

Spectrograph

Motivation

Spectroscopy is the study of the interaction between matter and radiated (or absorbed) energy. The energy dependent (color dependent) emission and/or absorption of light by a certain medium give insight into the internal structure of the atoms or molecules of this medium. Spectroscopic studies were of essential importance for the development of quantum mechanics and are very useful tools in modern analysis. In order to get to the information encoded in the radiation of interest, the light must be split up into its frequency components; the instruments that perform this task are called spectrographs or spectrometers. In this laboratory exercise, different spectrographs will be introduced and characterized; additionally, a molecular spectrum will be recorded and analyzed.

Wikipedia Keywords (for preparation at home)

spectrograph, dispersion, optical resolution, spectral resolution, energy levels, diatomic molecules, molecular spectra, vibronic spectroscopy, dissociation energy

Literatur

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Introduction

Spectrographs

Spectrographs are used to split up light into a frequency spectrum; the obtained signal is displayed on a screen or recorded with a camera. Prisms or gratings are used as dispersive elements (dispersion = the phenomenon where an optical property depends on the frequency of the radiation).

The light, which is to be examined, must illuminate the narrow entrance slit of the spectrograph. A collimator lens collects the light passing through the slit and creates a parallel light bundle. This parallel beam either passes through one or more prisms or is diffracted by one or more gratings, which leads to a frequency dependent angular deflection of the light. After traversing through the dispersive element(s), the rays of a certain frequency are still parallel, but rays of different frequencies spread at different angles. A camera lens finally focusses (ideally) all the parallel beams of the different frequencies into one plane, where either the screen or the recording device can be placed. Each frequency of the incoming light will create a spatially separated (ideally) image of the slit (= spectral lines) in the previously mentioned focal plane.

In practice, the entrance slit cannot be made infinitely small, and the lenses have a finite size and are not free of aberrations, which lead to a certain width of a line stemming from a single frequency; i.e. lines that lie very close to each other may overlap. Furthermore, the dispersive elements themselves have a limited resolution power, which is the quality criterion of a spectrograph and is defined as the quotient of the wavelength λ , divided by the smallest separable wavelength difference $\Delta\lambda$ between two lines (Rayleigh criterion) at that wavelength.

$$resolution = \frac{\lambda}{\Delta\lambda}$$

This way, higher numbers correspond to better devices.

In order to be able to relate spectral lines of a recorded spectrum to certain wavelengths, the recorded spectrum must be compared to a known line spectrum. This spectrum must be recorded using the same alignments of the instrument. Since 1960, the red line of the ^{86}Kr isotope has been defined as a basis with a wavelength of $\lambda = 605.7802106 \text{ nm}$. Additionally, more than 300 lines of an iron spectrum (iron arc lamp) are connected to this standard, which are usually used as references. When undertaking exact measurements, one must consider that the experimentally determined wavelengths usually refer to standard conditions (air, 15°C, 760 Torr) while theoretically predicted values generally refer to vacuum conditions.

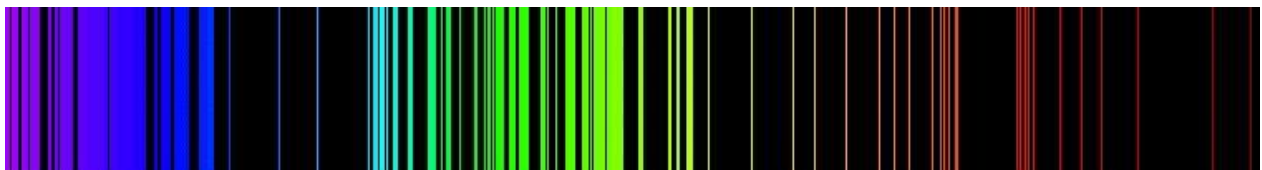


Fig. 1: Iron spectrum.

Prisms

Following the Fresnel equations, light that falls on the interface of a prism is transmitted and/or reflected. The respective intensity depends on the incident angle and the refractive index of the prism. The transmitted light beams are deflected when passing through the prism, obeying the well-known law of refraction:

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2(\lambda)}{n_1(\lambda)} \quad \text{with} \quad n_{\text{air}} \approx 1 \quad n_{\text{prism}} \approx 1.5$$

The frequency (or wavelength) dependence of the refractive index $n = n(\nu)$ leads to the dispersive property of a prism. When using materials with normal dispersion (dispersion: $dn/d\nu > 0$), the deflection of longer wavelengths (red) is smaller than that for shorter wavelengths (blue). Within the visible range, the refractive index n of glass changes by about 1 %, which leads to an angular splitting of 1-5° between red and blue light in a single prism. To enlarge the splitting, multiple prisms can be used (3 in this exercise).

The theoretical resolution power of a prism can be calculated using:

$$\frac{\lambda}{\Delta\lambda} = t \frac{dn}{d\lambda} \quad \text{with} \quad t \dots \text{base length of the prism} \quad \frac{dn}{d\lambda} \dots \text{material dispersion}$$

but can normally not be reached due to the before mentioned practical limitations.

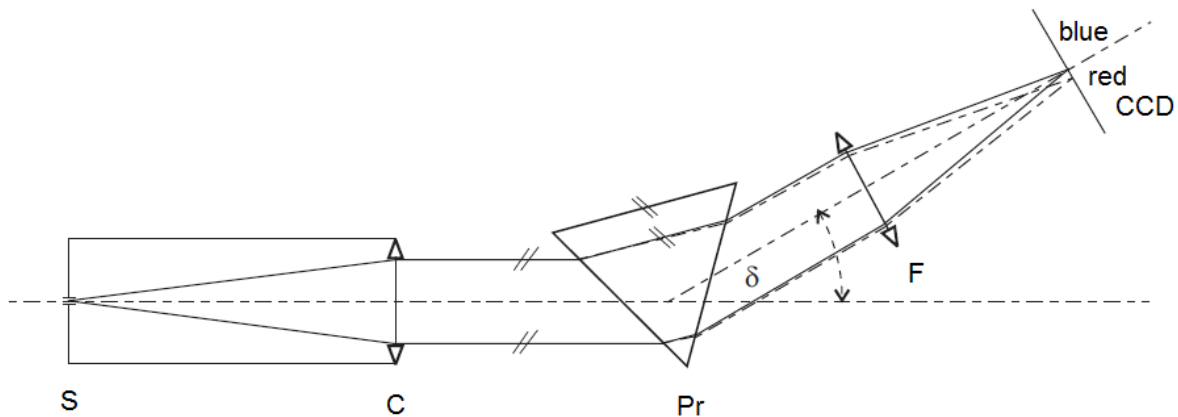


Fig. 2: Setup of a simple prism spectrograph with slit “S”, condenser lens “C”, prism “Pr”, focusing lens “F” and CCD-chip of the digital camera (taken from Ref. 7 and modified).

Gratings

When monochromatic light falls on a grating orthogonally, the diffracted light will have maxima at certain angles θ_m given by:

$$d \sin(\theta_m) = m \lambda$$

Gratings with narrower slits lead to a wider split-up of the peaks and the more slits are illuminated, the sharper the peaks become. If a grating is illuminated with light consisting of more than one frequency, all orders higher than zero split up into a frequency spectrum, with the violet side being closer to the zeroth order; the higher the order, the larger the frequency splitting is. These principles hold true for reflection gratings as well as for transmission gratings.

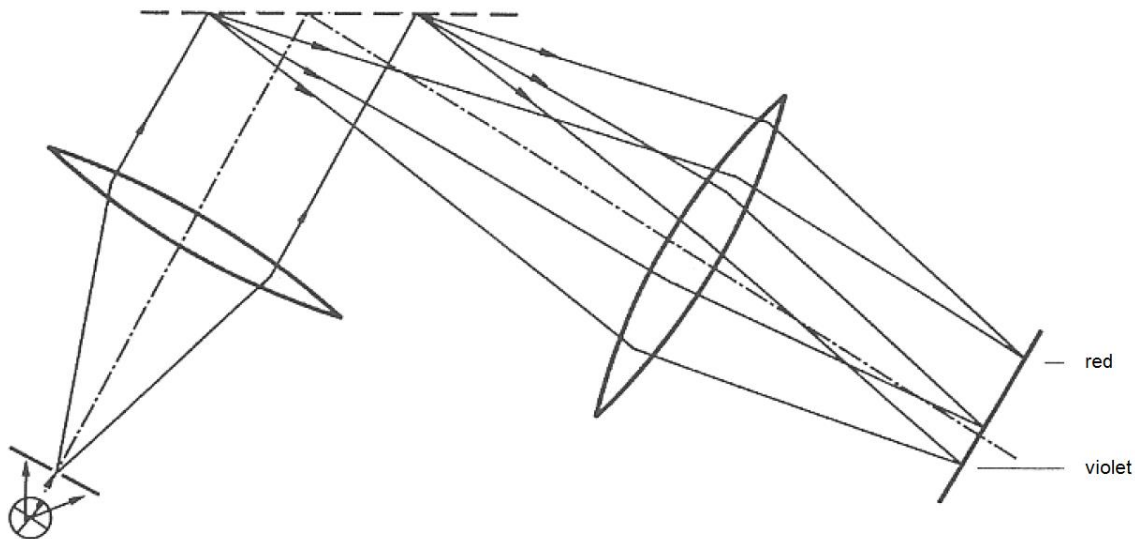


Fig. 3: Setup of a simple grating spectrograph (taken from Ref. 7 and modified).

The resolution power of a grating can be estimated by:

$$\frac{\lambda}{\Delta\lambda} = kN \quad k \dots \text{order} \quad N \dots \text{number of illuminated grating-lines}$$

As very simple gratings CDs, DVDs or blue ray discs can be used (bonus exercise in this laboratory). The following table gives the track pitch of the different media:

CD	1600 nm
DVD	740 nm
Blue ray disk	320 nm

Determination of molecule constants from the recorded spectra

This section is a summary of chapter M2 in Ref. 5. In contrast to single atoms, which only possess electronic energy levels, molecules are able to absorb and emit energy additionally in form of oscillatory or rotational energy. Following the laws of quantum mechanics, these energies are quantized as well; only discrete energy levels are possible. These extra-possibilities increase the variety of emitted spectral lines enormously. Therefore, molecule spectra are much more complicated than atomic spectra and can mostly only be interpreted using theoretical models. Even though these models only describe some aspects of the spectra, using them it is possible to gain important molecule parameters (e.g. momenta of inertia, binding force constants, equilibrium core distances, etc.) with their help.

In the visible range of molecule spectra, a structuring in so-called spectral bands (deutsch: Banden) is striking. These bands consist of many close lying spectral lines, which get closer and closer to each other towards the band edge. The different bands correspond to certain electronic transitions and the various lines within these bands correspond to states with different initial or final oscillatory or rotational energy.

Oscillatory energy levels are defined by:

$$E_{\text{harm}} = \hbar\omega_0 \left(v + \frac{1}{2} \right) \quad \text{for a harmonic oscillator, or}$$
$$E_{\text{Morse}} = k_1 \left(v + \frac{1}{2} \right) - k_2 \left(v + \frac{1}{2} \right)^2 \quad \text{for the more accurate Morse-potential}$$

Where v is the oscillatory quantum number and k_1 and k_2 are constants. This means that in reality the oscillatory levels are not equidistant. The higher the oscillatory quantum number v , the closer the levels are. In the Morse-potential as in real molecules, the potential is not infinitely high on one side. Therefore the maximum oscillatory quantum number is not infinity and there is a finite distance between the highest two levels.

There are selection rules for allowed transitions which state that $\Delta v = \pm 1$. This only holds true for the harmonic oscillator, in reality also $\Delta v = \pm 2, \pm 3, \pm 4, \text{ etc.}$ are possible with decreasing likelihood. If an electronic and an oscillatory transition occur simultaneously, no numeric rules can be stated anymore. Instead, predictions following the Franck-Condon-principle are possible. This principle states that the electronic transition happens so fast, that the relative position of the cores does not change during the transition. The transitions preferentially happen at distances where both, the upper and the lower levels, possess a high probability density. The transition possibility from one state v'' to another v' can be given by the Franck-Condon-factor:

$$f_{\text{FC}}(v', v'') = \left| \int \Psi_{v'} \Psi_{v''}^* dr \right|^2$$

The energy difference between two levels in a combined electronic and oscillatory transition is given by:

$$\Delta E = \Delta E_{\text{elec}} + E_{\text{Morse}}(v') - E_{\text{Morse}}(v'')$$

Translated to wavenumbers $\bar{\nu}$ this yields:

$$\bar{\nu} = \bar{\nu}_{00} + \left[a' \left(v' + \frac{1}{2} \right) - b' \left(v' + \frac{1}{2} \right)^2 \right] - \left[a'' \left(v'' + \frac{1}{2} \right) - b'' \left(v'' + \frac{1}{2} \right)^2 \right]$$

At room temperature, all absorbing molecules are in the oscillatory ground state $v'' = 0$. In the spectrum, the actual oscillatory quantum number is unknown, but neighboring lines differ by one. The quantum numbers v' of subsequent lines can be written as $v' = N + i$, where i is introduced as the running number. This simplifies the previous equation to:

$$\bar{\nu} = \bar{\nu}_0 + ai - bi^2 \quad \text{or for the difference between neighboring levels} \quad \Delta\bar{\nu}_i = A - Bi$$

Hence, when plotting $\Delta\bar{\nu}_i$ over the running number i , a linear fit can be employed. The intersection of the fitted straight line with $\Delta\bar{\nu}_i = 0$ gives the running number for the edge, with which the edge energy can be calculated. By knowing the atomic excitation energy $E(J^*) = 0.97 \text{ eV}$, the dissociation energy of the ground state can be calculated.

Equipment and Setup

The laboratory is equipped with 2 Steinheil prism-spectrographs with various possible modifications. This instrument can be adjusted to yield sharp images of spectra in a plane where formerly a photographic plate was placed. To match today's technical possibilities, the experiment was upgraded and now the images are taken with digital cameras that are connected to computers to allow direct image processing (MATLAB). Different spectral-lamps with a series of bright lines in the visible range provide the reference lines to determine the dispersion curve of the spectrograph. For the detection of the iodine absorption lines, iodine cells are illuminated with halogen-lamps. To illuminate the entrance slit of the spectrograph in an (close to) optimal way, various lenses with different focal lengths are available.

Practical aspects

Illumination of the entrance slit

In spectroscopic observations, an optimal illumination of the entrance slit of the spectrograph is crucial in order to get bright spectral lines. Depending on the particular problem, the light source can either be imaged onto the slit to be able to relate a certain part of every spectral line to a certain part of the light source, or the slit can be illuminated with a parallel beam of light (light source in the focus of objective lens) to get a completely homogeneous illumination of the slit. When producing an image, one has to consider that the frames of the lenses limit the light bundle that can be used for imaging.

Dispersion relation

In order to determine the dispersion relation of the spectrograph in the current settings a reference spectrum of an Hg-Cd-lamp or a Cs-lamp is recorded.

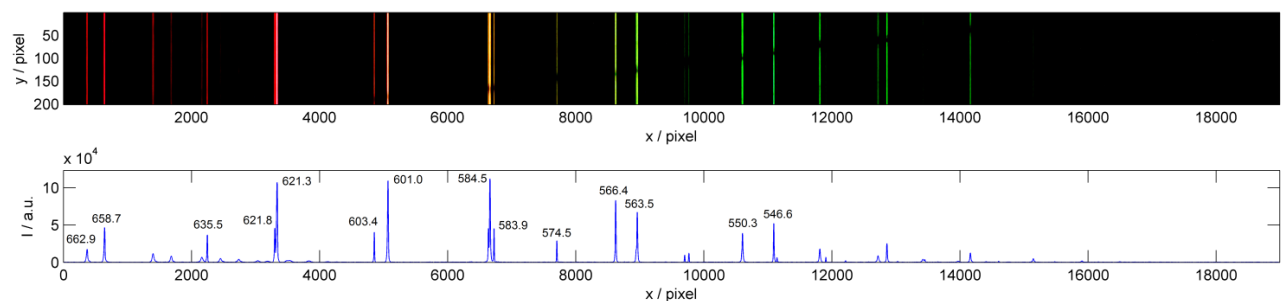


Fig. 4. Cs – reference spectrum as recorded. The numbers in the lower graph correspond to the wavelength of the respective peaks in nm.

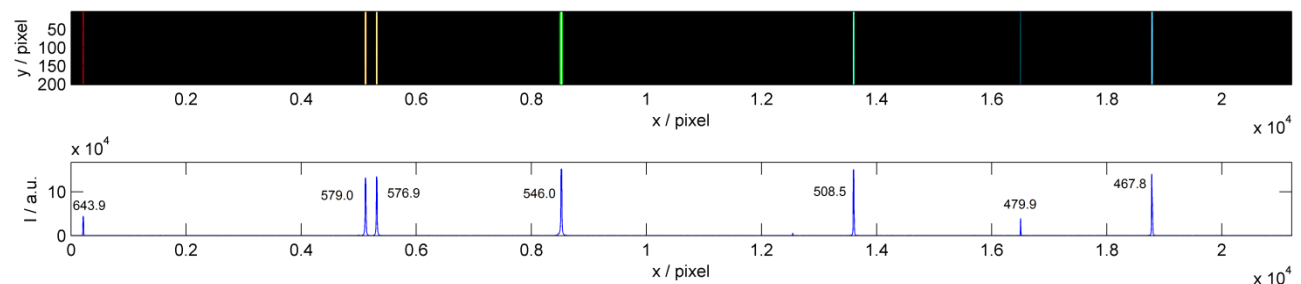


Fig. 5. Hg-Cd – reference spectrum as recorded. The numbers in the lower graph correspond to the wavelength of the respective peaks in nm.

With this knowledge, the recorded spectrum (intensity over pixels) can be converted into a physically meaningful spectrum (intensity over wavelength / frequency / wave number). To do this, the recorded peaks are plotted in a diagram where the x-axis corresponds to the pixel position and the y-axis to the physical quantity of interest. Then a quadratic fit is employed, which yields an equation for λ , ν or $\bar{\nu}$ as a function of the pixel-number.

Knowing the dispersion relation, all other spectra recorded under the same conditions can be converted. A conversion in intensity over wavenumbers makes sense for the analysis of the oscillation bands as described above.

Questions

Sketch and explain the experimental setup (think about the light path and where to put lenses, etc.)

What is important when adjusting the entrance slit of the spectrograph (in terms of sharpness and brightness)?

How do the spectral resolution and the brightness of the lines depend on the incident angle of the light beam on the prisms (keyword: Fresnel equations)?

What is the reason for frequency dependent deflection of the beam using a prism / grating?

Why do spectral lines appear slightly curved in the focal plane of the prism spectrograph and which direction (red or violet) does the curvature point towards? (consider the light path inside the spectrograph in 3D)

How can the position of a spectral line be translated into the wavelength of this line?

How do atomic and molecular spectra generally look like?

How do the potential curves and energy levels of diatomic molecules generally look like?

What is stated by the Franck-Condon-principle and what can be stated about transition probabilities?

Why is the absorption strongest in the vibrational band with $v'' = 0$?

Exercises

Adjusting of the prism spectrograph

Use the bright lines of the Hg-Cd-lamp to adjust the prisms and the focal plane such that the spectrum shows up as bright and sharp as possible using scotch tape as screen. The width of the slit can be adjusted by carefully turning the micrometer screw. When you have found good settings, attach the digital camera and correct for the new image plane (readjust the distance to the camera lens only, not the tilt). Finally, fine-tune the tilt of the detector plane with the camera attached. If larger corrections are needed, dismount the camera and look at the full spectrum again to make sure that the whole spectrum is sharp in the image plane. Due to the size of the CCD-chip, only a section of the spectrum will fit on one image; i.e. a panorama using multiple pictures must be recorded to image the whole spectrum. **When shifting the camera into a new position for the next image in the panorama, do not change any other settings!**

Absorption measurements with the iodine cell

The light of the halogen lamp must be directed through the iodine cell with as little reflections as possible, so that the slit is homogeneously and brightly illuminated. Handle the iodine cells carefully as they are the last remaining cells at the institute! In order to be able to evaluate the absorption spectrum, a reference must be recorded using the same settings of the spectrograph. It is best practice to record one part of the reference spectrum first, then to record the absorption spectrum in the exact same position. After recording these 2 images, the camera can be shifted to a new position and the procedure can be repeated. In the new position, there must be a certain overlap with the previous image in order to be able to merge the separated images into one spectrum.

Analysis of the obtained spectra (using MATLAB)

With the availability of computer-aided measurement technology, processing raw data with the computer became increasingly important. Therefore, the evaluation of the recorded images is a main part of the exercise and will be conducted within the time of the lesson using MATLAB. The following tasks should be completed:

1. Merging of the recorded images in order to create a composite spectrum covering the whole spectral range.
2. Determination of the dispersion relation of the spectrograph using the reference-spectrum.
3. Determination of the resolution power of the prism spectrograph and the USB grating spectrograph.
4. Determination of the wavelength of the band edges in the iodine absorption spectrum.
5. Determination of the dissociation energy of the iodine molecule in the ground state.

BONUS:

- Build your own Spectrograph using a CD or DVD. Repeat some of the measurements conducted with the other devices.