

Studijní text pro fyzikální praktikum Experimentální metody FPP II.

Úloha: Absorpční laserová spektroskopie

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1.1 Absorption spectroscopy

Absorption spectroscopy is based on principle that the absorption of radiation by a quantum system (atom, molecule etc.) is connected with transition of the quantum system between two discrete energy levels. In the following paragraphs, basic equations for absorption spectroscopy will be listed with short introduction to the topic, followed by sections on absorption line broadenings, ion number density determination from measured absorption and cavity ring-down spectroscopy.

1.1.1 Introduction to absorption spectroscopy

Monochromatic light of initial intensity I_0 passing through homogenous absorbing medium losses its intensity according to the Lambert-Beer law [Beer, 1852]:

$$\frac{dI(x, \nu)}{dx} = -\alpha(\nu)I(x, \nu), \quad (1.1)$$

where $I(x, \nu)$ is the intensity of the light of frequency ν at position x from the beginning of the absorbing medium and $\alpha(\nu)$ is the absorption coefficient. If $\alpha(\nu)$ is independent on x then the solution of equation (1.1) is:

$$I(L, \nu) = I_0 \exp(-\alpha(\nu)L), \quad (1.2)$$

where L is the distance traveled in the absorbing medium. The spectral line is characterized by its cross-section of photo-absorption:

$$\alpha(x, \nu) = N(x)\sigma(\nu), \quad (1.3)$$

where $N(x)$ is the number density of the absorbing particles at position x . The shape of the absorption line is characterized by the line-shape function $g(\nu)$ defined as:

$$\sigma(\nu) = Sg(\nu), \quad (1.4)$$

where S is the integral absorption coefficients (spectral line intensity) giving the strength of the absorption line. The line-shape function is normalized to unity:

$$\int_0^{\infty} g(\nu) d\nu = 1. \quad (1.5)$$

The Absorbance is defined as:

$$A(\nu) = -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right). \quad (1.6)$$

Caution has to be exercised because it is sometimes defined with decimal logarithm. Taking into account the solution of the Lambert-Beer law (1.2), equation (1.6) can be rewritten as:

$$A(\nu) = \alpha(\nu)L. \quad (1.7)$$

If the absorbing medium is not homogenous and contains more absorbing species the absorbance can be expressed as:

$$A(\nu) = \sum_j \sigma_j(\nu) \int_0^L N_j(x) dx, \quad (1.8)$$

where the sum is over all absorbing species present, σ_j is the cross section of photo-absorption of specie with concentration $N_j(x)$.

1.1.2 Broadenings of spectral lines

During the evaluation of the number density from the absorption lines one has to take into account the proper line-shape. In afterglow plasma, several processes (broadenings) can change the line-shape of the measured absorption line. The three most important are: the lifetime broadening, collisional broadening and Doppler broadening.

The lifetime broadening is a result of finite lifetime of the quantum states involved in the transition (the lifetime is the inverse value of the rate at which the energy level is depopulated to other states). The resulting line-shape is a Lorentzian function [Bernath, 2005]:

$$g(\nu) = \frac{\frac{\Delta\nu}{2\pi}}{(\nu - \nu_{nm})^2 + \left(\frac{\Delta\nu}{2}\right)^2}, \quad (1.9)$$

where $\nu_{nm} = (E_n - E_m)/h$ is the frequency of the transitions (lifetime broadening is symmetrical around this transitions), E_n and E_m are energy of the upper and lower state, h is Planck constant and

$$\Delta\nu = \frac{1}{2\pi} \left(\frac{1}{\tau_n} + \frac{1}{\tau_m} \right), \quad (1.10)$$

where τ_n and τ_m are lifetimes of upper and lower state. In plasmatic experiments, this type of broadening can be usually neglected in comparison with other ones.

The collisions of observed particles also cause broadening of the spectral line. If the collision is inelastic, the observed particle is excited/deexcited to other energy level leading to change in the lifetime of participating energy levels (see above). The elastic collisions lead to a random change of the wave function phase and the resulting line-shape of the absorption line is again Lorentzian function with half-width:

$$\Delta\nu = \frac{f_{col}}{2\pi}, \quad (1.11)$$

where f_{col} is the collision frequency. At low pressures (few hundreds Pa) this type of broadening is negligible in comparison with Doppler broadening. Typical values of pressure broadenings are 10 MHz per 100 Pa [Bernath, 2005]. At higher pressures (above 1000 Pa) the collisional broadening starts to play a role and has to be taken into account.

The movement of the observed particles with respect to the light source (detector) results in a shift in a frequency of the light absorbed (emitted) by the moving particle because of the Doppler effect. The observed line-shape is a result of an average of line-shape functions of all particles. Assuming Maxwell-Boltzman particle velocity distribution the resulting line-shape function is a Gaussian function:

$$g(\nu) = \frac{1}{\sqrt{2\pi}\sigma_D} \exp\left(-\frac{(\nu - \nu_{nm})^2}{2\sigma_D^2}\right), \quad (1.12)$$

where

$$\sigma_D = \nu_{nm} \sqrt{\frac{k_B T_{kin}}{Mc^2}}, \quad (1.13)$$

where k_B is the Boltzman constant, T_{kin} is the kinetic temperature of the particles, M is their mass and c is the speed of light. The full width at half maximum is obtained by multiplying σ_D with a factor of $2(2\ln 2)^{1/2} \approx 2.35$. From (1.13) the kinetic temperature can be computed as:

$$T_{\text{kin}} = \frac{\sigma_D^2 M c^2}{v_{\text{nm}}^2 k_B}. \quad (1.14)$$

In some cases there could be collisional and Doppler broadening taking part at the same time. Then fitting of the Voigt profile [Bernath, 2005] is used to obtain the contribution of Doppler and collisional broadening to the final line-shape.

1.1.3 Determination of number density

To measure the effective recombination rate coefficients, the knowledge of number density of recombining ions is desired. As in absorption spectroscopy the measured quantity is absorbance, some parameters connecting it with number density of absorbing species has to be known - integral absorption coefficient S or other quantity associated with it (e.g. Einstein coefficient of spontaneous emission A_{nm}). Following the derivation in ref. [Rothman et al., 1998] the absorption coefficient can be written as:

$$\alpha(\nu) = \left(1 - \frac{g_m N_n}{g_n N_m}\right) \frac{g_n}{g_m} N_m A_{\text{nm}} \frac{c}{8\pi \nu_{\text{nm}}^2} g(\nu), \quad (1.15)$$

where $g(\nu)$ is again the line-shape function, N_n and N_m are population of the upper and lower state respectively, g_n and g_m are their statistical weights, A_{nm} is Einstein coefficient of spontaneous emission. Under assumption that the upper state is not populated, the absorption coefficient at the center of the absorption line will be:

$$\alpha(\nu_{\text{nm}}) = \frac{g_n}{g_m} N_m A_{\text{nm}} \frac{c}{8\pi \nu_{\text{nm}}^2} g(\nu_{\text{nm}}). \quad (1.16)$$

Equation (1.16) gives the number density of one state only. Assuming Maxwell-Boltzman distribution an integral absorption coefficient can be derived from equation (1.15):

$$S = \frac{c \tilde{g}_n (2J_n + 1)}{8\pi \nu_{\text{nm}}^2 Q(T)} \exp\left(-\frac{E_m}{k_B T}\right) \left(1 - \exp\left(-\frac{E_n - E_m}{k_B T}\right)\right) A_{\text{nm}}, \quad (1.17)$$

where \tilde{g}_n is the nuclear spin degeneracy factor of the upper state, J_n is the rotational quantum number of the upper state, E_m and E_n are energies of the lower and upper state respectively, T is temperature and $Q(T)$ is partition function. If transition frequency ν_{nm} is expressed in cm^{-1} then equation (1.17) changes to:

$$S = C \frac{\tilde{g}_n (2J_n + 1)}{\nu_{nm}^2 Q(T)} \exp\left(-\frac{E_m}{k_B T}\right) \left(1 - \exp\left(-\frac{E_n - E_m}{k_B T}\right)\right) A_{nm}, \quad (1.18)$$

where $C = 1/(8\pi c) = 1.3266 \times 10^{-12} \text{ cm}^{-1}\text{s}$ and S has the dimension of $[\text{cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})]$ (commonly referred to as HITRAN unit [Rothman *et al.*, 1998]).

The partition function used in equations (1.17) and (1.18) corresponds to the internal state of the studied ionic specie at given temperature and is defined as:

$$Q(T) = \sum_k g_k \exp\left(-\frac{E_k}{k_B T}\right), \quad (1.19)$$

where g_k is the statistical weight of the state of energy E_k . To determine the partition function an accurate energy level list is necessary. At low temperature (such as in presented experiments) the number of levels needed for computation of $Q(T)$ is limited and the energy levels of many quantum systems are known with sufficient precision. The partition functions are usually fitted by an analytical function such as:

$$\log_{10} Q(T) = \sum_{n=0}^6 a_n (\log_{10} T)^n, \quad (1.20)$$

where T is in Kelvins.

The overall number density of the ionic specie probed N can then be computed from the measured absorbance A at the peak center of the Doppler broadened line by using equations (1.3), (1.4), (1.7) and (1.12):

$$N = \frac{A \sqrt{2\pi} \sigma_D(T)}{S(T)L}, \quad (1.21)$$

where L is the distance the light traveled in the absorbing medium.

1.1.4 References

Beer A.: *Annalen der Physik und Chemie* **86**, 78, 1852.

Bernath P. F.: *Spectra of Atoms and Molecules*. Oxford University Press, Oxford, 2005.

Rothman L. S. et al.: *J. Quant. Spectrosc. Radiat. Transfer* **110**, 533, 2009.

Table 5 Certified Wavelengths for SRM 2519

The table lists the vacuum wavelengths of line centers in the $\text{H}^{13}\text{C}^{14}\text{N } 2\nu_3$ band for the 13.3 kPa (100 Torr) SRM cell pressure. The 21 lines that were measured at NIST are certified with an expanded uncertainty (coverage factor $k = 2$) of ± 0.0006 nm. These lines are shown in the table with a (6) indicating the uncertainty in the last digit. The remaining line centers listed are the literature values from Ref. [1]. These values are certified with an expanded uncertainty of ± 0.003 nm, where the uncertainty is dominated by the pressure shift uncertainty.

R Branch	wavelength (nm)	P Branch	wavelength (nm)
25	1528.054	1	1543.1148(6)
24	1528.4862(6)	2	1543.809
23	1528.9271(6)	3	1544.515
22	1529.376	4	1545.2314(6)
21	1529.8376(6)	5	1545.9563(6)
20	1530.306	6	1546.690
19	1530.786	7	1547.435
18	1531.2764(6)	8	1548.190
17	1531.774	9	1548.9554(6)
16	1532.283	10	1549.7302(6)
15	1532.8024(6)	11	1550.5149(6)
14	1533.329	12	1551.311
13	1533.867	13	1552.116
12	1534.4159(6)	14	1552.931
11	1534.972	15	1553.756
10	1535.5401(6)	16	1554.5892(6)
9	1536.1170(6)	17	1555.4346(6)
8	1536.7034(6)	18	1556.292
7	1537.2997(6)	19	1557.157
6	1537.907	20	1558.033
5	1538.5224(6)	21	1558.919
4	1539.149	22	1559.814
3	1539.786	23	1560.7185(6)
2	1540.431	24	1561.6344(6)
1	1541.087	25	1562.563
0	1541.753		

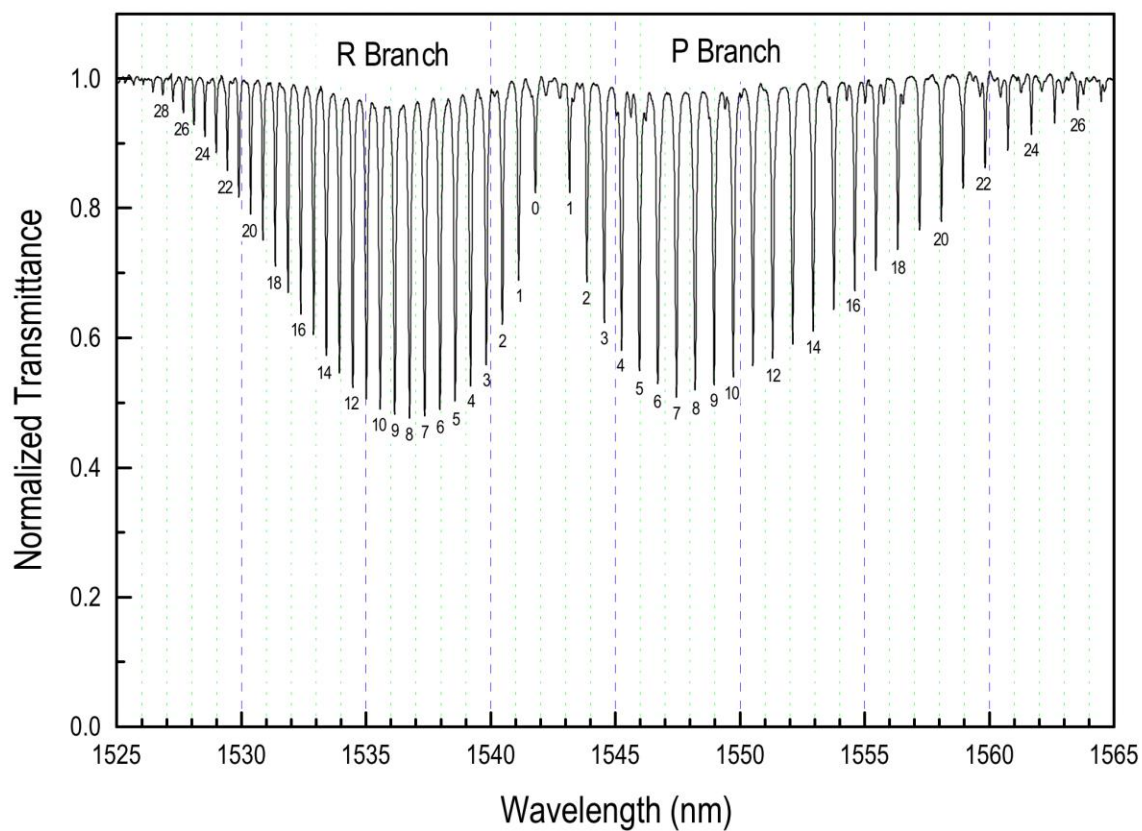


Figure 1. Hydrogen cyanide (H¹³C¹⁴N) spectrum taken by passing LED light through a SRM unit and recording the spectrum of the transmitted light using an optical spectrum analyzer with 0.05 nm resolution. The figure shows the recorded spectrum divided by the LED spectrum. The HCN gas pressure is 13 kPa and the optical path length through the gas is 22.5 cm.