IRS Infrared Spectroscopy Experiments

Location:	HCI H290	Group:	25
Date:	March 30 2021, 13:00 Uhr	Assistant:	**Luis Fábregas Ibáñez**
Report deadline:	April 23 2021		*luis.fabregas@phys.chem.ethz.ch*

How to prepare to the introduction

Read the document [1] as a good preparation to the IR experiment. Additional recommended references are listed at the end of this task list.

Experiments

Note: Spectrometer settings and sample details have to be recorded clearly. Each team works strictly independently to collect its own data (preparing solutions, measuring spectra) unless otherwise specified. Measurements are made with Bruker Alpha FT-IR spectrometers, equipped with ATR and Transmission modules, respectively.

A — Measurement basics

With the ATR module measure the IR absorption spectrum of pure liquid or solid substance. Background and sample interferograms are measured and, with the spectrometer software, processed to obtain the single intensity spectra and finally the transmission and the absorption spectrum of the sample. With this example, explain and illustrate the route from the interferograms to the absorption spectrum.
Compare the absorption spectrum with one taken from literature [2]. Assign prominent bands in the spectrum to the vibration of certain functional groups.

B — Verification of measurement reproducibility

Check, with liquid and solid samples, whether the ATR technique gives reproducible spectra (with respect to absorbance values and wavenumber positions of individual peaks). Take 3 measurements of each substance, replacing the sample between the measurements.

C — Absorption spectrum of liquid DMSO exposed to ambient air

DMSO is a highly hygroscopic substance and tends to absorb water by simple exposition to ambient air. IR allows us to monitor this phenomenon. Prepare a sample of fresh DMSO and measure 10 absorption spectra by waiting (e.g. 3 minutes) between measurements (without changing the sample).
Plot all spectra, identify the water wavenumbers, and plot the absorbance values A against time t. Find an appropriate model function $A(\phi_t)$ that fits the data.

D — Absorption spectra and identification of plastics

ATR-IR spectroscopy has a lot of industrial applications, one of them being quality control. Databases exist to identify *e.g.* polymers [3,4].
Measure absorption spectra of selected polymer samples. Draw the spectra in an overview for easy identification or differentiation. Assign prominent bands in the spectra to the vibration of certain functional groups.

E — Absorption spectra of binary solutions of water and ethanol

IR spectra of binary solutions of water (w) and ethanol (e) strongly depend on the composition. Prepare 12 binary solutions (including pure substances) with known volume fractions $\phi_e = V_e/(V_e + V_w)$ and measure the absorption spectra of these samples with the ATR technique. Plot all spectra (full range and details) and discuss the spectral changes.
At a selected wavenumber determine absorbance values A and plot them against ϕ_e. Find an appropriate model function $A(\phi_e)$ that fits the data. Repeat the procedure with absorbance data taken at two other wavenumbers.
Measure the absorption spectrum of a sample of a liquor (*e.g.* wine, grappa, whisky, etc. feel free to bring a sample from home) and determine the alcohol content using the above calibration graphs.

F — Vibrational spectra and transition energies of isotopomers

Measure the IR absorption spectrum of a compound (*e.g.* H_2O or $CHCl_3$) and of its deuterated analogon. Verify (by calculation of the reduced masses μ) the shift of the vibration wavenumber upon isotopic substitution [1].

G — Rotational-vibrational spectra of diatomic molecules

At high resolution, IR absorption spectra of small molecules may be observed with discrete rotational-vibrational transitions, see [1]. Aim of this experiment is to prepare several gaseous samples, to measure well-resolved spectra in a gas cell and to study and analyze the spectra of diatomic molecules to obtain specific molecular parameters such as bond lengths with high precision.
The discrete vibrational-rotational energy levels of a diatomic molecule can be described by

$$E_{\text{vib,rot}} = h\nu_0 \left(v + \tfrac{1}{2}\right) - h\nu_0 x_\text{e} \left(v + \tfrac{1}{2}\right)^2 + hc \left(B_\text{e} - \alpha(v + \tfrac{1}{2})\right) J(J+1) \quad ,$$

$$B_\text{e} = \frac{h}{8\pi^2 \mu c R_\text{e}^2} \quad ,$$

v and J: vibrational and rotational quantum number, respectively, ν_0: frequency of the harmonic vibration, x_e: anharmonicity constant, B_e: equilibrium rotational constant, α: rotation-vibration constant, R_e: equilibrium bond length.
Rotation-vibration absorption transitions $(v = 0, J'') \rightarrow (v = 1, J')$ within the fundamental vibration transition occur at discrete transition wavenumbers

$$\tilde{\nu} = \frac{E_{v=1,J'} - E_{v=0,J''}}{hc} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_\text{e} + \left(B_\text{e} - \tfrac{3}{2}\alpha\right) J'(J'+1) - \left(B_\text{e} - \tfrac{1}{2}\alpha\right) J''(J''+1) \quad .$$

A simple method uses two differences of out of four transitions, *e.g.*

transition	ΔJ	change of J	transition	ΔJ	change of J
$R(0)$ transition	$+1$	$J'' = 0 \rightarrow J' = 1$	$P(1)$ transition	-1	$J'' = 1 \rightarrow J' = 0$
$R(1)$ transition	$+1$	$J'' = 1 \rightarrow J' = 2$	$P(1)$ transition	-1	$J'' = 2 \rightarrow J' = 1$

Explicit expressions of $\tilde{\nu}$ for each of the four transitions are given in [1]. In the experiment you will determine the wavenumbers of these transitions from the absorption spectrum and further calculate the equilibrium bond length R_e of the molecule.

Literature

[1] E. Meister, *Infrarotspektroskopie* (provisorische Versuchsanleitung), ETH ZÃ¼rich (5.4.2020).

[2] J. Coates, Interpretation of Infrared Spectra, A Practical Approach, in: R.A. Meyers, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, 2006.

[3] SDBS Spectral Database for Organic Compounds, National Institute of Advanced Industrial Science and Technology (AIST), Japan.
sdbs.db.aist.go.jp/sdbs (9.3.2020).

[4] *Polymer Sample Identification Using Quest ATR*, Specac Application Note 42, *www.specac.com/en/documents/application-notes/polymer-identification-quest-application-note* (9.3.2020).

Lab report

Consult the appendices B and C in the praktikum book and the document *Lab Report Correction Checklist* when preparing your report! The report should present quantitative as well as qualitative findings of your experiments, clearly described and with context to theory and literature references. Just consider your report a research paper!
Deadline to hand in the signed report (per email to `luis.fabregas@phys.chem.ethz.ch` and C.C. to `erich.meister@phys.chem.ethz.ch`) is **April 23 2021**.
Please add to your report:
- This task list
- copies of your lab journal
- program codes used
- all regression summaries

Please attach a ZIP file with all measured data, R files and report PDF to the email.