Delta F' \) and \( \Delta F'' \) (tab. 6).

\[^2\Delta k = \frac{\partial k(\omega)}{\partial \omega} \Delta \omega\]
Table 5: The wave numbers for the $P$ and $R$ branches. The number $J$ is the rotational quantum number of the lower state corresponding to $v = 0$, which is $J''$.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$P(J)$ [cm$^{-1}$]</th>
<th>$R(J)$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2994±2</td>
<td>3034±2</td>
</tr>
<tr>
<td>2</td>
<td>2986±2</td>
<td>3044±2</td>
</tr>
<tr>
<td>3</td>
<td>2976±2</td>
<td>3055±2</td>
</tr>
<tr>
<td>4</td>
<td>2964±2</td>
<td>3065±2</td>
</tr>
<tr>
<td>5</td>
<td>2954±2</td>
<td>3073±2</td>
</tr>
<tr>
<td>6</td>
<td>2943±2</td>
<td>3083±2</td>
</tr>
<tr>
<td>7</td>
<td>2931±2</td>
<td>3093±2</td>
</tr>
<tr>
<td>8</td>
<td>2921±2</td>
<td>3103±2</td>
</tr>
<tr>
<td>9</td>
<td>2911±2</td>
<td>3113±2</td>
</tr>
<tr>
<td>10</td>
<td>2901±2</td>
<td>3119±2</td>
</tr>
<tr>
<td>11</td>
<td>2891±2</td>
<td>3129±2</td>
</tr>
<tr>
<td>12</td>
<td>2881±2</td>
<td>3137±2</td>
</tr>
<tr>
<td>13</td>
<td>2869±2</td>
<td>3145±2</td>
</tr>
</tbody>
</table>

Table 6: The wave numbers for the $P$ and $R$ branches. The number $J$ is the rotation number of the lower state corresponding to $v = 0$, which is $J''$

We then plot $\frac{\Delta F}{J+\frac{1}{2}}$ over $(J + \frac{1}{2})^2$ and fit linear according to eq. (9). From the linear fit we get fit parameters:

$$a'' = -(0.0156 \pm 0.002) \text{ cm}^{-1} \text{ and } b'' = (22.7722 \pm 0.1642) \text{ cm}^{-1},$$

$$a' = -(0.0136 \pm 0.002) \text{ cm}^{-1} \text{ and } b' = (22.499 \pm 0.1869) \text{ cm}^{-1}.$$
With the formulas from evaluation, eqs. (10-17), we can calculate all the molecular values. We also used eq. (5) and the data from tab. 6 to calculate \( \bar{\nu}_0 \).
According to eq. (18), the most intense peak in the spectrum should be at $J_{max} \approx 2.5$. In the measurement, the most intense were at about $J \approx 7$. This is a grave deviation.

A little mystery is the missing peak between the Q peak and the first frequency in the P branch of the “high energy” band. At first we suspected it had somehow been covered by the Q branch or been suppressed for some other reason. When we fitted the data under the assumption that the missing peak was just suppressed and respected it in the counting of $J$, we got completely inadequate results (not even a linear dependence). We then started counting just at the second (first visible) peak (see the original spectrum in the appendix), leaving out the missing one. Since we got better results this way, the question arises, why there is such a large gap between Q and P(1).

7 Discussion

The experiment itself was comfortable since nothing had to be calibrated or adjusted. Certainly, the spectrometer in use wasn’t state of the art but the resolution proved certainly sufficient to display the rotational bands of methane.

The CO$_2$ spectroscopy was most successful, but since we only had to identify the respective frequencies, the task wasn’t challenging enough to conclude about our spectroscopic skills.

That was certainly different in methane. First of all, the “low energy” band was not good enough for evaluation. Possibly, we should have adjusted the test gas pressure and the different settings at the recorder and the spectrometer a little further. The mystery about the hidden peak could not be solved and is our main source of concern about the validity of the measured values.

Unfortunately, we were unable to find literature values for CH$_4$. Comparison to other molecules (especially CH, which we believe to have a similar spectrum) shows that our gained data are in the correct order of magnitude, so grave errors seem not to have occurred.

It is very unfortunate that we could not measure HCl which is supposed to show a very demonstrative spectrum. It would also be nice to have a way of recording the spectra digitally.

References
