

Introduction to Raman Spectroscopy

Johannes Kiefer

**Technische Thermodynamik
Universität Bremen, Germany**



- Rotational and vibrational spectra in a nutshell
- Raman spectroscopy
 - Raman effect and Raman activity
 - Instrumentation
 - Signal analysis
 - Potential problems (and how they can be overcome)
- Applications (after the break)

Fundamentals of Vibrational Spectroscopy

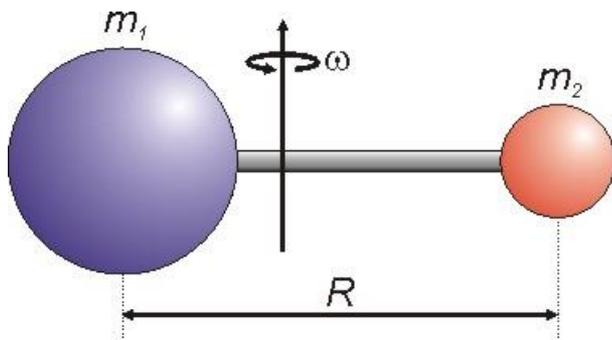


- Spectroscopy utilises energetic interactions between light and matter
- Molecular structure
 - Rotational structure
 - Vibrational structure
 - Overtone and combination bands

Fundamentals: Rotational Structure



Rotation of a diatomic molecule – classical rigid rotor



- m_1, m_2 : masses
- R : distance
- ω : angular velocity

Important quantities:

reduced mass:
$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

moment of inertia:
$$\Theta = m_1 R_1^2 + m_2 R_2^2 = \mu R^2$$

angular momentum:
$$L = \Theta \cdot \omega$$

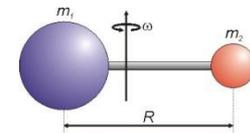
rotational energy:
$$E_{rot} = \frac{1}{2} \cdot \Theta \cdot \omega^2$$

However: arbitrary rotational energy is not possible in “molecular reality”

Fundamentals: Rotational Structure

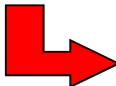


Rotation of a diatomic molecule – classical rigid rotor



Introduction of rotational quantum number J to describe the “real molecule”

$$L = \Theta \cdot \omega \qquad L^2 = \left(\frac{h}{2\pi} \right)^2 \cdot J(J+1) = \hbar^2 \cdot J(J+1) \qquad J = 0, 1, 2, \dots$$

 $E_{rot} = \frac{1}{2} \cdot \Theta \cdot \omega^2 = \frac{\hbar^2}{2\Theta} \cdot J(J+1)$ **quantised rotational energy of rigid rotor**

for spectroscopy we introduce $F(J) = \frac{E_{rot}}{hc} = B \cdot J(J+1)$

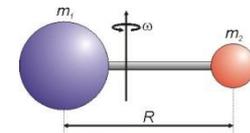
with the rotational constant $B = \frac{h}{8\pi^2 c \Theta}$ in the unit [cm⁻¹]

Note: in a real molecule there are (2J+1) degenerated sub-levels characterized by the magnetic quantum number $M = J, J-1, \dots, -J$

Fundamentals: Rotational Structure



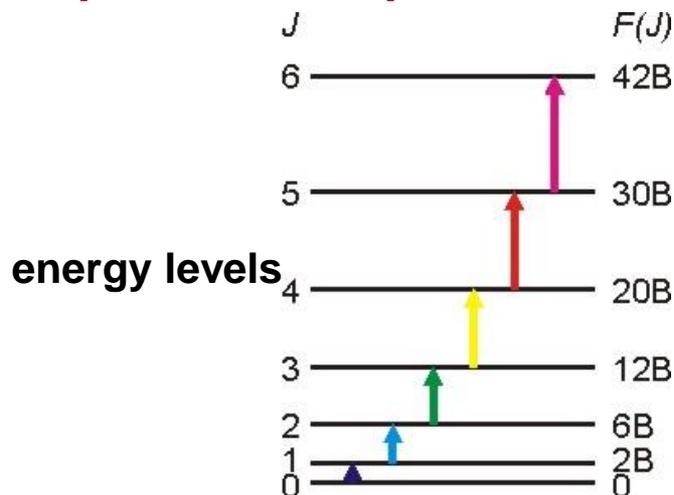
Rotation of a diatomic molecule – classical rigid rotor



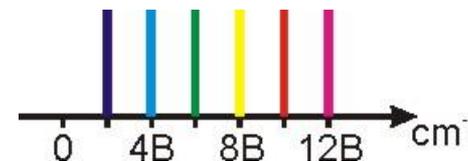
Pure rotational spectrum:

- selection rule for optical transition: $\Delta J = \pm 1$ (and $\Delta M = 0, \pm 1$)
- spectral line energy: $h\nu = E(J+1) - E(J)$
or in terms of wave numbers $\bar{\nu}_{J \rightarrow J+1} = F(J+1) - F(J) = 2B(J+1)$

→ spectrum of equidistant lines on the wavenumber scale (distance: $2B$)



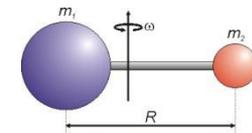
resulting spectrum



Fundamentals: Rotational Structure



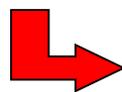
Rotation of a diatomic molecule – classical rigid rotor

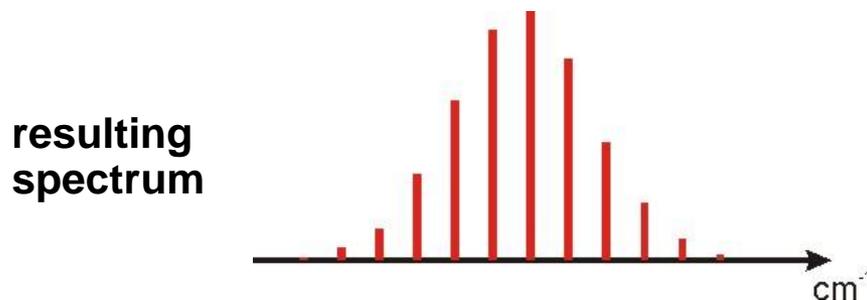


Line intensities:

- assumption: constant transition probability
- dependence on degree of degeneration: recall magnetic sublevels $(2J+1)$
- dependence on population distribution: Boltzmann

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} \cdot e^{-(E_J - E_0)/kT} = (2J + 1) \cdot e^{-BhcJ(J+1)/kT}$$

 spectrum of equidistant lines with intensity distribution



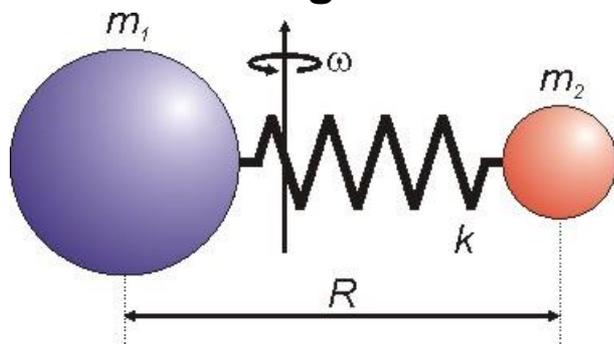
However: in a real molecule the internuclear distance is not constant

Fundamentals: Rotational Structure



Rotation of a diatomic molecule – classical non-rigid rotor

In a real molecule the distance R between the nuclei depends on the angular velocity due to centrifugal force \Rightarrow the higher ω the higher R



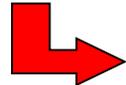
m_1, m_2 : masses

R : distance

ω : angular velocity

k : spring constant (Hooke's law)

Balance of forces: $\mu R \omega^2 = k(R - R_e)$ centrifugal force = spring force
 R_e internuclear distance at equilibrium

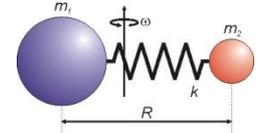
 energy of system:
$$E_{rot} = \frac{L^2}{2\mu R_e} - \frac{L^4}{2k\mu^2 R_e^6}$$

Again: arbitrary rotational energy is not possible in “molecular reality”

Fundamentals: Rotational Structure



Rotation of a diatomic molecule – classical non-rigid rotor



Introduction of rotational quantum number J to describe the “real molecule”

$$E_{rot} = \frac{\hbar^2}{2\mu R_e^2} \cdot J(J+1) - \frac{\hbar^4}{2k\mu^2 R_e^6} \cdot J^2(J+1)^2 \quad \text{quantized rotational energy of non-rigid rotor}$$

for spectroscopy we introduce $F(J) = \frac{E_{rot}}{hc} = B \cdot J(J+1) - D \cdot J^2(J+1)^2$

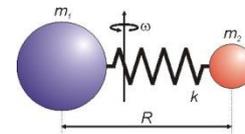
with the centrifugal stretching constant $D = \frac{\hbar}{4\pi k \Theta^2 R_e^2 c}$ in the unit $[\text{cm}^{-1}]$

Note: the ratio $D/B \approx 10^{-3} \dots 10^{-4} \Rightarrow D$ can be neglected for small J values

Fundamentals: Rotational Structure

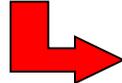


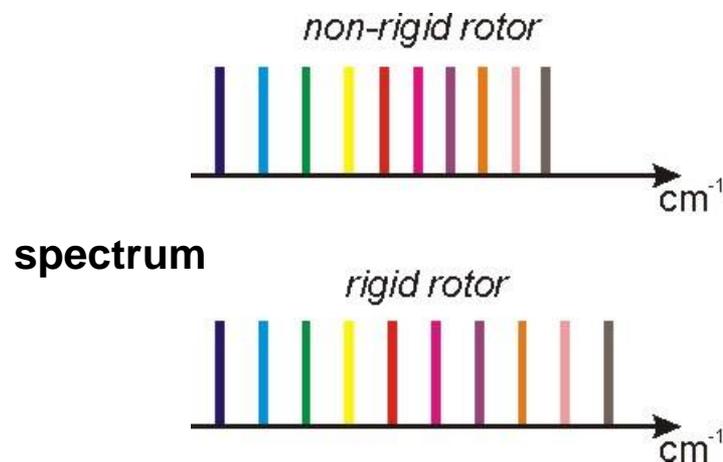
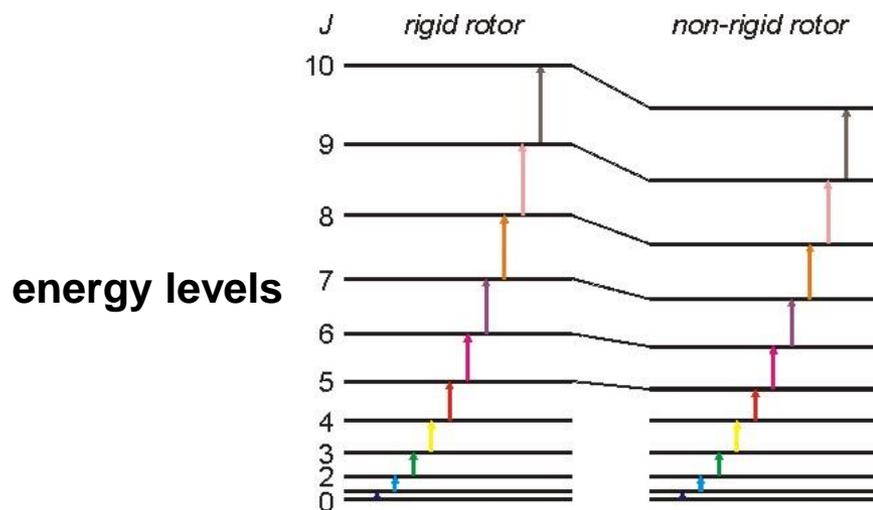
Rotation of a diatomic molecule – classical non-rigid rotor



Pure rotational spectrum:

- selection rule for optical transition: $\Delta J = \pm 1$ (and $\Delta M = 0, \pm 1$)
 - spectral line energy: $h\nu = E(J+1) - E(J)$
- or in terms of wave numbers $\bar{\nu}_{J \rightarrow J+1} = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3$

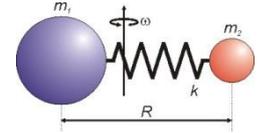
 **spectrum of non-equidistant lines**



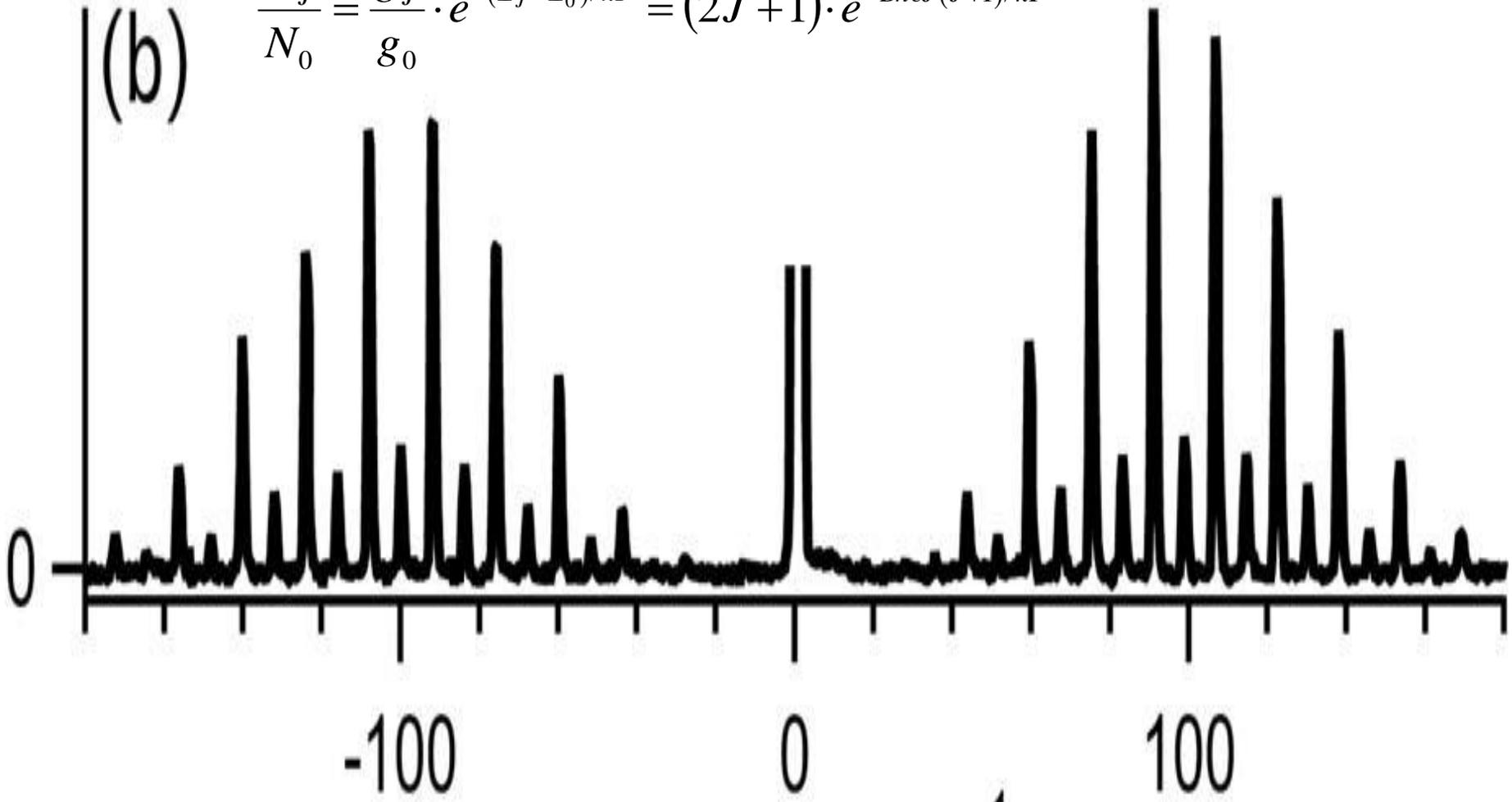
Fundamentals: Rotational Structure



Example: Nitrogen



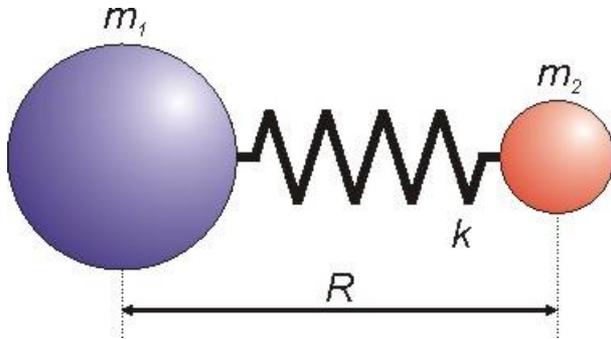
$$\frac{N_J}{N_0} = \frac{g_J}{g_0} \cdot e^{-(E_J - E_0)/kT} = (2J + 1) \cdot e^{-BhcJ(J+1)/kT}$$



Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – classical harmonic oscillator



- m_1, m_2 : masses
- R : distance
- ω : oscillation frequency
- k : spring constant (Hooke's law)

As a first approximation the system can be described by Hooke's law:

$$F = -k \cdot (R - R_e)$$

R_e internuclear distance at equilibrium

F Force

assuming pure Coulomb interactions:

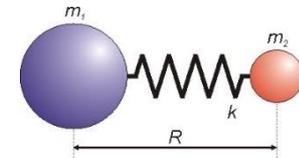
$$k = \frac{dF}{dr} = \frac{2e^2}{4\pi\epsilon_0 R_e^3}$$

eigenfrequency: $\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$ with the reduced mass $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$

Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – classical harmonic oscillator



Introducing the potential V (corresponding to the potential energy in a spring)

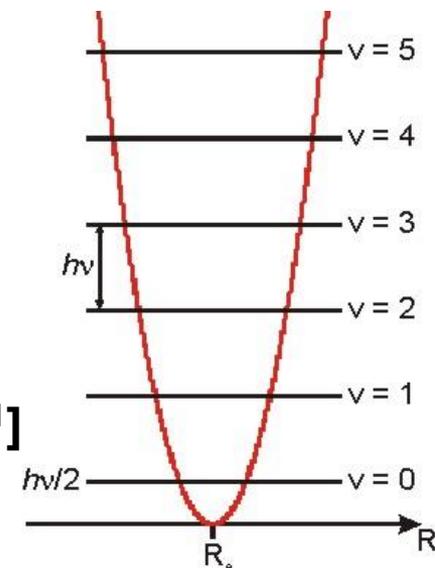
$V = \frac{k}{2} \cdot (R - R_e)^2$ which is basically a parabolic curve.

Further introducing the vibrational quantum number v , the energy levels are

given by $E_{vib} = \hbar\omega \cdot \left(v + \frac{1}{2} \right)$ with $v = 0, 1, 2, \dots$

for spectroscopy we introduce $G(v) = \frac{E_{vib}}{hc} = \omega_e \left(v + \frac{1}{2} \right)$

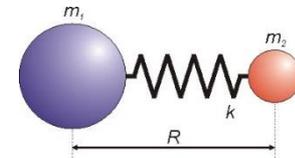
with the vibrational constant $\omega_e = \frac{\hbar\omega}{hc} = \bar{\nu}_e$ in the unit $[\text{cm}^{-1}]$



Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – classical harmonic oscillator



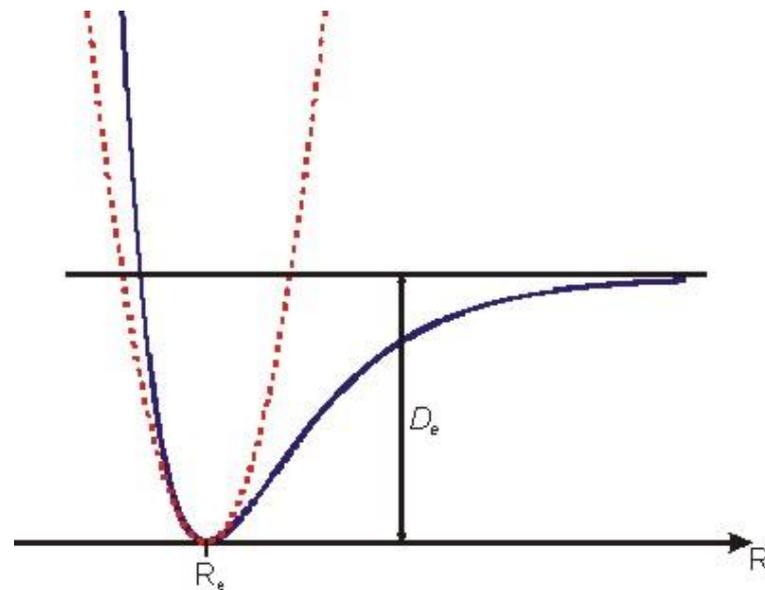
In reality the potential is not a parabolic curve:

- not only the Coulomb potential acts when $R < R_e \Rightarrow$ steeper slope
- weakening of bonding when $R > R_e \Rightarrow$ flatter slope

Morse potential: $V = D_e \cdot \left[1 - e^{-a(R-R_e)}\right]^2$

energy of dissociation D_e

molecule specific parameter $a = \omega_e \cdot \left(\frac{\mu}{2D_e}\right)^{1/2}$

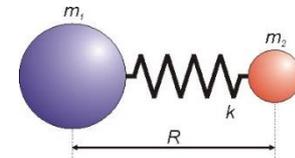


Note: for $R \approx R_e$ the harmonic oscillator potential is in good agreement with the anharmonic one

Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – classical harmonic oscillator



energy of the anharmonic oscillator

$$E_{vib} = \hbar\omega_e \cdot \left(v + \frac{1}{2}\right) - x_e \hbar\omega_e \cdot \left(v + \frac{1}{2}\right)^2$$

↑
 $2\pi\nu_e$

NOT the vibrational constant!

$$G(v) = \bar{\nu}_e \cdot \left(v + \frac{1}{2}\right) - x_e \bar{\nu}_e \cdot \left(v + \frac{1}{2}\right)^2$$

with the anharmonicity constant $x_e = \frac{\hbar\omega_e}{4D_e}$ (typically ~0.01)

selection rules:

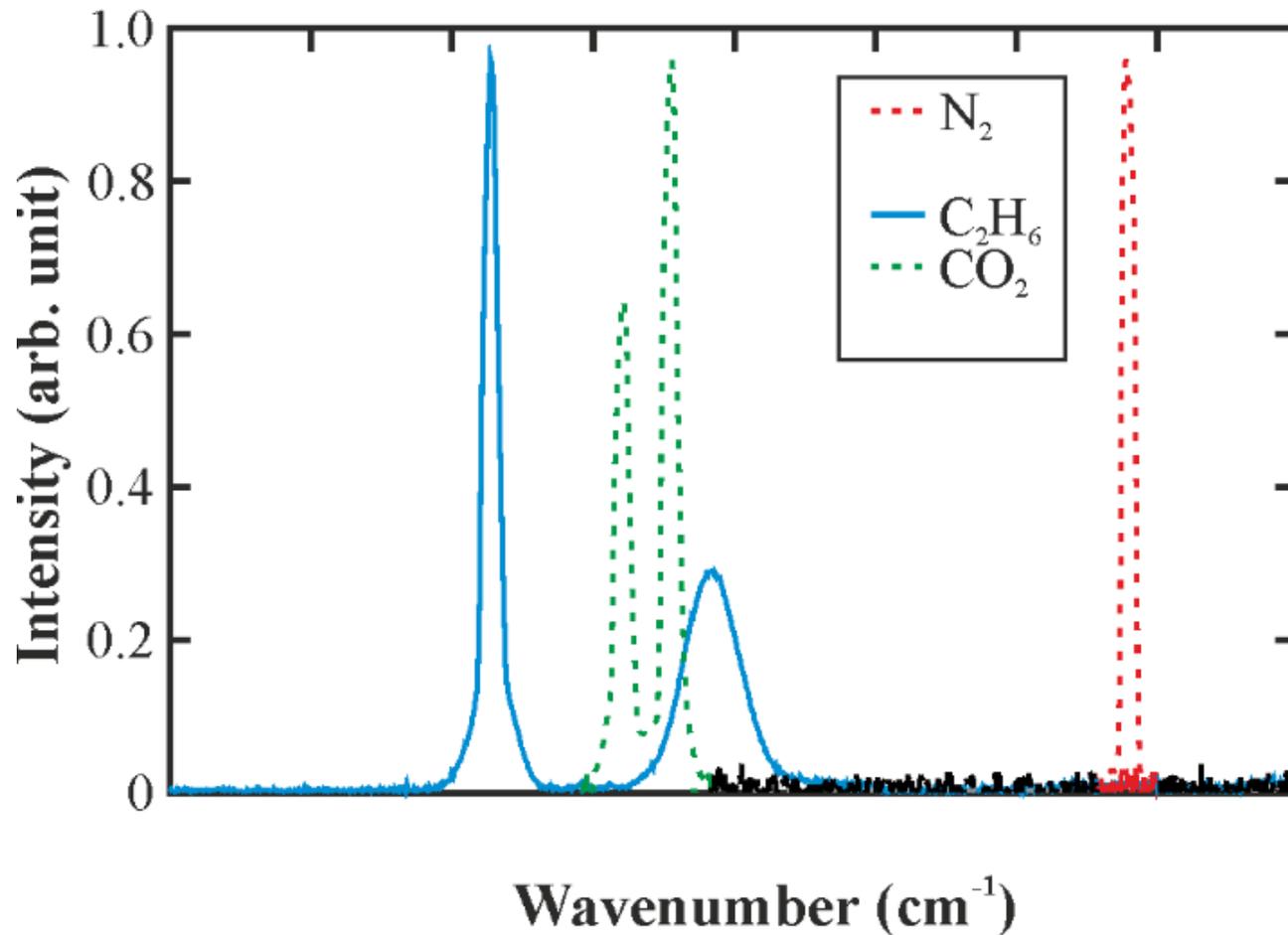
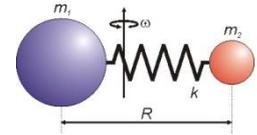
- harmonic oscillator: $\Delta v = \pm 1$
- anharmonic oscillator: $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ (overtone vibrations possible)

Note: the vibrational energy levels are not equidistant

Fundamentals: Vibrational Structure



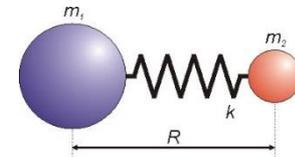
Example: Nitrogen, Ethane and Carbon dioxide



Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – classical harmonic oscillator



molecular vibration and rotation exert influence on each other

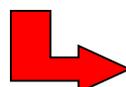
simplest approximation: rigid rotor + harmonic oscillator

$$E(v, J) = E_{vib}(v) + E_{rot}(J) = \hbar\omega \cdot \left(v + \frac{1}{2} \right) + BhcJ \cdot (J + 1)$$

vibrations much faster than rotation (~1000 oscillation during one rotation)

⇒ rotation with averaged internuclear distance R

averaged R increases with v ⇒ increasing moment of inertia ⇒ rotational constant B decreases

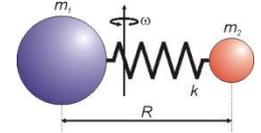
 rot. stretching (non-rigid rotor) + vib. stretching (anharmonic oscillator)

Note: vibration and rotation are strongly coupled with each other

Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – rovibrational structure



solution: introduction of a modified rotational constant

$$B_v = B_e - \alpha \cdot \left(v + \frac{1}{2} \right) + (\text{higher order terms})$$

B_e : theoretical rotational constant when no vibration occurs

α : molecule specific number ($\alpha \ll B_e$)

and a modified stretching constant

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

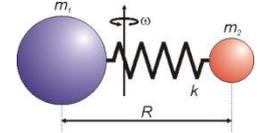
D : theoretical stretching constant when no vibration occurs

β : molecule specific number ($\beta \ll D$)

Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – rovibrational structure



the coupled rovibrational energy is given by

$$E(v, J) = \hbar\omega_e \cdot \left(v + \frac{1}{2}\right) - x_e \hbar\omega_e \cdot \left(v + \frac{1}{2}\right)^2 + B_v hcJ \cdot (J + 1) - D_v hcJ^2 \cdot (J + 1)^2$$

or for the spectroscopist

$$T(v, J) = G(v) + F(v, J) = \bar{\nu}_e \cdot \left(v + \frac{1}{2}\right) - x_e \bar{\nu}_e \cdot \left(v + \frac{1}{2}\right)^2 + B_v J(J + 1) - D_v [J(J + 1)]^2$$

the energy of an optical transition can be calculated by

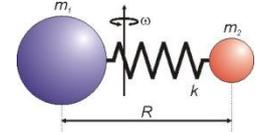
$$\Delta E = \underbrace{E(\text{final state}) - E(\text{initial state})}_{\text{molecular information}} = \underbrace{h\nu}_{\text{measured quantity}}$$

Note: terms of higher order are usually neglected but must be included especially when higher vibrational/rotational states are considered

Fundamentals: Vibrational Structure



Vibration of a diatomic molecule – rovibrational structure



nomenclature of optical transitions: according to the rotational quantum number change

$$\Delta J = 0 \quad : \quad \text{Q branch}$$

$$\Delta J = +2 \quad : \quad \text{S branch}$$

$$\Delta J = -2 \quad : \quad \text{O branch}$$

$$\Delta J = +1 \quad : \quad \text{R branch}$$

$$\Delta J = -1 \quad : \quad \text{P branch}$$

Note: the appearance of the individual branches corresponds to the selection rules which are dependent on the molecule geometry

Fundamentals: Vibrational Structure

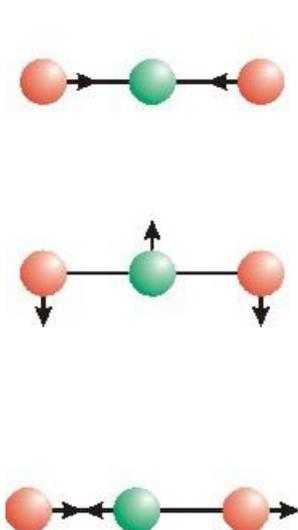


Vibration of polyatomic molecules

- in diatomic molecules there is only stretching vibration
- in polyatomic molecules deformation vibrations occur
- normal vibrational modes of triatomic molecules:

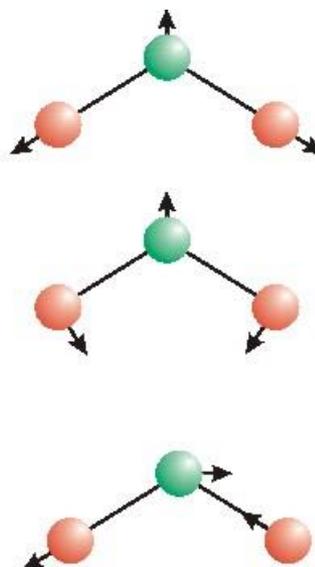
linear molecule

example: CO_2



angulate molecule

example: H_2O



Note: the normal modes do not influence each other

Fundamentals: Vibrational Structure



Vibration of polyatomic molecules

wavenumber range (cm ⁻¹)	vibrating group	remark
1400	C-H	scissoring
< 1500	C-X	X: halogenide
1650	C=C	
1700	C=O	
2200–2500	C≡C	
2349	CO ₂	
2850–3200	C-H	stretching
3100–3500	N-H	
3200–3600	O-H	usually broad band



Overtone vibrations

- assuming the harmonic oscillator the selection rule for vibrational modes is $\Delta v = \pm 1$
- in the anharmonic oscillator (this means for real molecules) additional transitions are allowed: $\Delta v = \pm 2, \pm 3, \dots$, which are called overtone bands
- the transition probability of overtone vibrations is much lower than that of normal modes

Note: the frequency of an overtone vibration is less than the doubled normal mode

Fundamentals: Vibrational Structure



Spectral ranges

regime	transitions	wavelength (μm)	wavenumber (cm^{-1})
NIR	overtone and combination bands	0.7-2.5	14300-4000
MIR	normal vibrational modes	2.5-50	4000-200
FIR	pure rotational	50-1000	200-10



- Rotational and vibrational spectra in a nutshell
- **Raman spectroscopy**
 - Raman effect and Raman activity
 - Instrumentation
 - Signal analysis
 - Potential problems (and how they can be overcome)
- Applications (after the break)

Raman Spectroscopy: Fundamentals



Fundamentals

- Raman spectroscopy is spectroscopy of **scattered light**
- When a molecule is exposed to an electric field, electrons and nuclei are forced to move in opposite directions \Rightarrow a **dipole moment is induced**

$$\mu = \alpha E$$

μ : induced dipole moment

α : molecular polarizability

E : electric field strength

- A vibration is **Raman active** only if the molecular polarizability is modulated by the normal vibration

$$\left(\frac{\partial \alpha}{\partial q} \right)_0 \neq 0$$

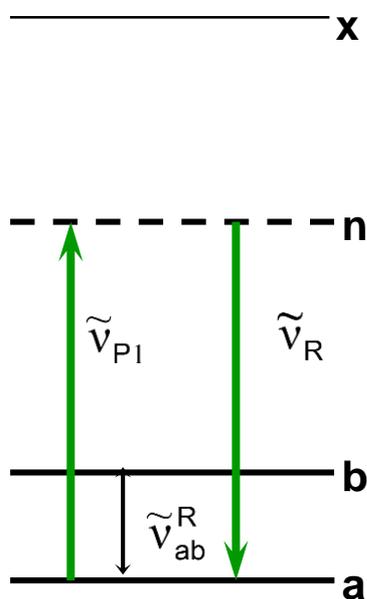
q : normal coordinate

Raman Spectroscopy: Fundamentals

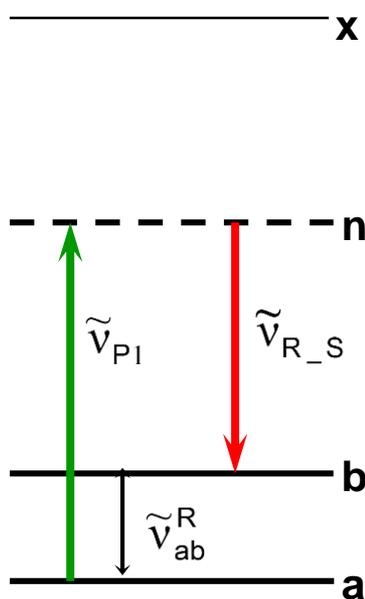


Fundamentals

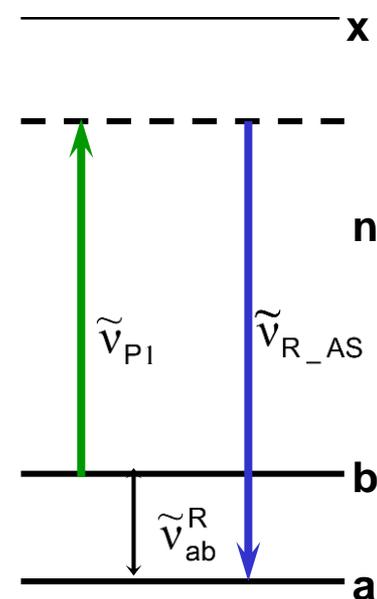
- A common scheme illustrating light scattering at molecules is



(i) Rayleigh



(ii) Raman Stokes



(ii) Raman anti-Stokes

**Albert Einstein about the difference between IR and Raman spectroscopy:
“Insert 10 cents into a Coke machine and receive a Coke: INFRARED; insert 1
Dollar and receive a Coke and 90 cents change: RAMAN”**



Experimental arrangement: light source

- A big advantage in Raman spectroscopy is the non-resonant excitation
⇒ lasers of arbitrary wavelength can be used
- The scattering cross section is strongly dependent on the laser wavelength

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)_{Raman} \propto \frac{(\tilde{\nu}_0 - \Delta \tilde{\nu}_R)^4}{\Delta \tilde{\nu}_R}$$

therefore short wavelengths deliver better signal-to-noise ratio.

- Gas diagnostics: Nd:YAG lasers (532nm, 355nm, 266nm); Excimer (248nm)
- Liquids and solids: Nd:YAG (1064nm), diode lasers (~800nm)

Note: at short wavelengths the molecules may be resonantly excited to a higher electronic state



Experimental arrangement: detectors

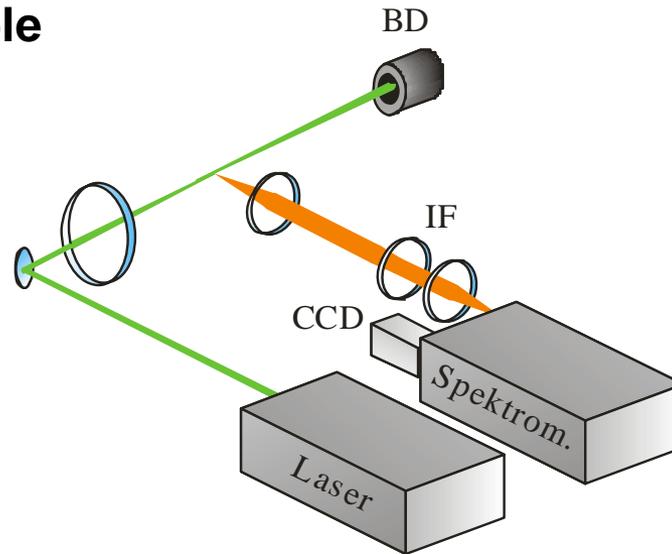
- Detectors employed for Raman spectroscopy are typically semiconductor based
- the signal is comparatively weak \Rightarrow intensified CCD cameras or back-illuminated CCD chips are common

Raman Spectroscopy: Instrumentation



Experimental arrangement: 90° detection

- The detection perpendicular to the laser beam path way is the most often used method for Raman spectroscopy
- high spatial resolution possible, well defined measurement volume
- experimentally simple



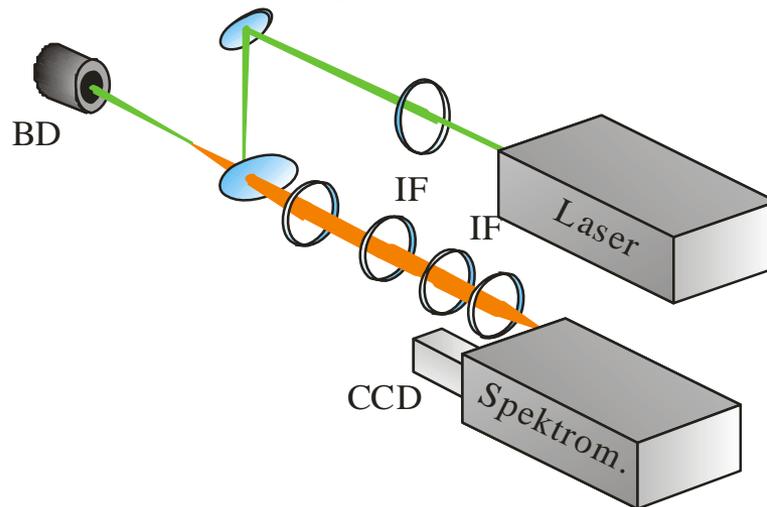
Note: the 90° detection scheme requires at least three optical accesses to the object of investigation

Raman Spectroscopy: Instrumentation



Experimental arrangement: backscattering detection

- The detection of the backscattered Raman signal can be arranged in a very compact setup
- spatial resolution only possible with additional spatial filtering
- Raman signals generated in the glass components may cause interferences



Note: in the backscattering scheme only two optical accesses to the object of investigation are necessary



Simple calibration of intensity vs. concentration

Sophisticated methods include

- **Chemometrics, e.g.,**
 - **Principal Component Analysis (PCA)**
 - **Partial least-squares regression (PLSR)**
 - **Principal Component Regression (PCR)**
- **Support vector machines (SVM)**
- **Artificial Neural Networks (ANN)**

Advantage: can deal with huge and highly complex data sets

Disadvantage: complicated and require large training data sets



Signal quantification by intensity ratio

- in general, the Raman signal intensity is given by

$$I = k I_0 n L \left(\frac{\partial \sigma}{\partial \Omega} \right)_{Raman} \Omega$$

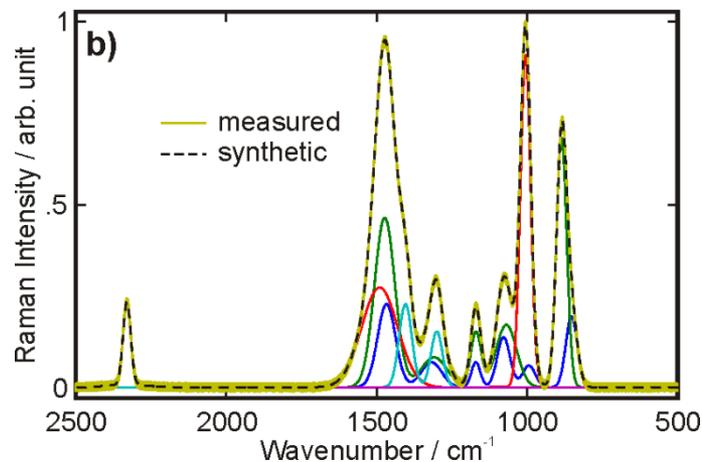
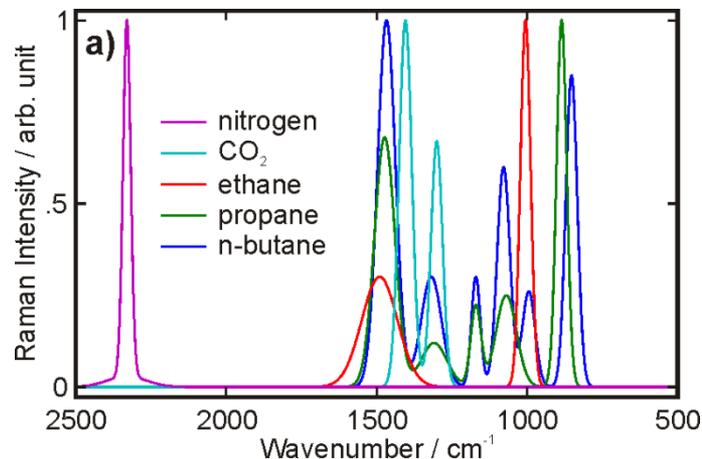
k	: calibration factor
I_0	: incident laser intensity
n	: number density
L	: probe volume length
Ω	: collection solid angle

- in order to correct for laser intensity fluctuations it is a common approach to determine concentration ratios (relative concentrations)

$$\frac{I_1}{I_2} = \frac{k I_0 n_1 L \left(\frac{\partial \sigma}{\partial \Omega} \right)_{Raman,1} \Omega}{k I_0 n_2 L \left(\frac{\partial \sigma}{\partial \Omega} \right)_{Raman,1} \Omega} = K \cdot \frac{n_1}{n_2}$$



Signal quantification by spectral soft modeling



Evaluation of mixture spectrum by fitting a synthetic spectrum generated from a superposition of pure component spectra

Zehentbauer, Kiefer
Chem. Today – Chimica Oggi 30 (2012) 54-57.

Note: the described procedures can be used only in gases and simple liquids

Applications: Natural Gas Analysis



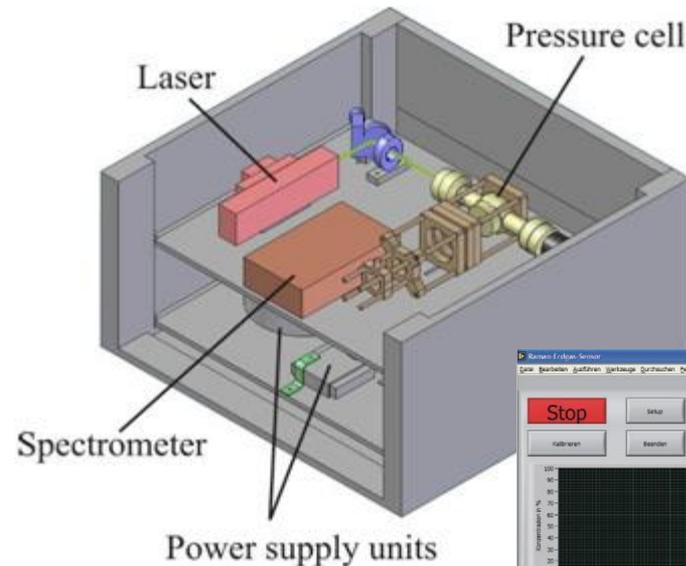
Background of project

- Combustion behaviour in gas turbines depends on fuel composition
- For process control the composition information must be provided with high accuracy and temporal resolution
- Nowadays: Technology in place
 - **Calorimetry**
 - ☞ only integral information about calorific value
 - ☞ not sufficient for control purposes
 - **Gas chromatography**
 - ☞ compositional information with high accuracy
 - ☞ time resolution in the order of minutes
 - ☞ not sufficient for control purposes

Applications: Natural Gas Analysis



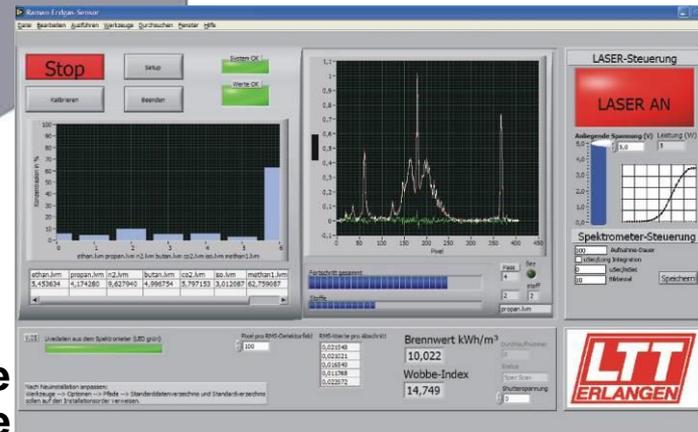
Raman based sensor for power plant applications



Schematic sensor setup

Application in gas turbine power plant

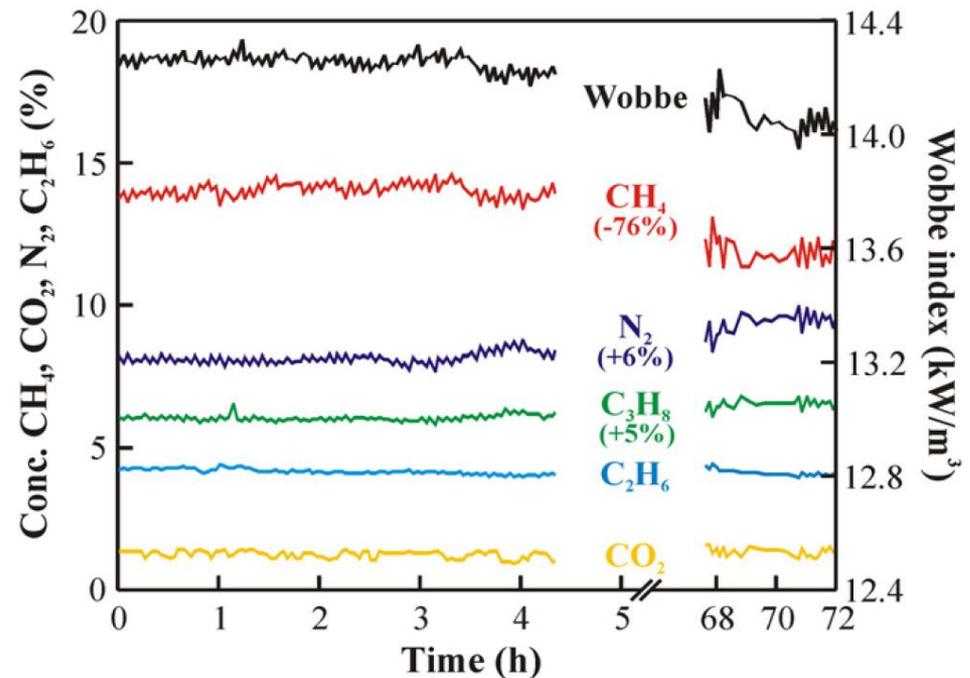
Control software user interface



Kiefer, Seeger, Steuer, Schorsch, Weigl, Leipertz
Meas. Sci. Technol. 19 (2008) 085408.



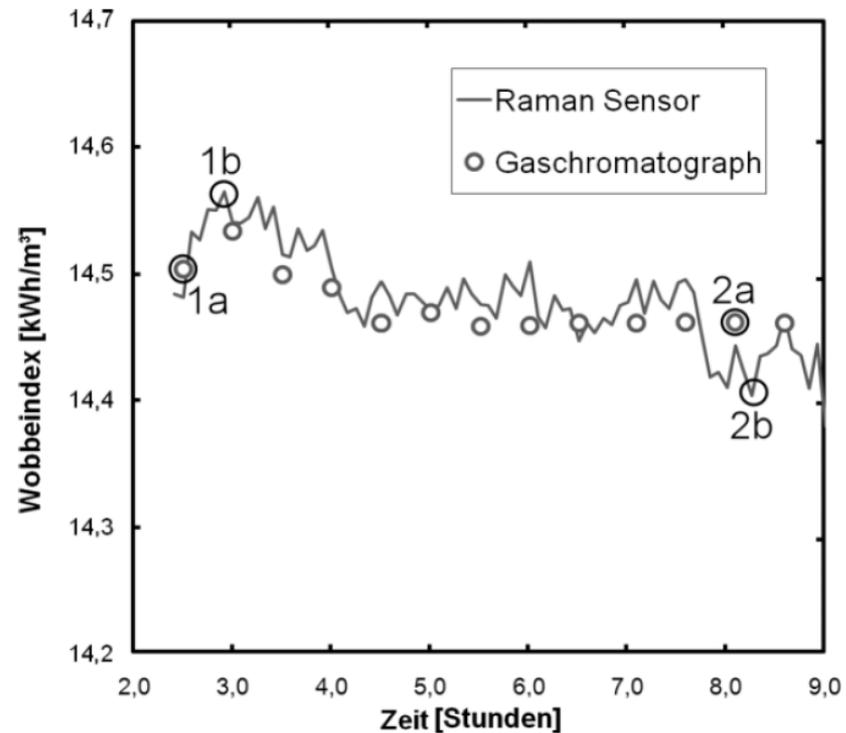
Raman based sensor for power plant applications



**Results from long term
measurement campaign in GT
power plant**

Kiefer, Seeger, Steuer, Schorsch, Weigl,
Leipertz
Meas. Sci. Technol. 19 (2008) 085408.

Raman based sensor for power plant applications



Comparison with GC

Schorsch, Kiefer, Steuer, Seeger,
Leipertz, Gonschorek, Abröll, Käß
Chem. Ing. Techn. 83 (2011) 247-253.



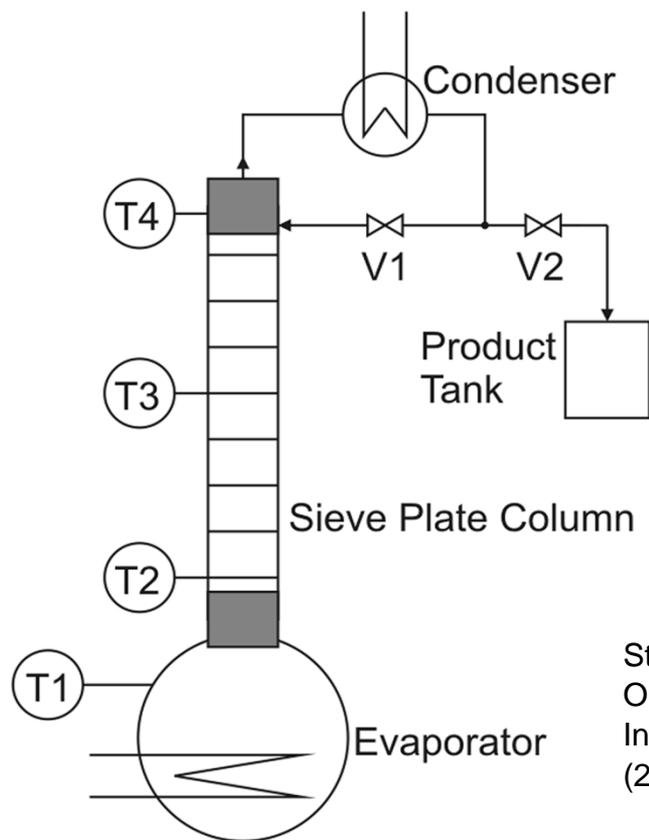
Background of project

- Distillation processes are of great importance, e.g., in the **petrochemical industry**
- **Compositional analysis is complicated and time consuming (GC, HPLC)**
 - **process control is difficult**
- **Multiple parameters influence product composition:**
 - **Feed composition**
 - **Heating strategy**
 - **Reflux strategy**
 - **Additives and impurities**
- **Aim of project:**
 - ☞ **Establish Raman spectroscopy as a tool for distillation column monitoring**
 - ☞ **Show potential for analysing mixtures of liquid hydrocarbons**

Applications: Distillation Process



Distillation facility



Struthers, Zehentbauer,
Ono-Sorhue, Kiefer
Ind. Eng. Chem. Res. 50
(2011) 12824–12830.

Figure 1. Schematic diagram of the distillation facility. T1–T4 are thermocouples, and V1 and V2 are valves to control the reflux ratio.

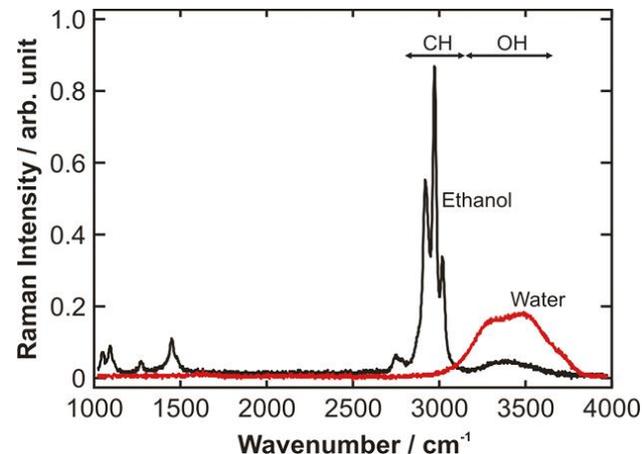


Figure 2. Experimental Raman spectra of pure ethanol and pure water. The spectral regions utilized for calibration are indicated by arrows.

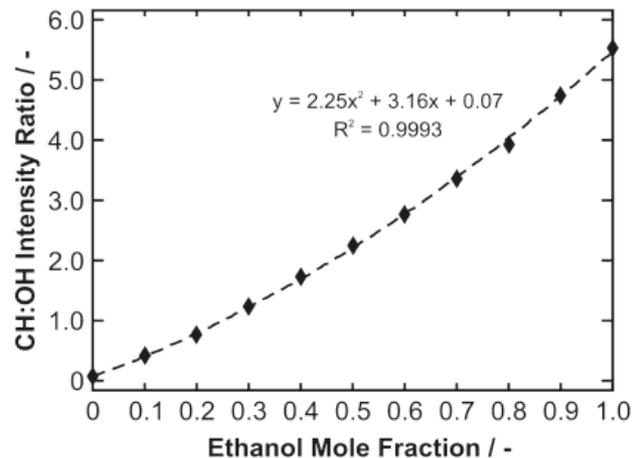
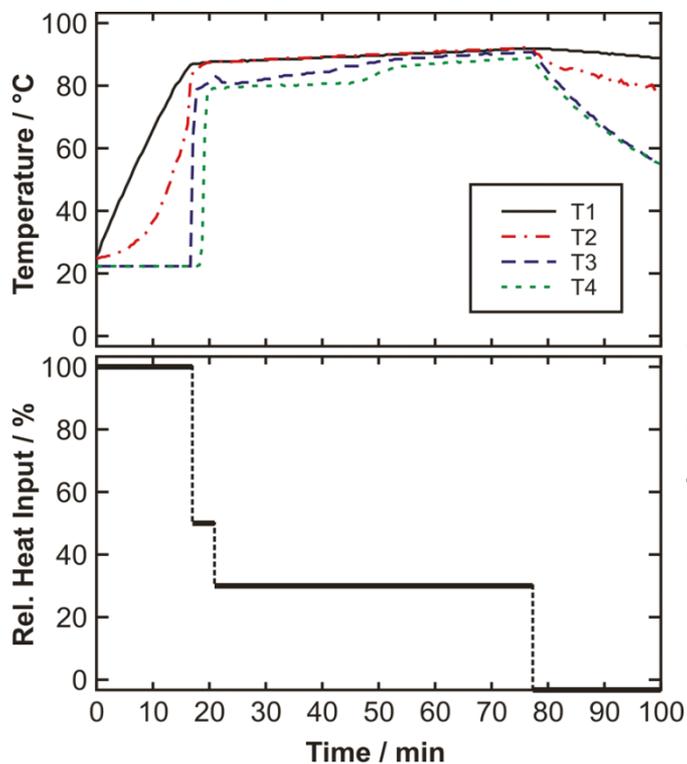


Figure 3. Calibration curve for binary ethanol/water mixtures. The diamonds represent experimental data; the dashed line is the best-fit second-order polynomial function.

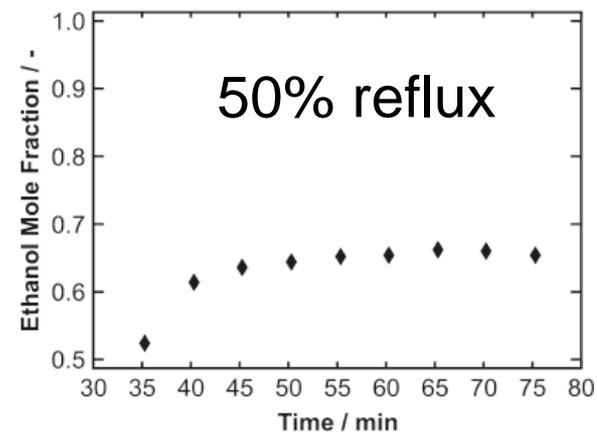
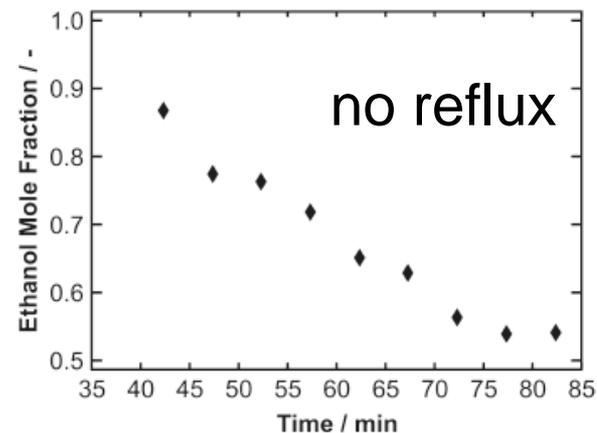


Product monitoring



Exemplary heating strategy and thermal column behaviour

Struthers, Zehentbauer, Ono-Sorhue, Kiefer
Ind. Eng. Chem. Res. 50 (2011) 12824–12830.





Hydrocarbon mixture analysis

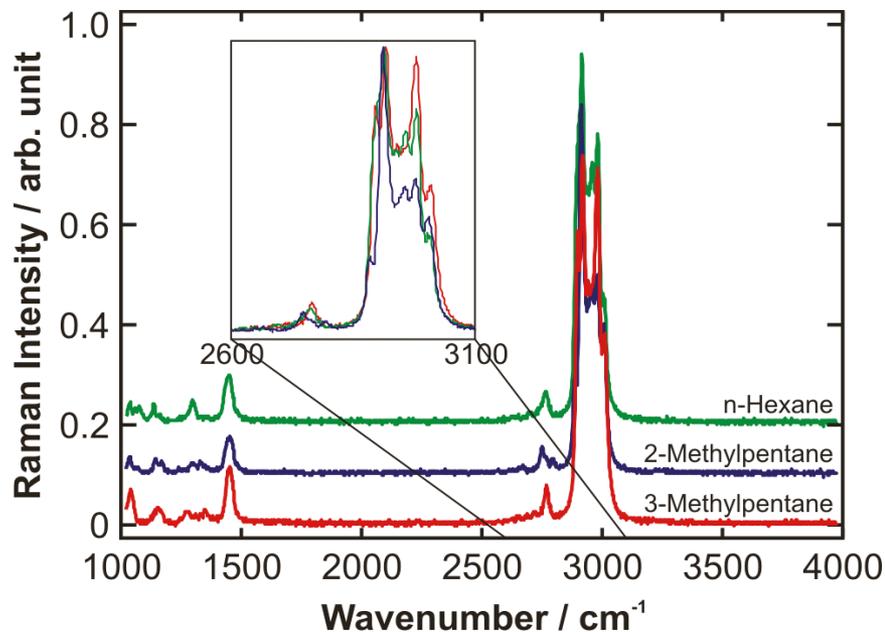


Figure 12. Raman spectra of pure *n*-hexane and its isomers 2-methylpentane and 3-methylpentane. The inset shows the enlarged CH stretching region.

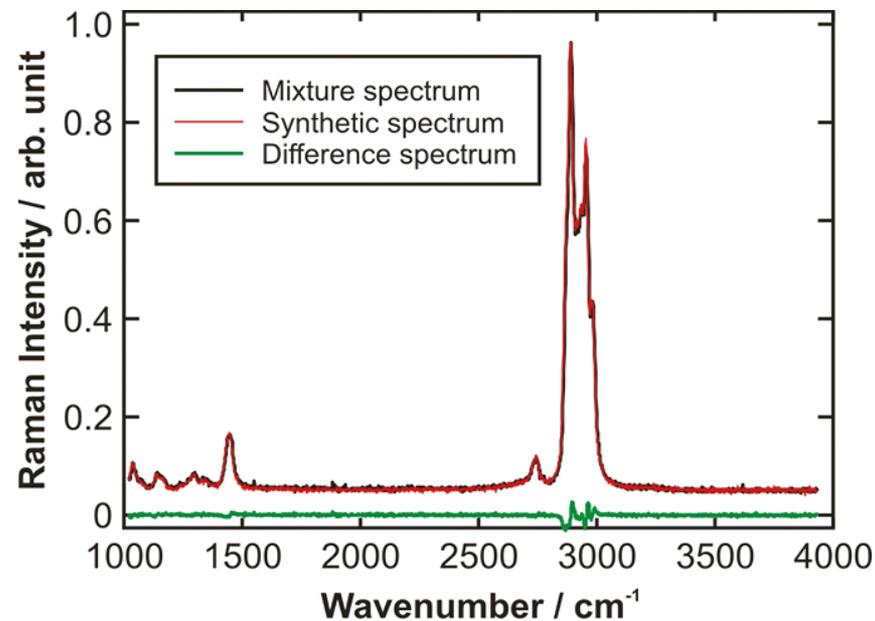


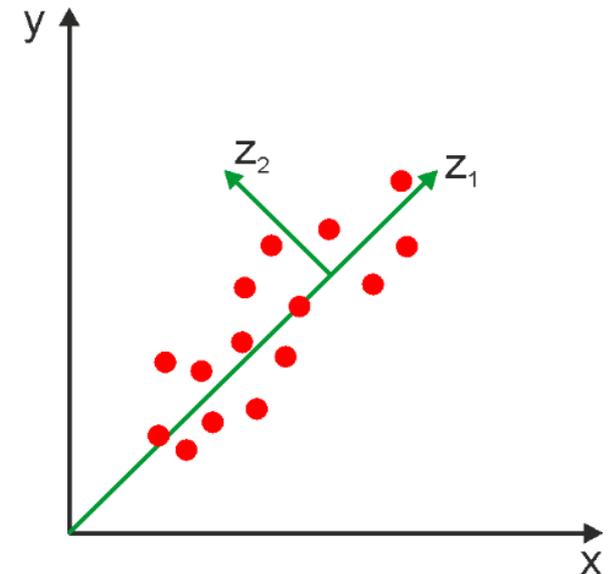
Figure 13. Experimental spectrum from a ternary mixture of hexane isomers and the best-fit synthetic spectrum. The difference between the two is indicated underneath.



Signal quantification by chemometrics

- PCA and PLSR of Scotch whisky

$$\begin{array}{c} (I \times J) \\ \text{X} \end{array} = \begin{array}{c} (I \times F) \\ \text{S} \end{array} * \begin{array}{c} (F \times J) \\ \text{L}' \end{array} + \begin{array}{c} (I \times J) \\ \text{E} \end{array}$$



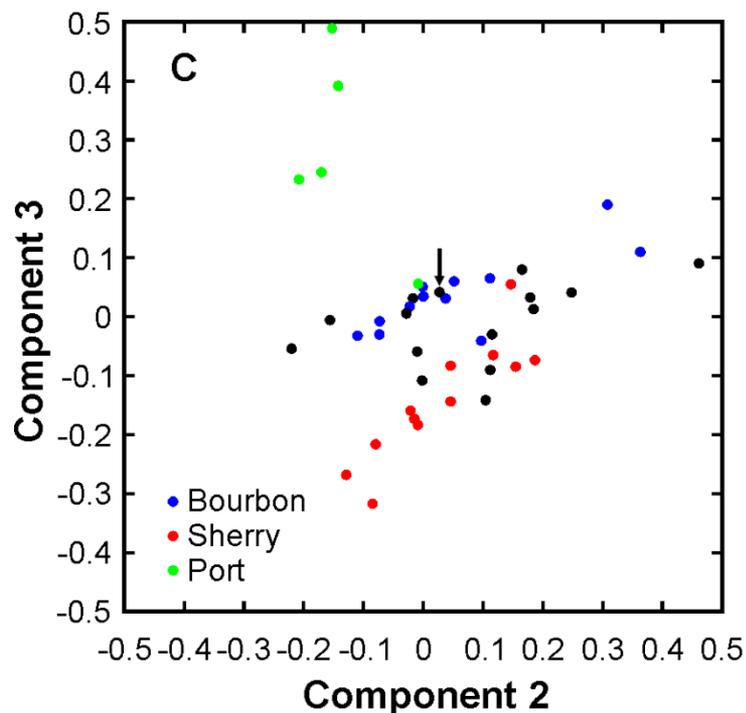
- The PCs can then be utilized in a regression analysis

Raman Spectroscopy: Composition Analysis

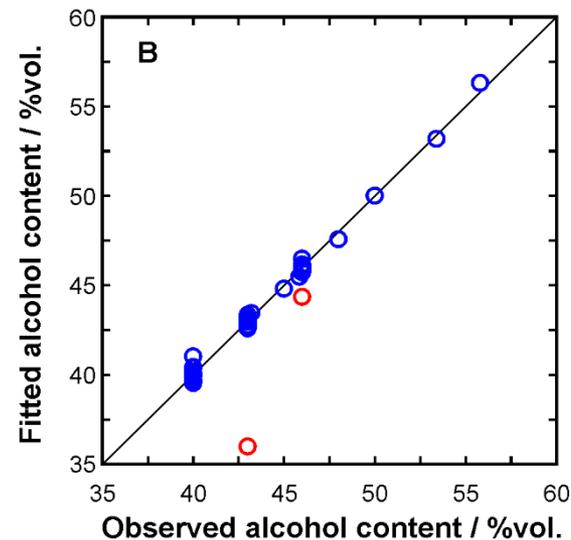
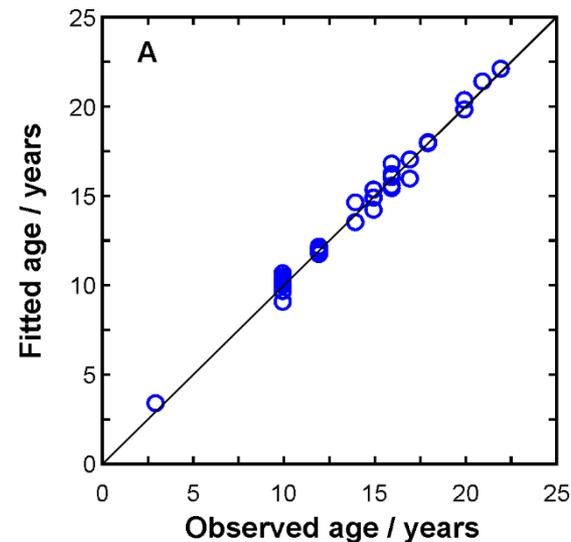


Signal quantification by chemometrics

- PCA and PLSR



PCA allows determination of cask type



PLSR

Kiefer, Cromwell, Analytical Methods 9 (2017) 511–518.

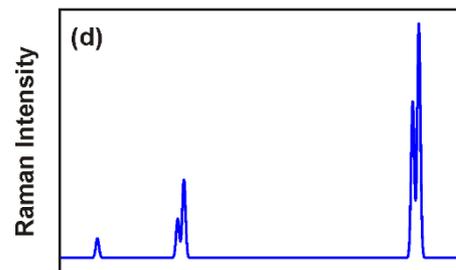
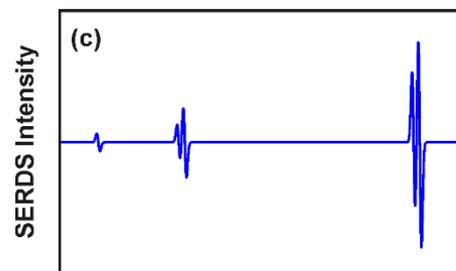
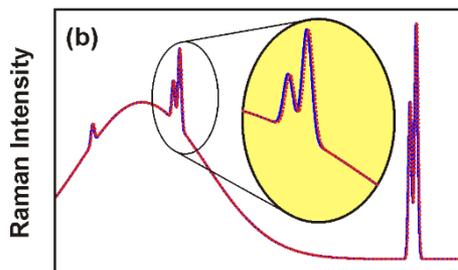
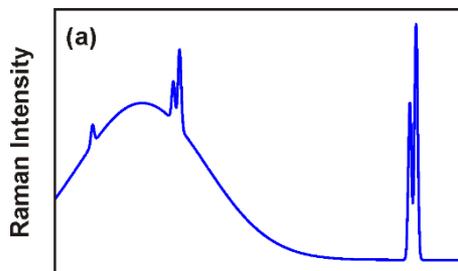
Raman Spectroscopy: Problems



Potential problems and how to solve them

- Fluorescence and elastically scattered light
 - Post-processing: baseline correction

- Experimental: SERDS

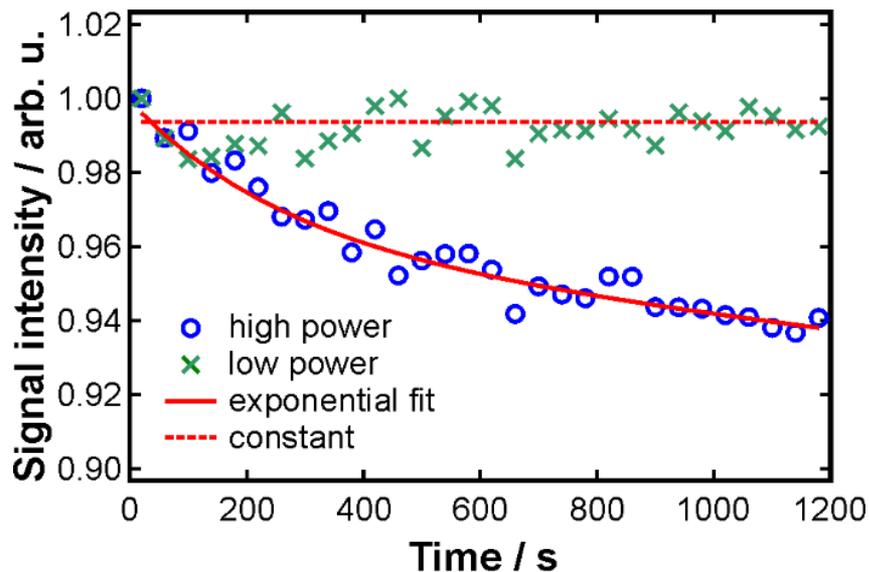


Raman Spectroscopy: Problems



Potential problems and how to solve them

- Sample Degradation



Kiefer, Cromwell, Analytical Methods 9 (2017) 511–518.



- Banwell and McCash, “Fundamentals of Molecular Spectroscopy”, McGraw Hill
- D. A. Long, „Raman Spectroscopy“, McGraw Hill Higher Education Gebundene, 1977
- J. Kiefer, “Recent Advances in the Characterization of Gaseous and Liquid Fuels by Vibrational Spectroscopy”, *Energies* 8 (2015) 3165-3197; doi:10.3390/en8043165

Raman Spectroscopy for Underwater Sensing

Johannes Kiefer

**Technische Thermodynamik
Universität Bremen, Germany**



- Raman Spectroscopy in aqueous systems
- Raman spectroscopy in sea water
- Applications

Raman Spectroscopy in aqueous systems



- Water has a low Raman scattering cross section

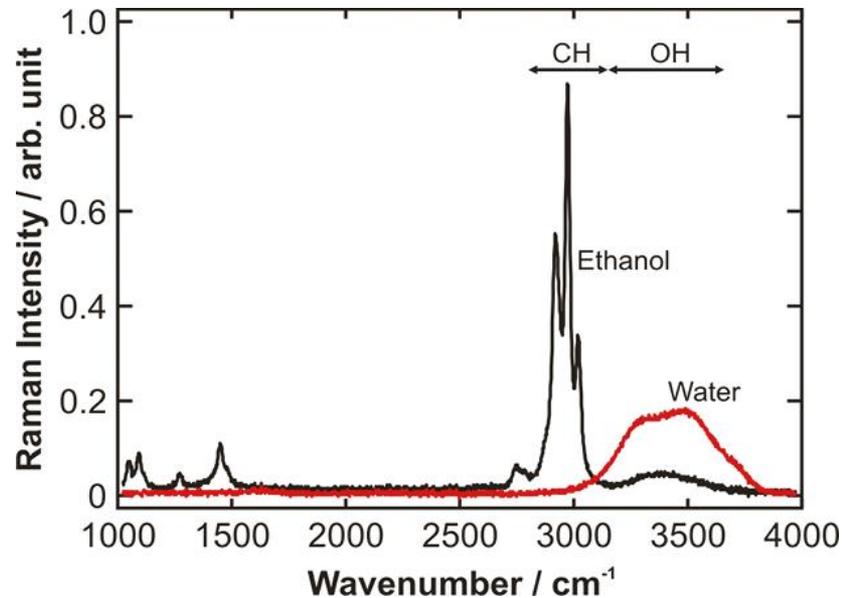


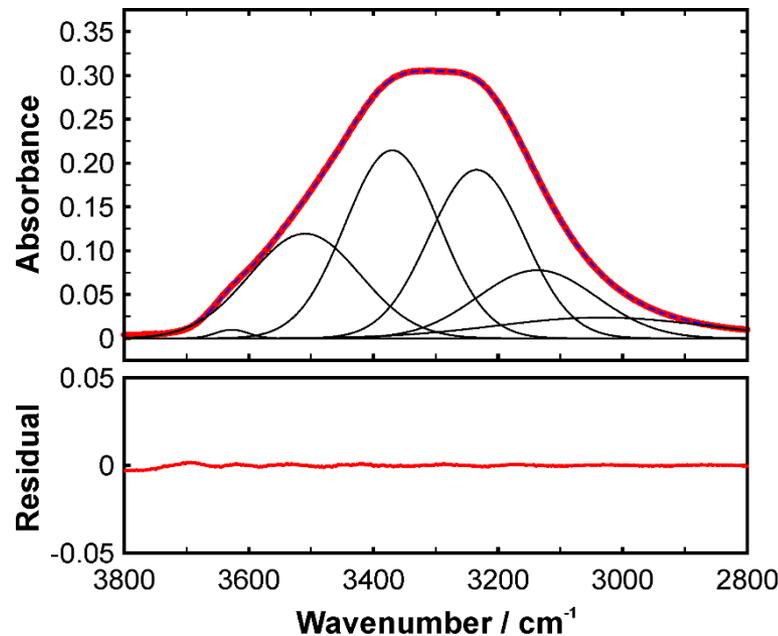
Figure 2. Experimental Raman spectra of pure ethanol and pure water. The spectral regions utilized for calibration are indicated by arrows.

Struthers, Zehentbauer,
Ono-Sorhue, Kiefer
Ind. Eng. Chem. Res. 50
(2011) 12824–12830.

➤ Advantageous for dynamic range of measurement



- OH stretching band



V.M. Wallace, N.R. Dhumal, F.M. Zehentbauer, H.J. Kim, J. Kiefer, *Journal of Physical Chemistry B* 119, 14780-14789 (2015).

- Advantageous because of rich information
- Disadvantageous because of complexity

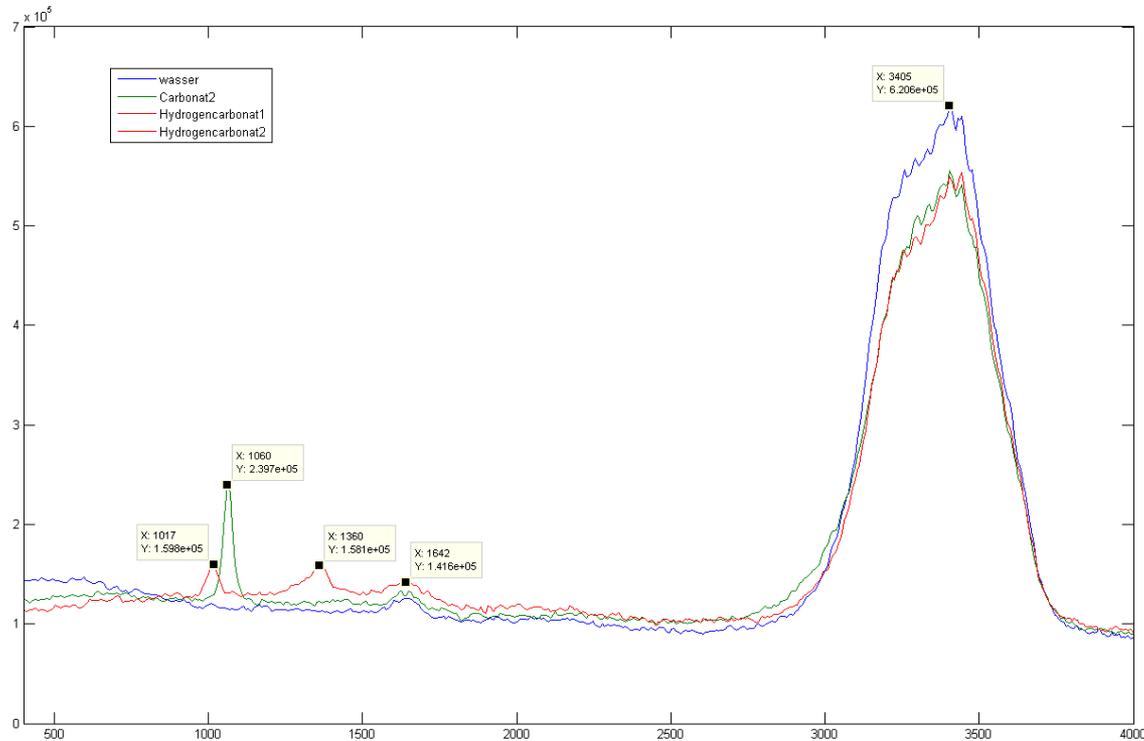


- Sea water contains a large variety of chemical substances (and other stuff...)
 - Dissolved salts
 - Cations: sodium, potassium, magnesium, ...
 - Anions: carbonate, chloride, bromide, sulfate, ...
 - Dissolved gases
 - Nitrogen, oxygen, carbon dioxide, methane, ...
 - Liquids
 - Carbon dioxide, hydrocarbons, ...
 - Microorganisms, small animals, ...

Raman Spectroscopy in sea water



- Salts
 - Molecular anions (carbonate, hydrogencarbonate, sulfate, nitrate) have their own vibrational signature



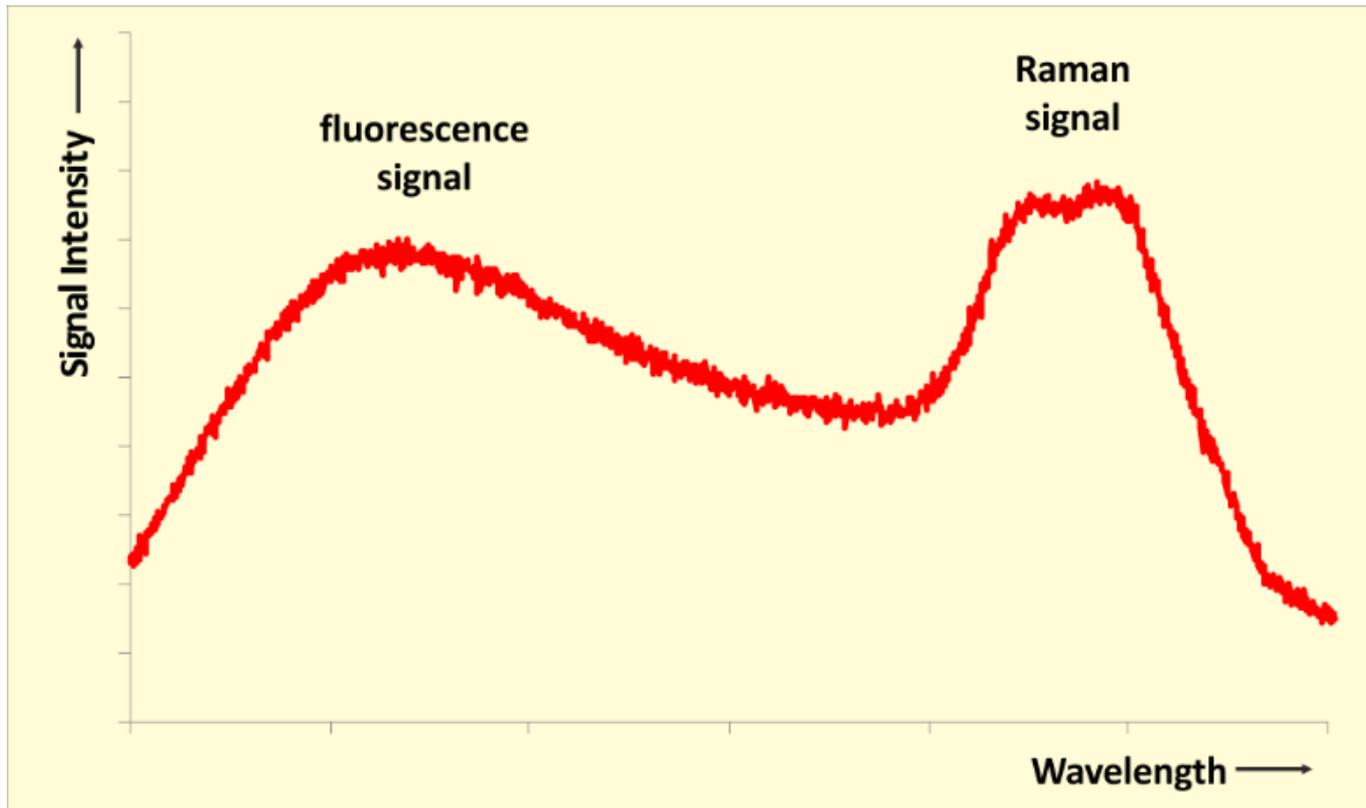


- Dissolved gases and liquids

Raman Spectroscopy in sea water



- Organic substances
 - Possibility of fluorescence interference





- Raman Spectroscopy in aqueous systems
- Raman spectroscopy in sea water
- Applications

Details on Subsea Raman can be found in:



- J.D. Pasteris, B. Wopenda, J.J. Freeman, P.G. Brewer, S.N. White, E.T. Peltzer, G.E. Malby,
“Raman Spectroscopy in the Deep Ocean: Successes and Challenges”
Applied Spectroscopy 58 (2004) 195A-208A.
<http://journals.sagepub.com/doi/pdf/10.1366/0003702041389319>
- X. Zhang, W.J. Kirkwood, P.M. Walz, E.T. Peltzer, P.G. Brewer,
„A Review of Advances in Deep-Ocean Raman Spectroscopy”
Applied Spectroscopy 66 (2012) 237-249
<http://journals.sagepub.com/doi/full/10.1366/11-06539>

Note: These Focal Point Articles are free for download from the website of Applied Spectroscopy.