

## Physical laboratory 3

### Task F Atomic and molecular optical emission spectra

#### Tasks

1. Identify spectral lines emitted by electrode material vapours in an arc discharge and determine their intensity. Calculate the temperature of the arc discharge from the Boltzmann slope.
2. Determine the rotation temperature of the OH radical from the measured molecular spectrum.

#### Introduction

Substances excited to some of its higher levels can transmit their energy to their surroundings in the form of radiation. The excitation can occur due to their non-zero temperature, chemical reactions, collisions with fast electrons, energetic photons, radioactive radiation and many other processes. If the substance is excited to high-enough levels, the emitted radiation can lie in the visible region (approx. 400–700 nm) or in the region of even shorter wavelengths. The energy is radiated in energy portions (quanta)  $h\nu = hc/\lambda$  due to spontaneous or stimulated transitions of electrons from higher to lower energy levels. We can observe individual spectral lines in the spectra of substances with discreet well-separated energy levels such as free atoms.<sup>1</sup> If clusters of lines with close energies exist in the structure of the substance, we can see groups of close-lying lines forming the so-called molecular bands characteristic for emission of materials formed from several atoms. When the substance contains a large number of energy levels covering a large energy interval and lying very close together, as is typical for condensed matter, the optical emission spectrum will be continuous. Moreover, if this substance is in thermal equilibrium, the spectrum can be close to that of a radiating black body.

The electromagnetic spectrum emitted by a substance carries a lot of information about the said substance. Optical emission spectroscopy (OES) studies the visible light spontaneously emitted by a substance. For example, OES is often used in plasma physics to determine particle

<sup>1</sup>Even a seemingly simple spectral line can have different spectral shapes and, if it is actually an overlap of spectral lines with nearly identical wavelengths, an inner structure. Also, magnetic and electric fields, collisions with other particles and the lifetime of the excited state can also influence the spectral shape of a line.

concentrations (electrons, excited species or even ground-state species). OES belongs to non-invasive methods of studying radiating objects. This means that we do not interfere with the studied effect by the spectrometer. We only capture the intensity of the radiation emitted by the studied object – we acquire the optical emission spectrum.

This laboratory is divided into two parts. In the first part, you will work with the spectrum of free atoms (iron evaporated by an electric arc discharge). As previously described, a spectrum of an atomic gas is composed of different spectral lines, each corresponding to an electron transition between two exactly defined energy levels. In such a case, the calculation of the excitation temperature of the atoms is the most basic application of OES. In the second part of the laboratory, you will work with the spectrum of OH excited in a plasma. OH, being a diatomic particle, exhibits a different type of optical spectrum. The spectrum of a discharge containing molecular gasses is composed of (taking into account the limited resolution of a spectrometer) band structures – spectral bands. Such bands form by overlapping lines corresponding to transitions between levels whose energy is the sum of electronic, vibrational and rotational contributions. From the intensities of the spectral lines, it is possible to calculate the different temperatures – excitation temperature, vibration temperature and rotation temperature. As the rotational quanta are very small, an equilibrium between the rotational states and the particles' thermodynamic (temperature) movement takes place effectively. That is why the rotation temperature (therefore a temperature describing the excitation of rotational states) measured in the plasma approximately corresponds to the translational temperature (the real temperature of neutral gas) in the plasma.

## Atomic spectra

### Spectral line intensity

The intensity of a spectral line of the wavelength  $\lambda_{mn}$  arising by an electron transition from the upper level  $m$  of the energy  $E_m$  the bottom  $n$  level of energy  $E_n$  can be written as

$$I_{mn} = \frac{hc}{4\pi\lambda_{mn}} \cdot A_{mn} \frac{g_m}{\sigma} \cdot \exp\left(-\frac{E_m}{kT}\right), \quad (1)$$

where  $E_m$  is the excitation energy of the upper level,  $A_{mn}$  is the transition probability from the  $m$  level to the  $n$  level,  $g_m$  is the statistical weight of the upper energy level,  $\sigma$  is the total number of states,  $h$  is the Planck's constant,  $c$  is the speed of light,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature of the radiating body under thermodynamic equilibrium. The energy difference between the upper and bottom levels governs the light quantum energy of the corresponding frequency or wavelength:

$$(E_m - E_n) = h\nu_{mn} = \frac{hc}{\lambda_{mn}}. \quad (2)$$

From the measurements, we can usually determine only the relative intensity of the spectral lines. For the relative intensity of the spectral line (in arbitrary units) we can write

$$I_{mn} \sim \frac{A_{mn}g_m}{\lambda_m} \cdot \exp\left(-\frac{E_m}{kT}\right). \quad (3)$$

Which we can rewrite into

$$\frac{I_{mn}\lambda_{mn}}{A_{mn}g_m} \sim \exp\left(-\frac{E_m}{kT}\right) \quad (4)$$

and after using the logarithm rule into

$$\ln\left(\frac{I_{mn} \cdot \lambda_{mn}}{A_{mn}g_m}\right) \sim \left(-\frac{E_m}{kT}\right). \quad (5)$$

We can experimentally measure the relative intensities of the spectral lines  $I_{mn}$  and their wavelengths  $\lambda_{mn}$ . For each line, we also know the  $A_{mn}g_m$  (the product of the upper  $m$  level transition probability and its statistical weight) and the excitation energy  $E_m$  of the upper energy quantum state  $m$ , which are tabulated.

If we make the Boltzmann plot

$$y = \ln \left( \frac{I_{mn}\lambda_{mn}}{A_{mn}g_m} \right) = f(E_m), \quad (6)$$

we can fit it by a line with the slope  $\tan \alpha = -1/kT$ , from which we can unambiguously determine the absolute temperature of a radiating body  $T$ .

### Acquisition of arc discharge spectrum

Grating spectrometers (fig. 1) are the most commonly used devices for the acquisition of the atomic line spectra. The radiation is brought in by optical fibres often manufactured from silica glass to transmit also near UV range radiation. The radiation passes through an entrance slit, and (after a possible reflection from a mirror) it impacts a rotatable grating. The grating decomposes the light and the diffracted radiation then (after another possible reflection from a mirror for prolonging of the optical path and resolution enhancement) it goes to the detector. CCD camera, ICCD camera or a photomultiplier are typically used detectors. The spectrometer settings and measured data saving are usually done directly by a computer and a special electronic communication unit of the spectrometer.

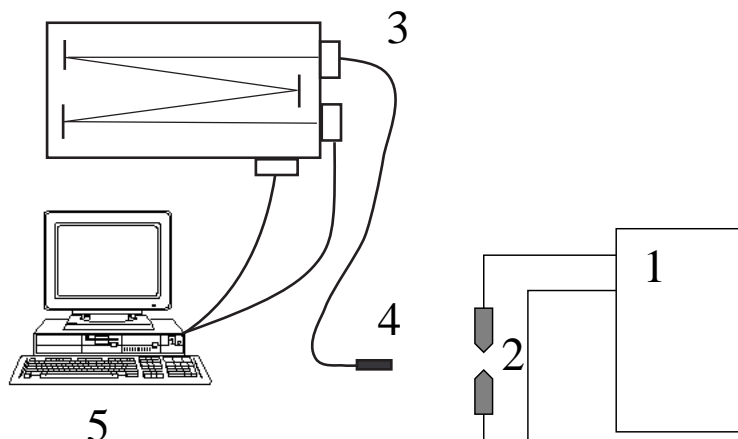


Figure 1: Schematic diagram of spectrum acquisition by a grating spectrometer. 1 - power source, 2 - arc discharge, 3 - spectrometer, 4 - optical fibre, 5 - computer.

### Evaluation of measured spectrum

When evaluating the measured spectra, the first step is to identify the individual spectral lines. Wavelengths of selected iron atom spectral lines are summarised in table 1. Keep in mind that spectrometers do not measure the wavelengths absolutely precisely, and the measured wavelengths can be shifted compared to their actual values.

Moreover, the effect of the background radiation and the dark current (i.e. current generated by the detector while no light is going to the detector) need to be removed from the measurement. A simple option how to subtract the background from the measured signal is by subtracting the spectrum intensity measured in the close vicinity of the studied line where no part of the studied

| $\lambda_{mn}$ | $E_m$ | $A_{mn}g_m \times 10^8$ |
|----------------|-------|-------------------------|
| [nm]           | [eV]  | [s <sup>-1</sup> ]      |
| 429.413        | 4.371 | 0.71                    |
| 429.924        | 5.308 | 5.2                     |
| 430.791        | 4.434 | 5.9                     |
| 431.509        | 5.070 | 1.5                     |
| 432.576        | 4.473 | 6.1                     |
| 433.705        | 4.415 | 0.23                    |
| 435.274        | 5.070 | 1.0                     |
| 436.977        | 5.882 | 2.2                     |
| 437.593        | 2.832 | 0.0094                  |
| 438.357        | 4.312 | 7.7                     |
| 440.475        | 4.371 | 4.4                     |
| 441.512        | 4.415 | 2.8                     |
| 442.731        | 2.851 | 0.0099                  |
| 444.234        | 4.988 | 1.1                     |
| 444.320        | 5.647 | 1.9                     |
| 444.772        | 5.009 | 1.1                     |
| 445.912        | 4.955 | 1.0                     |
| 446.165        | 2.865 | 0.0052                  |
| 446.655        | 5.606 | 5.3                     |
| 447.602        | 5.614 | 5.4                     |
| 448.217        | 2.875 | 0.0053                  |
| 449.457        | 4.955 | 1.22                    |
| 452.862        | 4.913 | 1.8                     |
| 453.115        | 4.220 | 0.076                   |
| 460.294        | 4.177 | 0.088                   |
| 473.678        | 5.828 | 2.5                     |
| 485.975        | 5.426 | 1.3                     |
| 487.132        | 5.409 | 3.7                     |
| 487.215        | 5.426 | 2.2                     |
| 487.822        | 5.426 | 0.77                    |

Table 1: Selected spectral line constants.

line (or any other line) lies from the line intensity itself. The relative line intensity can be then calculated by integrating the measured signal throughout the whole line.

After identifying the lines and determining their intensity, it is possible to construct the Boltzmann plot and calculate the excitation temperature of the radiating atoms from the slope of the line.

## Molecular spectra

### Quantum description of a diatomic molecule state

#### Electron state classification

The electronic state of a free atom can be described by the quantum numbers  $L$ ,  $S$  and  $J$  made by summing up the moments  $l$ ,  $s$  and  $j$  of all the electrons in the atom.

A magnetic moment arises from the movement of every electron in the shell of the atom or a molecule. The magnetic interaction between the spin and orbital momenta of the individual

electrons lead to their mutual intertwining. Such spin-orbital interactions can be approximately described, for example, by the Russell-Saunders spin-orbital coupling.

A model of a free atom with the Russell-Saunders coupling can be even extended to describe the electronic state of a diatomic molecule. The orbital and spin momenta corresponding to individual electrons are coupled into resultant orbital  $L$  and spin  $S$  momenta of the whole molecule. If the charges of the atomic cores are small, the vectors of  $L$  and  $S$  are lying in the direction of the electric field they create, and the spin-orbital coupling is very weak.

The resultant orbital momentum of the electrons carries out a precession movement around the axis between the two atomic cores, and the projection of this moment onto this axis can have only  $\Lambda\hbar$  values. The quantum number  $\Lambda$  can be

$$\Lambda = 0, 1, 2, \dots \quad (7)$$

All electron states with  $\Lambda > 0$  are twice degenerate. This corresponds to two possible rotation directions of the momentum rotation with the same projection onto the inter-core axis.

We describe the states with  $\Lambda=0, 1, 2, 3, 4\dots$  using the terms  $\Sigma, \Pi, \Delta, \Phi, \Gamma\dots$  analogically to a free atom.

The coupling of the magnetic moment  $S$  into the inter-core axis is caused by a magnetic field created by the moving electrons, unlike in the previous case, where the cause was the electric field between the atomic cores in the molecule. The resultant spin momentum carries out precession movement around the axis between the two atomic cores, and the projection of this moment onto this axis can have only the values of  $\Sigma\hbar$ . The quantum number  $\Sigma$  is an analogue to the quantum number  $s$  in a free atom and can take on values of

$$\Sigma = S, S - 1, \dots, -S \quad (8)$$

The total number of the molecule spin momentum orientations corresponds to the multiplicity of the state  $(2S+1)$ . This number is typically shown in the left superscript above the term symbol of the energy state – for example  ${}^3\Pi$ .

The projection of the total momentum arising from the spin-orbital coupling onto the inter-core axis can take on values of  $\Omega\hbar$ , where the quantum number  $\Omega$  can be

$$\Omega = \Lambda + \Sigma. \quad (9)$$

If  $\Lambda=1, \Sigma=1, 0, -1$ , then  $\Omega=2, 1, 0$ . This is generally denoted as  ${}^3\Pi_2, {}^3\Pi_1$  a  ${}^3\Pi_0$ . Due to the influence of the spin-orbital coupling, states with different values of  $\Omega$  have different energies. This results in the state of  ${}^3\Pi$  being a triplet.

The energy states of a free atom can be described by the quantum numbers  $L, S$  and  $J$  analogically to the quantum numbers  $\Lambda, \Sigma$  and  $\Omega$  of a diatomic molecule. However, such a set of these three numbers is not enough to describe a molecule's electronic state and to introduce the transition selection rules. We need to add one (in the case of a heteronuclear molecule) or two (for a homonuclear molecule) characteristics considering the symmetry of the electron wave function  $\psi_e$ .

For a diatomic molecule, it is necessary to establish if its  $\psi_e$  is symmetrical or antisymmetrical with respect to any plane containing the inter-core axis. Symmetrical states are denoted by a right superscript  $+$ , any antisymmetrical ones by a right superscript  $-$ . These symbols are only used for the  $\Sigma$  states. States with  $\Lambda > 0$  are always twice degenerated in this regard.

For a homonuclear molecule, it needs to be established if it is symmetrical or antisymmetrical with respect to the centre mass of the molecule. Symmetrical states are denoted by a  $g$  right subscript and those antisymmetrical by right subscript  $u$ .

## Selection rules

A free atom excited to a higher energy state than its ground state can relax back to its ground state by radiating one or more photons. The change in the electronic states while radiating a photon is governed by selection rules giving the probability of all of the many possible transitions.

| n | Selection rule  | Transition examples                             |   |
|---|---|---|---|
|   |   | allowed   | forbidden                                       |
| 1 | $\Delta\Lambda = 0, \pm 1$  | $\Sigma - \Sigma, \Pi - \Sigma, \Delta - \Pi$   | $\Delta - \Sigma, \Phi - \Pi, \Phi - \Sigma$    |
| 2 | $\Delta S = 0$  | ${}^3\Sigma - {}^3\Sigma, {}^3\Pi - {}^3\Sigma$ | ${}^3\Sigma - {}^1\Sigma, {}^3\Pi - {}^1\Sigma$ |
| 3 | $+$ $\not\leftrightarrow$ $-$ , $+$ $\leftrightarrow$ $+$ , $-$ $\leftrightarrow$ $-$ | $\Sigma^+ - \Sigma^+, \Sigma^- - \Sigma^-$      | $\Sigma^+ - \Sigma^-, \Sigma^- - \Sigma^+$      |
| 4 | $g \leftrightarrow u, u \not\leftrightarrow u, g \not\leftrightarrow g$               | $\Sigma_u^+ - \Sigma_g^+, \Pi_g - \Sigma_u^+$   | $\Sigma_g^+ - \Sigma_g^+, \Pi_u - \Sigma_u^-$   |

Table 2: Selection rules for a spontaneous electron transition between two states derived from the dipole approximation for Hund's coupling  $a$  in a diatomic molecule.

The selection rules valid for the electronic state transitions of a diatomic molecule derived by the electric dipole approximation, including examples of allowed and forbidden transitions, are shown in table 2.

The validity of the selection rule no. 2 in table 2 decreases with the increase of the core charge of the molecule. For example, a triplet-singlet transition is strictly forbidden for molecular hydrogen. However, for example, the  $a^3\Pi - X^1\Sigma^+$  forbidden transition can be weakly observed in the CO molecule.

## Diatomic molecule spectrum

### Diatomic molecule as a vibrating rotor

The total energy of a diatomic molecule can be separated into mechanical energy and internal energy. The mechanical energy is the sum of the kinetic energy of the translation movement and the potential energy. The internal energy is composed of, amongst others, the energy connected to the electronic state, rotation energy and vibration energy. The energy related to the rotation and vibration of the molecule is quantised, unlike the kinetic energy.

If the interaction between the vibration and rotation can be neglected, the energy of the molecule  $E$  in a given electronic-vibration-rotation state is the sum of the energies corresponding to the electronic state ( $E_e$ ), vibration state ( $E_v(\nu)$ ) and rotation state ( $E_r(N)$ ):

$$E = E_e + E_v(\nu) + E_r(N). \quad (10)$$

The vibration energy of a diatomic molecule is proportional to the vibration quantum number  $\nu$  taking on non-negative integer values. The vibration energy in the anharmonic oscillator approximation can be written as

$$E_v(\nu) = hcG_\nu = hc[\omega_e(\nu + \frac{1}{2}) - x_e\omega_e(\nu + \frac{1}{2})^2 + y_e\omega_e(\nu + \frac{1}{2})^3 \dots] \quad (11)$$

The vibration wavenumber  $\omega_e$ , the anharmonicity constants  $x_e$ ,  $y_e$  and also the vibration term  $G_\nu$  in this equation are dependent on the electronic state of the vibrating molecule.

The rotation energy of a diatomic molecule is proportional to the rotation quantum number  $N$  that, just like  $\nu$ , takes on non-negative integer values. The rotation energy in the nonrigid rotor approximation can be written as

$$E_r(N) = hc[B_\nu N(N+1) - D_e N^2(N+1)^2 + \dots] \quad (12)$$

where  $B_\nu$  and  $D_e$  are rotation constants corresponding to the given electronic state of the molecule. As the mean atomic core distance and well as the mean momentum of the molecule increase with increasing vibration quantum number  $\nu$ , the rotation constants depend on the vibration state of the molecule. Rotation constant  $B_\nu$  can be written as

$$B_\nu = B_e - \alpha_e(\nu + \frac{1}{2}), \quad (13)$$

| n | Selection rule        | Transition examples              |                              |
|---|-----------------------|----------------------------------|------------------------------|
|   |                       | allowed                          | forbidden                    |
| 1 | $\Delta\nu$ unlimited | $\Pi(\nu = 3) - \Pi(\nu = 1)$    | -                            |
| 2 | $\Delta N = 0, \pm 1$ | $\Sigma(N = 9) - \Sigma(N = 10)$ | $\Pi(N = 5) - \Sigma(N = 2)$ |

Table 3: Selection rules for changes of the rotation and vibration quantum number for simultaneous spontaneous electron-vibration-rotation transition.

where  $B_e$  and  $\alpha_e$  are tabulated spectroscopic constants depending on the electronic state of the molecule.

Electronic relaxations of a molecule by a spontaneous transition of an electron from a higher energy state to a lower one are governed by transition rules shown in table 2. Based on this table, it is possible to predict lower electronic states for any given upper state. The rotation and vibration state of the molecule can also change during the electronic relaxation of the molecule. Corresponding selection rules, including examples, are shown in table 3. In the optical spectrum, instead of the classical atomic lines, we can observe molecular rotation-vibration bands. Given high enough resolution in these bands, we can find the vibration sequences, vibration progressions and rotation R, P and Q branches. The principle behind these structures is shown in figures 2 and 3.

### Interpretation of molecular potential energy curves

Figure 4 shows two potential energy curves corresponding to two different states of an  $I_2$  molecule. The  $^1\Sigma$  state is the ground state and the  $^3\Pi$  state is the lowest excited state. The description of these states and curves using the spectral terms reveals that the  $^3\Pi$  state is a metastable state (meaning it has a long lifetime) as the transition from this state to the ground state is against

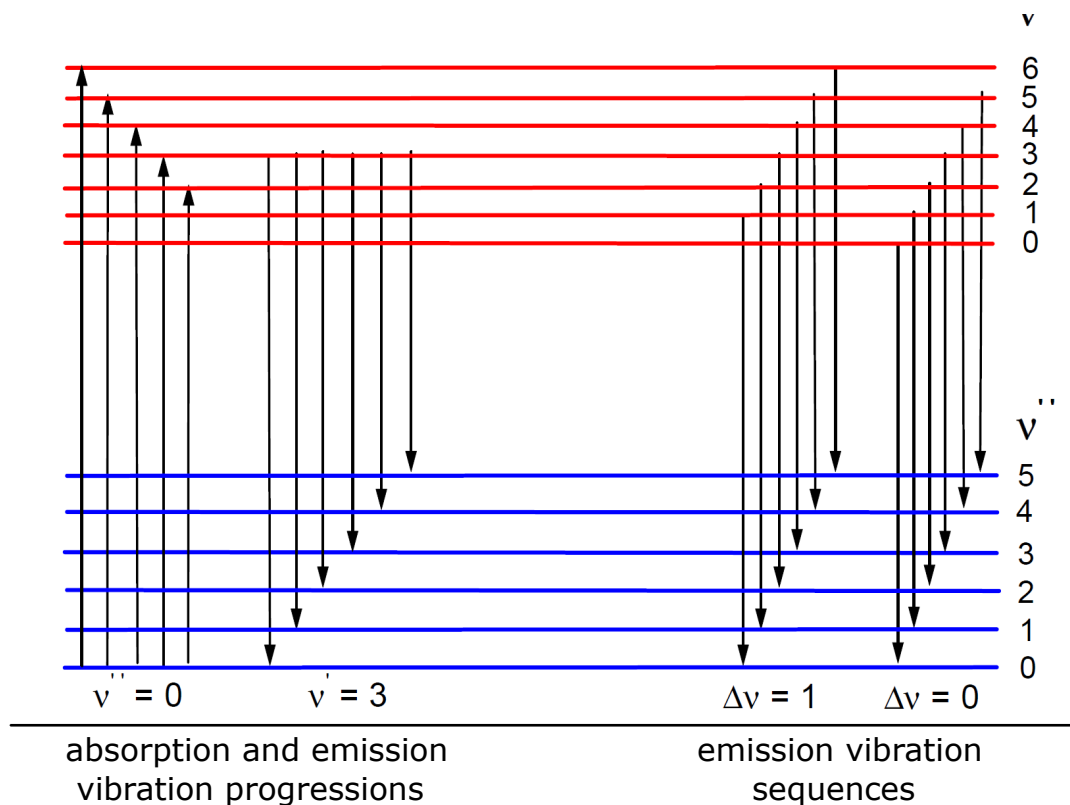


Figure 2: Formation principle of the vibration progressions and sequences.

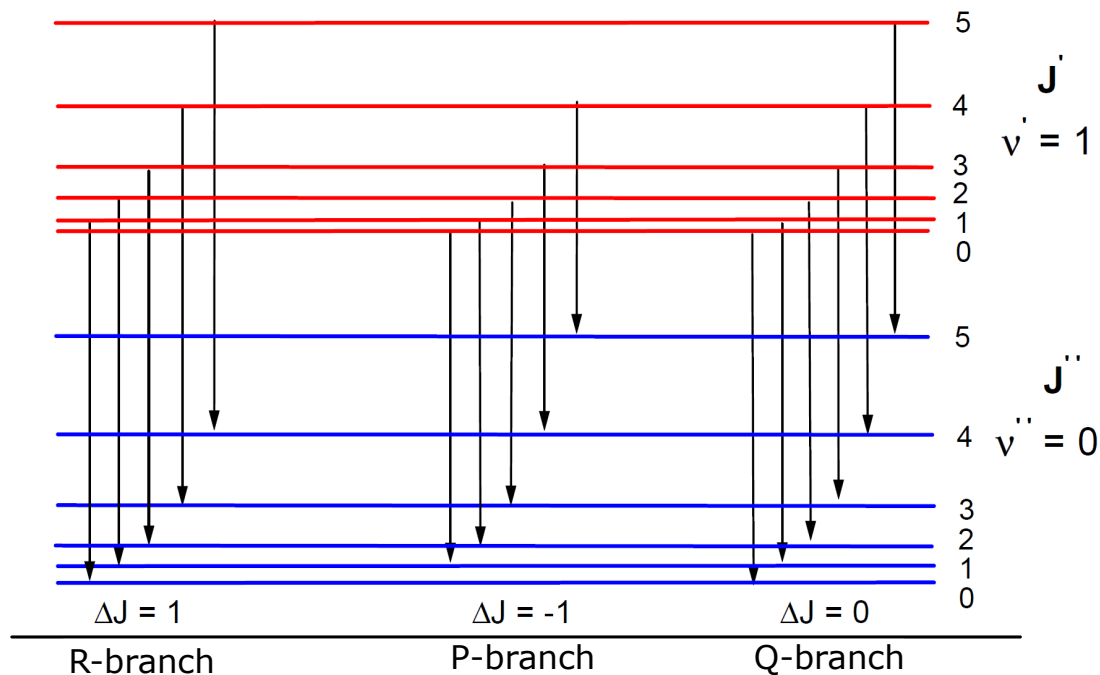


Figure 3: Principle of formation of the R, P and Q rotation branches for the case of  $J=N$ .

the  $\Delta S = 0$  selection rule. Only the vibration states are usually shown in the potential energy curves. The rotation states are not. The base state curves are not in the shape of a parabola. Therefore, the anharmonic oscillator approximation was used for its calculation. More than 80 vibration states correspond to the base state of the  $I_2$  molecule.  $D_e$  is the dissociation energy of the base state. If such energy is introduced to the  $I_2$  molecule, the energy of its vibrations is so high that the molecule tears apart into two I atoms (it dissociates) in the  $^2P_{3/2}$  states. Lower energy is needed for the dissociation of the  $I_2$  molecule in its excited  $^3\Pi$  state. If this state is dissociated, two I atoms are created, and one of them is in the  $^2P_{3/2}$  state and the other one in the  $^2P_{1/2}$  state. Yet more information can be derived from the potential energy curves. By using the Franck-Condon principle, it is possible to determine what vibration states will be preferentially excited by electron impact, what transitions will be the most intensive in the optical spectrum, etc.

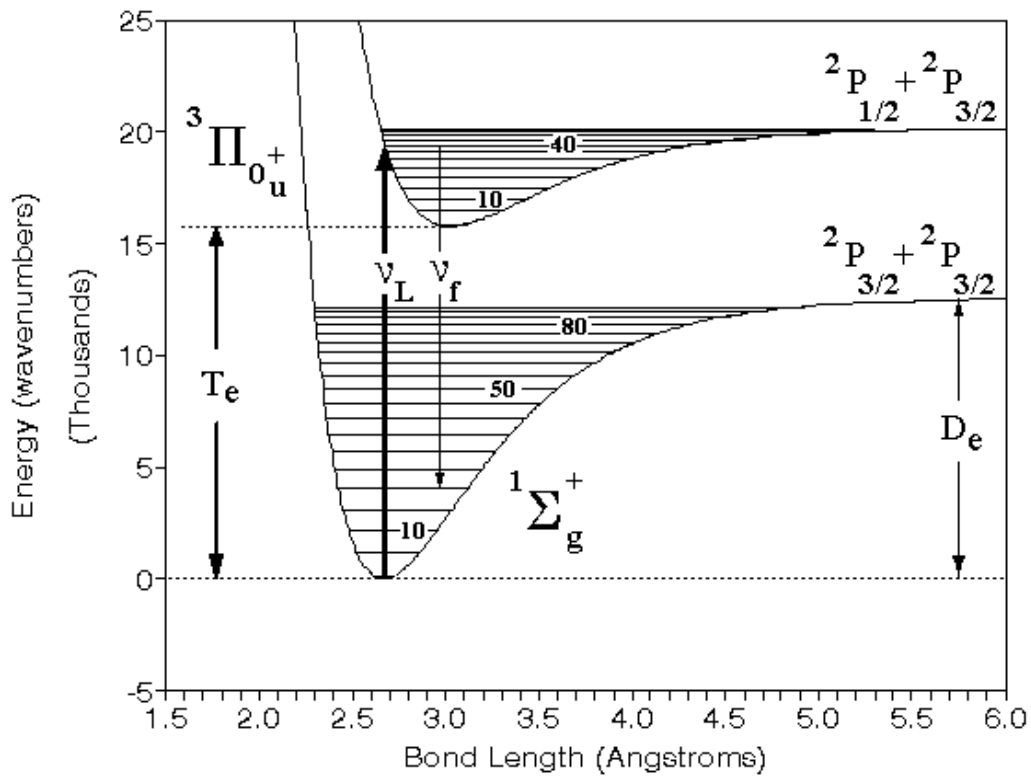
### Rotation line intensity

The rotation quanta are much smaller than the vibration or electronic quanta. Therefore also rotation states will be excited if a vibration state is excited. The intensity of a rotation line is given by the following formula 14.

$$I_{n''v''J''}^{n'v'J'} = C_{n''v''J''} \tilde{\nu}^4 S_{J',J''} e^{-\frac{B_{v'} N'(N'+1)hc}{kT}} \quad (14)$$

$I_{n''v''J''}^{n'v'J'}$  is the spectral line intensity,  $B_{v'}$  is the rotation constant of the upper vibration state,  $N'$  is the rotation quantum number of the upper state.  $J'$  is the quantum number for the total momentum.  $N' = J' - 1/2$  for the case of the laboratory measurements. Both the numbers  $J'$  and  $N'$  are used in molecular spectroscopy. In some works, these different quantum numbers can be mistaken, leading to errors in the measured data evaluation.  $C$  is a constant with the same value for all rotation lines of a single branch,  $\tilde{\nu}^4$  is the wavenumber of the studied line,  $S_{J',J''}$  is the Hönl-London intensity factor of the given transition,  $k$  is the Boltzmann constant,  $h$  the Planck constant,  $c$  is the speed of light and  $T$  the sought for temperature. By performing the logarithm of 14 we will get the Boltzmann plot – a linear dependence of  $\ln \frac{I_{n''v''J''}^{n'v'J'}}{\tilde{\nu}^4 S_{J',J''}}$  on  $N'(N'+1)$ .



Figure 4: Potential energy curves of the I<sub>2</sub> molecule.

$$\ln \frac{I_{n'v'J'}}{n'^4 S_{J'J''}} = -\frac{B_{v'}hc}{kT} N'(N'+1) + const \quad (15)$$

The rotation temperature can be calculated from the slope of the Boltzmann plot.

| $N'$ | $J'$ | $S_{J'J''}$ | $\lambda[\text{nm}]$ |
|------|------|-------------|----------------------|
| 1    | 3/2  | 0.563       | 307.843              |
| 2    | 5/2  | 1.065       | 307.996              |
| 4    | 9/2  | 2.100       | 308.326              |
| 5    | 11/2 | 2.640       | 308.512              |
| 6    | 13/2 | 3.160       | 308.733              |

Table 4: Rotation quantum numbers, intensity factors and wavelengths of selected spectral lines of the OH radical.

## Experimental procedure

1. The task is to evaluate the atomic spectrum of iron vapours measured in an arc discharge and the molecular spectrum of OH radical measured in a non-isothermic low-temperature plasma. Derive the corresponding temperature (excitation in the case of iron atoms and rotation in the case of OH radicals) from both spectra. Correct lines need to be identified, the background needs to be subtracted, and the relative intensity of the lines needs to be calculated. This data is used in the Boltzmann plot, and the temperature is derived from the

slope of the plot. You can use hereafter described *Span* and *Lifbase* for the data evaluation. A brief manual for using these programs, for example, on the OH radical is shown in the following points. Iron atoms do not require *Lifbase* simulations. Their treatment in *Span* is the same. The data needed for the evaluation of the Boltzmann plot of the OH radical can be found in point 5.

2. Open the \*.spc file with the radical spectrum in *Span 1.7*. The OH  $A^2\Sigma^+ \rightarrow X^2\Pi$  transition was measured. The software can be freely downloaded from <http://physics.muni.cz/~zdenek/span/>. The measured spectra are typically shifted for up to several nanometres. An additional step is therefore needed for correct data analysis. In our case, we can use the OH radical spectrum simulated in *Lifbase 2.1* for correct spectral line identification. The simulated spectra give true wavelengths. This step is not needed in the case of the iron atoms, where the lines are much more separated.
3. Download *Lifbase 2.1* (<https://www.sri.com/contact/form/lifbase-o>) and run it. Input the desired molecule, OH (A-X) in our case, in the **Simulation** window. The wavelengths are given in angström, so set the simulated interval to 3050Å– 3140Å. Use the resolution of 0.15Å, tick the box for a thermalised systems and select **L'(Air)** in **Units**. Run the simulation by clicking the green button. In the simulated spectrum, determine (according to the wavelengths from table 4) the spectral lines with the quantum numbers 1, 2, 4, 5 and 6 necessary for the temperature calculation.
4. Identify the same 5 lines in the measured spectra using the simulated spectrum. In *Span 1.7* set the studied molecule: **Database** → **Select Molecules** → **Ohr**. Have only this molecule ticked as the presence of more molecules or atoms could be very confusing. Select the spectral line by a left mouse click and assign a correct identification to the line from the selection. *Span 1.7* shows you the  $J'$  quantum numbers in the selection (do not confuse these with  $N'$ ), simplifying the work. If you have at least one line identified, you can further ease your work by shifting (correcting) the spectrum to the correct wavelength interval by going to **Spectrum** → **Correct Wavelengths** → **From Lines in Graph**. Then identify the rest of the five spectral lines and repeat the wavelength correction. You can verify your result by adding the tabulated spectrum of the OH radical to the background by **Graph** → **Background** → **Add...** → **From database (minimum atomic and molecular line intensity = 0)**.
5. Determine the intensities of the selected five lines  $I_{n''v''J''}^{n'v'J'}$  with the rotation quantum numbers  $N'$  of 1, 2, 4, 5 a 6 (or  $J'$ : 3/2, 5/2, 9/2, 11/2 a 13/2) from the spectrum. Subtract the spectral background from their intensities. Determine their wavelengths and the wavenumbers  $\tilde{\nu}^A$ . The value of the rotation constant for the upper vibration state is  $B_{v'} = 1696.6 \text{ m}^{-1}$ . Determine the rotation temperature from the Boltzmann plot by using the herein shown formulae and tabulated constants. Verify your calculated temperature by calculation in *Span 1.7*: **Analysis** → **Temperature** → **From Graph**. The possible (small) difference in the calculated temperatures can arise from e.g. different spectroscopic constants.

### Summary of the spectrum treatment in *Span 1.7*

- Open *Span 1.7*
- Open the spectrum file by **File** → **Open** → 'OH-XX.SPC', while XX is the number of your assigned spectrum.
- Select the Ohr molecule in the database: **Database** → **Select Molecules** → **Ohr**
- Select a chosen spectral line by a left click. **Select spectral line** table will open. Find the correct line with its parameters closest to the ones in table 4, e.g. OHRI 307.84400 1 3/2. Confirm your selection by clicking **OK**.

- Shift the spectrum to the correct wavelength interval: **Spectrum** → **Correct Wavelengths** → **From Lines in Graph**.
- Identify the remaining lines.
- Verify your result by adding the tabulated OH radical spectrum to the background: **Graph** → **Background** → **Add...** → **From database** → **OK**.  
(minimum atomic and molecular line intensity = 0).
- Correct the background noise level to zero for determining the line intensities: **Spectrum** → **Correct Intensities** → **Manually in Graph** → **OK**. Shift the spectrum by the up and down arrows. To turn off the correction mode: **Spectrum** → **Correct Intensities** → **Manually in Graph**.
- Further line information can be found in: **Analysis** → **Peak Intensities** → **From Graph**, where the first column shows the wavelengths of the selected lines, the second and third column shows the line boundaries on the x axis and the fourth column shows the intensity.
- Verify the calculated rotation temperature by **Analysis** → **Temperature** → **From Graph**.

You can find more information about *Span 1.7* in **Help**.

## References

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