

Hoorcollege

Vibrational spectroscopy Theory & Practice

Lecturer: Dr. Jörg Matysik
Language: English
Literature: Syllabus
Doelgroep: MSc students in Chemistry.
Also MSc students of other fields & PhD students are welcome.

Programme (details see below):

1. Intellectual toolbox
METHODS
2. Infrared spectroscopy
3. Raman & Resonance Raman spectroscopy
4. Advanced & related methods
THEORY
5. Vibrational frequencies
6. Intensities
7. Linewidths

Start: Mon. 31 Aug 2009 in LCP16 at 11.00

Other dates: 4, 7, 11, 14, 18, 25, 28 Sept, 2, 5, 9, 12 Oct 2009.

Mondays 11-13, Fridays 13-15, always in LCP-16.

Date for vraaguur and tentamen will be announced later.

From each participant (or a team of two participants), a presentation of 15-20 min is expected.

Further information:

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The programme

1. Intellectual toolbox

1.1 From classical to quantum mechanics

Black body, limits of classical physics, Basics of quantum mechanics

1.2 Mechanical potentials & vibrations

Harmonic & Morse potentials, laws of Hooke & Newton, harmonic oscillator, types of molecular vibrations

1.3 Energy distribution

Maxwell & Boltzmann distributions, Molecular energy distribution, Eyring theory

1.4 Photophysics & Photochemistry

Absorption, Einstein factors, Lambert Beer, Fluorescence, Jablonsky diagrams, Laws of photochemistry, competing photochemical processes

1.5 Refraction, reflection & scattering

Snell's law, reflection, Rayleigh, Raman & Mie scattering

METHODS

2. Infrared (IR) spectroscopy

2.1 History & principle

2.2 Setup of a dispersive spectrometer

IR-radiation sources, monochromator, gratings, detectors, spectrometers

2.3 Setup of a Fourier-transform (FT) IR spectrometer

Spectrometer, interferogramme, Fourier-transformation, Michelson interferometer, apodisation, other interferometers

2.4 Sample states

Cuvettes, tablets, suspensions, low temperature, gasses,

2.5 IR in reflection & ATR

2.6 IR in emission

2.7 The IR spectrum

*First inspection, Examples: **some organic compounds***

3 Raman & Resonance Raman spectroscopy

3.1 Overture

History, principle, Feynman diagram, set-up, polarisability

3.2 The Resonance Raman (RR) effect

- *Excitation in the visible, example: haem*
- *excitation in the UV, example: cytochrome-c*
- *surface enhancement*

3.3 Time-resolved Raman spectroscopy

- *Spinning cell*
- *pulsed pump-probe, example: bacteriorhodopsin*
- *flowing cell, example: cyt-c oxidase*

3.4 Fourier-transform (FT) Raman

Jacquinot and multiplex advantages, sampling optics: Kubelka-Munk, sample arrangements: fiber optics, micro & 2D scanning arrangements, collecting optics.

3.5 Time-resolved FT spectroscopy

- *Low-temperature. Example: phytochrome*
- *rapid scan*
- *stroboscope technique*
- *step scan, example: bacteriorhodopsin*

4 Advanced & related methods

4.1 Rotations

4.2 Low-frequency modes: far-IR (FIR), Terahertz (THz)

*Measuring temperatures, modes between 400 and 10 cm^{-1} ,
Examples: Boson peaks in glasses
THz spectrometer, principles, THz imaging, examples:
retinal, HCl*

4.3 Overtones: Near-IR

4.4 IR chemiluminescence

Molecular beams, Eyring theory, basics of chemical reactions

4.5 Non-linear Raman processes

- *Stimulated Raman effect, femtosecond stimulated Raman, example: carotene*
- *Hyper Raman effect*

4.6 Two-dimensional vibrational spectroscopy

Comparison to NMR, Pump-probe, Cross-peaks due to mode coupling, Example: α -helical peptide

4.7 Other spectroscopic scattering methods

- Brillouin scattering, Fabry-Perot interferometer,
- Inelastic neutron scattering, example: **liquid water**

THEORY

5 Vibrational frequencies

5.1 Concepts for calculations

*Electronic structures, methods for computer calculations, di- & polyatomic molecules, normal mode analysis, Wilson's FG matrix method, number of vibrations, examples: **amide modes, open-chain tetrapyrroles***

5.2 Empirical rules

Stretching modes, inter-molecular interactions

5.3 Force constants

5.4 Isotope effects

5.5 Overtones and combination modes

*Fermi-resonances, example: **CO₂***

5.6 Symmetry of molecules

Point groups

5.7 Symmetry of vibrations

*Example: **water molecule**, character tables*

6. Intensities

6.1 Infrared intensities

Einstein coefficients, Transition dipole moment

6.2 Raman intensities: Classical molecule in classical field

6.3 Raman intensities: q.m. molecule in classical field

6.4 Raman intensities: q.m. description

- *Sum-over-states picture*
- *time-dependent picture*

7. Linewidths

7.1 Overtone

Information of a spectral line, linewidth & line shape

7.2 The natural linewidth

The Lorentz function, Rayleigh criterion

7.3 Broadening effects

*Doppler broadening, Gauss and Voigt functions,
molecular hits, aggregate states*

7.4 Molecular symmetry & rotational pattern

*The four forms of the spinning top, Examples: Ethine,
cyclopropane, water, ethene*

7.5 Homogeneous & inhomogeneous broadening

Example: Hydrogen-bonding of liquid water

7.6 Experimental broadening effects

Monochromator, interferometer, Raman laser

Last update: 20 May 2009