PROVISIONAL DOCUMENT

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMICAL DIVISION

COMMISSION ON SPECTROCHEMICAL AND OTHER OPTICAL PROCEDURES FOR ANALYSIS

Nomenclature, Symbols, Units, and Their Usage in Spectrochemical Analysis - XVII

LASER-BASED MOLECULAR SPECTROMETRY FOR CHEMICAL ANALYSIS: ABSORPTION

(IUPAC recommendations 1996)

Prepared for publication by

G. Gauglitz[1] and D. S. Moore[2]

[1]Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-72076 Tübingen, Germany

[2]Fresenius' Journal of Analytical Chemistry, Postfach 1261, D-65220 Taunusstein, Germany

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CONTENTS

Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis - XVII. Laser-based Molecular Spectrometry for Chemical Analysis: Absorption (IUPAC Recommendations 1996)

SYNOPSIS

This report is the 17th in a series on spectrochemical methods of analysis issued by IUPAC commission V.4. It is concerned with the principles of laser absorption spectroscopy and its application in the optical wavelength region. The present report has four main sections: fundamentals of laser absorption spectroscopy, Doppler-limited spectroscopy; sub-Doppler laser spectroscopy, and time-resolved laser spe ctroscopy

1 INTRODUCTION

A series of documents dealing with nomenclature, symbols and units used in spectrochemical analysis is issued by IUPAC.

Part I (Pure Appl. Chem., 30, 653-679 (1972)) is concerned mainly with general recommend a-tions in the field of emission spectrochemical analysis.

Part II (Pure Appl. Chem., 45, 99-103 (1976)) gives some basic rules on data interpretation.

Part III (Pure Appl. Chem. 45, 105-123 (1976)) deals extensively with the nomenclature of an a-lytical flame (atomic emission and absorption) spectroscopy and associated procedures.

Part IV (Pure Appl. Chem. 52, 2541-2552 (1980)) concerns X-ray emission (and fluorescence) spectroscopy.

Part V (Pure Appl. Chem. 57, 1453-1490 (1985)) deals with the classification and description of radiation sources.

Part VI (Pure Appl. Chem. 56, 231-345 (1984)) covers molecular luminescence spectroscopy.

Part VII (Pure Appl. Chem. 60, 1449-1460 (1988)) is concerned with molecular absorption spectroscopy (UV/VIS).

Part VIII (Pure Appl. Chem. 63, 735-746 (1991)) deals with a new nomenclature system for X-ray spectroscopy.

Part IX (Pure Appl. Chem. 67, 1725-1744 (1995)) covers fundamental aspects of spectral di s-persion and isol ation of radiation.

Part X (Pure Appl. Chem. 60, 1461-1472 (1988)) deals with sample preparation for ana lytical atomic spectroscopy and other related techniques.

Part XI (Pure Appl. Chem. 67, 1745-1760 (1995)) deals with the detection of radiation.

Part XII (Pure Appl. Chem. 64, 253-259 (1992)) deals with terms related to electrothermal a t-omization.

Part XIII (Pure Appl. Chem. 64, 261-264 (1992)) deals with terms related to chemical va pour generation.

Part XIV (Pure Appl. Chem.) deals with a general notation for laser-based atomic spectro s-copy

Part XV (Pure Appl. Chem. 67, 1913-1928 (1995)) Laser-based molecular spectroscopy for chemical analysis - Fundamentals

Part XVI (Pure Appl. Chem.) Laser-based molecular spectrometry for chemical analysis: lum i-nescence

Part XVIII (Pure Appl. Chem.) Laser-based molecular spectrometry for chemical analysis: R a-man scattering

This document, Part XVII, deals with the fundamentals and applications of laser absorption spectroscopy used in laser based molecular spectroscopy for chemical analysis.

Basic aspects of spectral resolution limited by the Doppler width of molecular absorption are treated, application of single mode or multi-mode lasers is discussed, approaches to high-resolution sub-Doppler laser spectroscopy are given, and applications are seen with this respect.

This document does not cover laser-induced effects causing luminescence which are covered in part XVI, scattering processes covered in part XVIII, or photo acoustic spectroscopy covered in part XIX.

2 FUNDAMENTALS

In absorption spectroscopy especially tunable lasers are used. Their applicability depends on their spectral resolution determined either by Doppler limitations, the frequency stabilization, or methods of sub-Doppler spectroscopy. Applications further depend on detection techniques with respect to feasibility in different spectral regions and their sensitivity.

2.1 Interaction radiation and matter

2.1.1 Oscillation model

According to the classical model of the refractive index the interaction between a medium and propagating radiation can be described by the model of a damped forced oscillation. According to this model the refractive index becomes a complex number in the range of resonance-frequency

$$\tilde{n} = n' - \mathrm{i}\, n'' \quad . \qquad \text{eq. (1)}$$

The dependence of the refractive index on wavelength is called the dispersion curve. Its imaginary part n'' relates to the absorption coefficient. The Kramers-Kronig dispersion equations combine absorption and dispersion by use of the complex refractive index. The transition moment (see Ref. 2) can be calculated by use of the time-dependent Schrödinger-equation and the wave-functions of the ground and exited states. Einstein and absorption coefficients (see [XV]) correlate to this transition moment.

2.1.2 Nonlinear absorption

The absorbed intensity is proportional to the intensity of the incident radiation in linear absorption. Using a laser one can obtain an irradiance large enough to significantly alter the population of the energy levels, resulting in nonlinear absorption. These saturation effects give rise to line-broadening (sec. 2.2.1.3).

2.1.3 Reflection

According to Fresnel's law the refracted radiant power is influenced by the complex refractive index of matter, the angle of incidence, and the azimuthal angle of polarization. The ratio of refractive indices at the interface between two media governs the amount of radiation penetrating the interface. Thus this radiation contains information on the medium's absorption spectrum. For exact intensity measurements reflections at all interfaces have to be taken into account.

2.2 Laser characteristics and absorption spectra

2.2.1 Line width

Both the line widths of the laser radiation [see [XV 2.6.2]) and the sample spectrum are important in absorption spectrometry.

The function of the intensity in the vicinity of n_0 is called the line profile. The frequency interval for the two frequencies at which the intensity is half the maximum is the full width at half maximum (FWHM), shortly called line width or half width. The regions outside this kernel are the line wings (see Fig. 1). The line width of a damped oscillator having a natural line width given by a Lorentzian profile corresponds to the natural line width dn .

$$\delta\nu = \frac{A_i}{2\pi} = \frac{1}{2\pi\tau_i} \qquad \text{eq. (2)}$$

or

$$\delta\omega = A_i = \frac{1}{\tau_i} \qquad \text{eq. (3)}$$

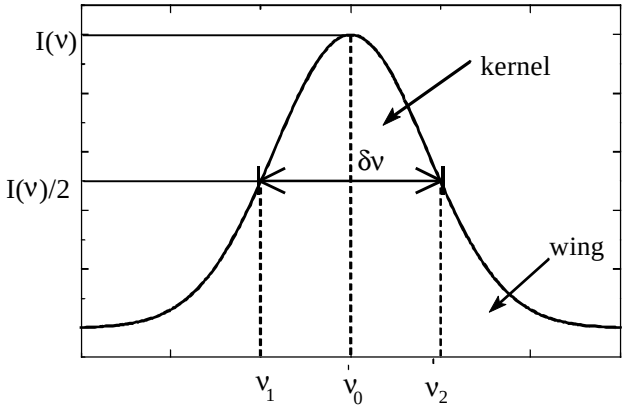


Fig. 1: Line profile: *natural line width* dn , kernel, and wings of a spectral line.

The natural line width correlates the Einstein coefficient A_i of spontaneous emission to the life time τ_i of a molecular level. If the lower state is an excited state also, both the uncertainties contribute to the line width.

2.2.1.1 Spectral resolution

The resolving power (see [I, IX]) is defined by

$$R = \left|\frac{l}{\Delta l}\right| = \left|\frac{n}{\Delta n}\right| \qquad \text{eq. (4)}$$

giving the minimal separation of closely spaced lines. According to the Rayleigh criterion the central diffraction maximum coincides with the first minimum of the other line (s. Fig. 2). Two lines are just resolved if the dip between the maxima drops to $8/\pi^2 \approx 0.8$ of I_{max}.

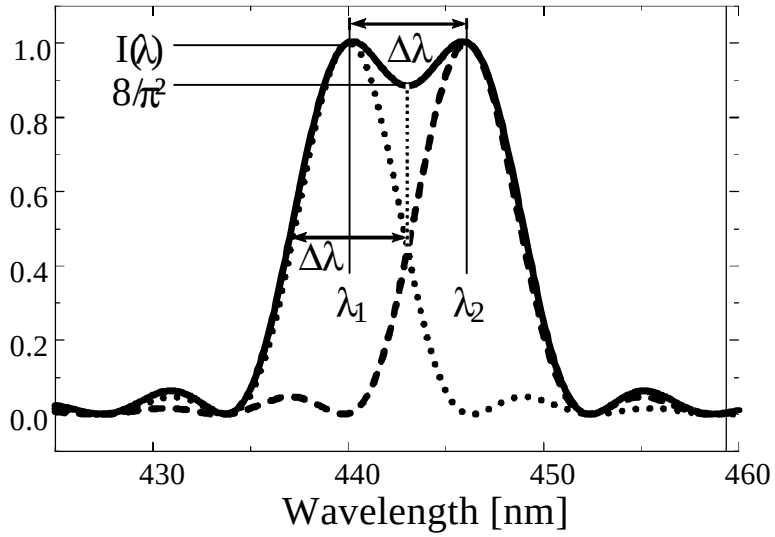
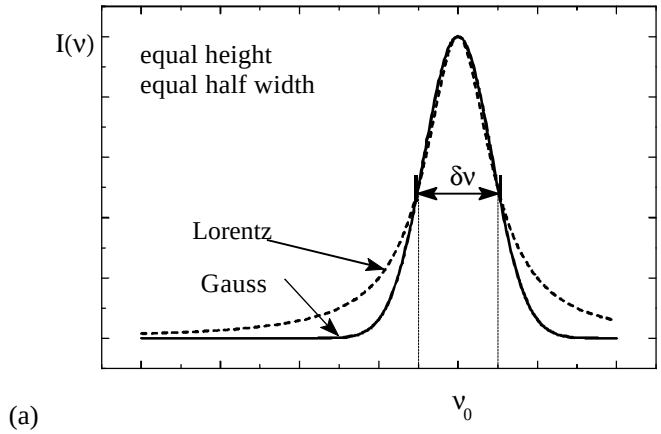


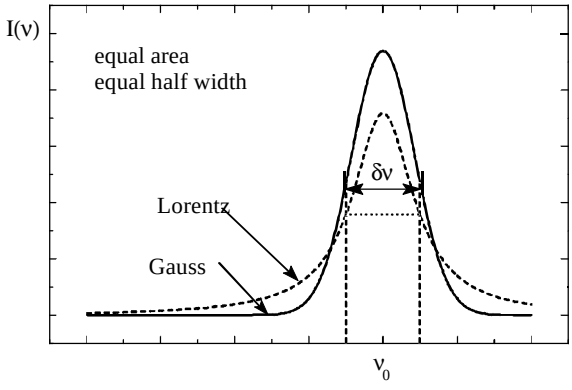
Fig. 2: Rayleigh criterion

2.2.1.2 Line profiles

The Doppler effect broadens the natural line (Lorentzian profile s. Fig. 3) profile due to the thermal motion of the absorbing or emitting *species*. This Doppler broadened spectral line exhibits a Gaussian profile, which exceeds the natural line width by approximately two orders of magnitude at ambient conditions (see [XVI]).



(a)



(b)

Fig. 3: Lorentzian and Gaussian line profile (a): equal heights , (b) equal areas.

Since not all the molecules with a definite velocity emit or absorb at the same frequency, the intensity profile is a convolution of Lorentzian and Gaussian profiles, called the Voigt profile (see Fig. 4; also [XVI]).

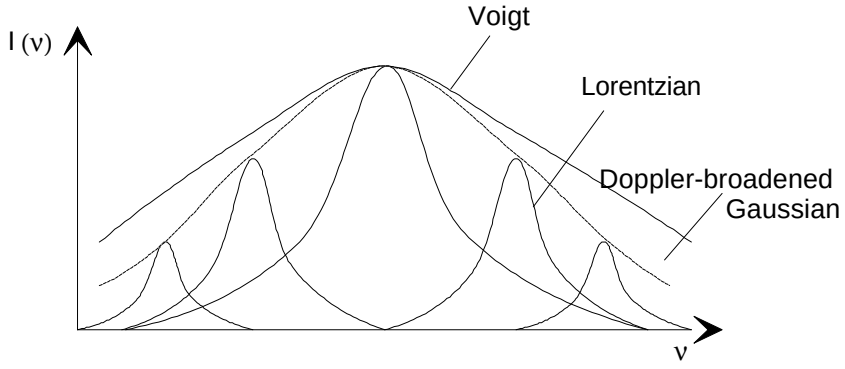


Fig. 4: Voigt line profile

2.2.1.3 Broadening of lines

The Lorentzian profile is given by homogeneous broadening which occurs if the probability of transition of absorption or emission is equal for all molecules in the considered level. Natural line broadening is an example. If the probability is not equal for all the molecules, but depends on their velocity, inhomogeneous line broadening occurs, which is a Doppler broadening.

Interaction between particles results in collision broadening which is due to a decrease in the excited-state lifetimes. Since pressure influences the collision rate, it causes pressure broadening Another broadening process is due to the time flight of molecules across the laser beam which is called time of flight broadening.

Saturation of the population densities causes an additional saturation broadening, which can be either homogeneous or inhomogeneous (sec. 3.2.2)

2.2.2 Polarization

According to the orientation of the molecules in the laser source, the radiative coupling of the two levels, and laser oscillator parameters, a laser exhibits polarisation properties (see [XV]). These properties can be used in laser induced dichroism and birefringence measurements. Other applications of polarized radiation are ellipsometry and surface plasmon resonance.

2.2.3 Fluctuations

Reduction of limits of decision and determination requires an increase of the signal-to-noise ratio of laser sources. It depends on the stability of intensity and wavelength (see [XV 5.1]).

2.2.3.1 Intensity

The intensity of a continuous wave source shows periodic and random fluctuations.

Long-term drifts may be caused by temperature and pressure changes either in the source or by thermal detuning of the resonator as well as effects of the mirrors, windows, and optical components.

Intensity stabilization is achieved either by a split beam with a servo loop controlling the discharge current. Fast fluctuations are reduced by use of a Pockels cell, whose transmittance is changed using feedback techniques.

2.2.3.2 Wavelength

For extreme wavelength stability only single-mode lasers can be used. In most multi-mode lasers only the time-averaged envelope of the spectral output profile is defined.

Long-term drifts are mainly caused by temperature or small pressure changes. The main contribution to short term fluctuations are the acoustical vibrations of the resonator system and refractive index fluctuations. By referencing to an atomic transition or using a Fabry-Perot interferometer these drifts may be reduced by feedback techniques.

2.3 Terms in quantitative analysis

In absorption spectroscopy both the intensity and laser property of the light source influence the limits of detection and limits of determination of a sample.

Whereas the limit of decision is defined as minimal significant signal according to calibration experiments, both the limit of detection and limit of determination (quantification) are defined as concentrations: The first is the minimal concentration corresponding to the minimal signal at the limit of decision; The latter includes the confidence intervals of the calibration curve and the analytical function (inverse of the calibration function). In some literature the three terms are correlated to 3σ, 6σ and 10σ values of the signal to noise ratio, where σ represents the statistically calculated standard deviation using a Gaussian distribution. This definition of terms is represented in Fig. 5.

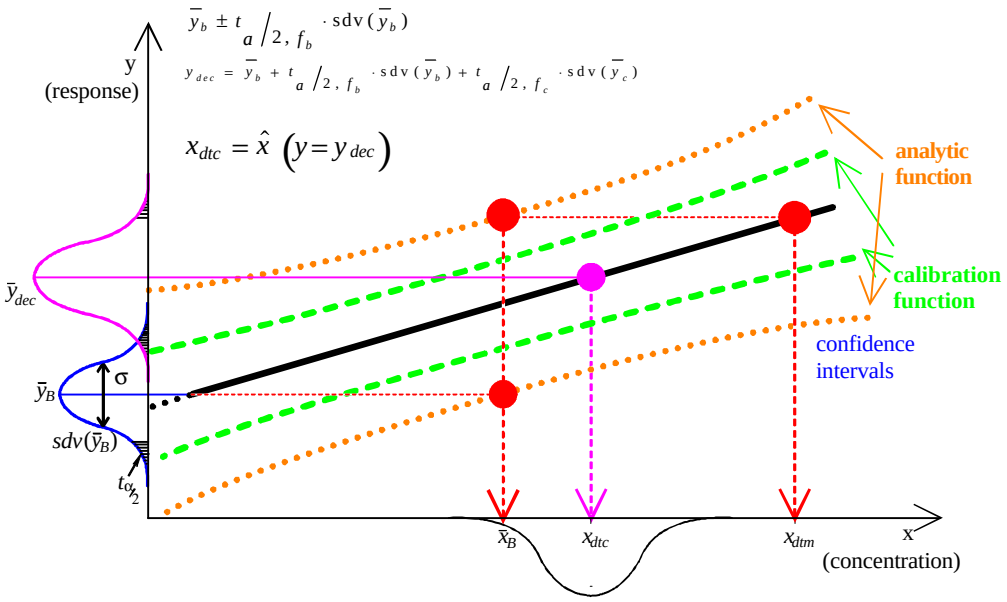


Fig. 5: Axis of signals vs. axis of concentration correlating, blank (y_b), limits of decision (y_{dec}), detection (x_{dec}), and determination (x_{dtm}).

3 IMPROVED TECHNIQUES IN MOLECULAR ABSORPTION SPECTROSCOPY

3.1 Doppler-limited absorption spectroscopy

In Doppler-limited absorption spectroscopy, the spectral resolution is limited by the width of lines in the molecular absorption or emission spectra, although the laser line width itself might be smaller.

In case of small absorption coefficients, a small difference of two large quantities has to be determined. This problem can be minimized: 1) by frequency modulation, tuning the laser through the absorption spectrum. The difference of transmitted intensities for two frequencies is detected

with a phase-sensitive detector (lock-in), timed to the modulation frequency *f*. This restricts frequency response to a narrow interval at *f*. This is superior to intensity modulation, or 2) directly monitoring the intensity absorbed rather than relying on the difference measurement. A further approach is intracavity absorption, placing the sample inside the resonator (3.1.3).

3.1.1 Excitation spectrum

In fluorescence excitation spectroscopy monitoring the fluorescence intensity during variation of the wavelength of excitation within the absorption band, even in the case of extremely small absorption coefficients or concentrations, a measurable signal proportional to the absorption band is obtained. Increasing the intensity of the excitation source amplifies the signal. The excitation spectrum resembles the absorption spectrum.

3.1.2 Photoacoustic spectroscopy

In an absorbing molecular transition, part of the absorbed laser intensity is transfered to thermal energy, which gives rise to temperature and pressure changes. In photoacoustic spectroscopy , periodic modulations of the laser beam produces pressure variations which can be detected by a microphone or other transducer.

3.1.3 Intracavity absorption

The detection sensitivity is manifold increased, if the sample is placed inside the cavity. Several effects can give rise to such amplification:

Q-factor amplification [V 6.2.3, XV 5.3] can be obtained via the multiple passes through the sample as long as saturation effects can be neglected and the absorption coefficient is small. Multiple reflections increase the finesse F^*, which is ratio of the free sprectral range dn of an interference filter or interferometer to the theoretical half width Δn given by

$$F^* = \frac{dn}{\Delta n} = \frac{p\sqrt{r}}{1-r} \quad , \qquad \text{eq. (5)}$$

which is determined by the reflectivity ρ and determines the resolving power R of an interferometer.

If the internal loss of the cavity is low, large enhancement factors are achieved for absorptive samples in case of laser beams matched to fundamental modes of an external passive resonator.

Just above threshold (see [XV] minor changes in intracavity losses drastically change laser output. Mode competition and mode coupling phenomena sensitively cause mode oscillations. One of the oscillating modes is tuned across the absorption spectrum into resonance, changing the laser frequency.

3.1.4 Ionisation spectroscopy

Absorption of photons by molecular transitions can be monitored by ionisation spectroscopy, detecting ions or electrons produced by photoionisation (by radiation), by collision induced ionisation (thermally), or by field ionisation (external electric field).

3.1.5 Strong external magnetic or electric field effects

In some cases it is preferable to tune the absorption lines of molecules with permanent magnetic or electric dipole moments using external fields rather than tuning the laser frequency in spectral regions where tunable laser sources do not exist.

3.1.5.1 Laser magnetic resonance spectroscopy

By an external magnetic field the molecular levels are split into the Zeeman levels. Laser magnetic resonance (LMR) spectroscopy is very sensitive, it allows determination of rotational co n-

stants, fine structure parameters, and magnetic moments of molecules, e.g. of radicals in low concentration in gases.

3.1.5.2 Stark spectroscopy

In Stark spectroscopy an external electric field is used to tune molecular absorption lines of small molecules with permanent electric dipole moment via the Stark shift. The quality of the determined molecular parameters is limited by the accuracy of the electric field measur ement.

3.1.6 Resonance methods and multi photon transitions

Optical-optical double resonance can be achieved by stepwise excitation cause by simultaneous interaction of two optical fields. This concept can be varied by combining photons of frequencies of different spectral ranges as optical-radio-frequency, microwave-infrared, or optical-microwave double resonance. Special selection rules govern the transition probability as for the two photon process of Raman scattering (see [XVIII]).

3.2 High resolution sub-Doppler laser spectroscopy

Most of these techniques require a tunable single-mode laser with bandwidth smaller than the desired spectral resolution. The laser frequency fluctuations have to be smaller than the natural line width $\delta\nu$ which requires frequency stabilization techniques. The basic principle of Doppler-free spectroscopy relies on the separation of molecules with small velocity distribution in the direction of the incident monochromatic wave or on a coherent preparation of a molecular state.

3.2.1 Molecular beam techniques

Produced in an oven, molecules pass through a small hole A and at a distance d a second slit B (diameter $b << d$) in a free pass forming a molecular beam with flux density approximately constant across the beam diameter.

The collimated molecular beam is crossed perpendicular with a monochromatic probe laser. The Doppler width is reduced by the factor which equals the collimation ratio of the beam. Especially for polyatomic molecules with their complex visible absorption spectra, the method is essential for the resolution of single lines.

By free expansion of a gas into a vacuum, molecular beams are internally cooled (internal cooling). The amount of cooling depends on the number of collisions during expansion. Only the lowest rotational-vibrational levels in the ground state are populated and only loosely bound molecules with small dissociation energies (van der Waals molecules) can be formed. Because of the perpendicular crossing this reduction of Doppler width is called geometrical cooling.

Molecular beam and probe laser radiation are collinear within an acceleration voltage between two electrodes thus reducing the longitudinal velocity distribution in acceleration cooling.

3.2.2 Saturation spectroscopy

By optical pumping with a monochromatic tunable laser, an inhomogeneously broadened m olecular transition is selectively saturated. A ‘hole’ is burned into the population distribution of the absorbing state (hole burning). In Fig. 6 the population distributions of the lower (i) and upper (k) state are given with the effect of this hole burning.

With the saturation parameter

$$S_0 = 2S/pg \qquad \text{eq. (6)}$$

at the center of the absorption line one can define a ratio

$$S = B_{ik}\,\rho_{ik}\,(\nu) / R \qquad \text{eq. (7)}$$

of the depletion absorption rate $B_{ik}\, r_{ik}(w)$ to the sum R of all relaxation processes refilling level i. B_{ik} represents the Einstein coefficient for the transition $i \rightarrow k$ and r is the energy density of the radiant field. Given a normalised homogeneous line profile of a molecular transition with line width

$$g_s = g \cdot \sqrt{1 + S_0} \quad (g = g_n + g_C) \qquad \text{eq. (8)}$$

where g_n is the natural line width and g_c the collisional broadening line width, and saturation broadening by strong fields, g_s is very much smaller than the Doppler width, if the interaction time of the molecules with the radiation is longer than spontaneous lifetime, and pressure as well as saturation broadening can be neglected at small laser intensities. This homogeneous line width represents the spectral width g_S which is called the Bennet hole. Probing the population with a second laser and using a mirror arrangement, the back and forth propagating wave interacts with different molecules. As long *as* $\nu \neq \nu_0$ two different waves are burnt into the population distribution. They merge together at $\nu = \nu_0$. When both waves interact with the same molecules (see Fig. 7), they are exposed to twice the intensity, forming a small dip in the center ('Lamb dip').

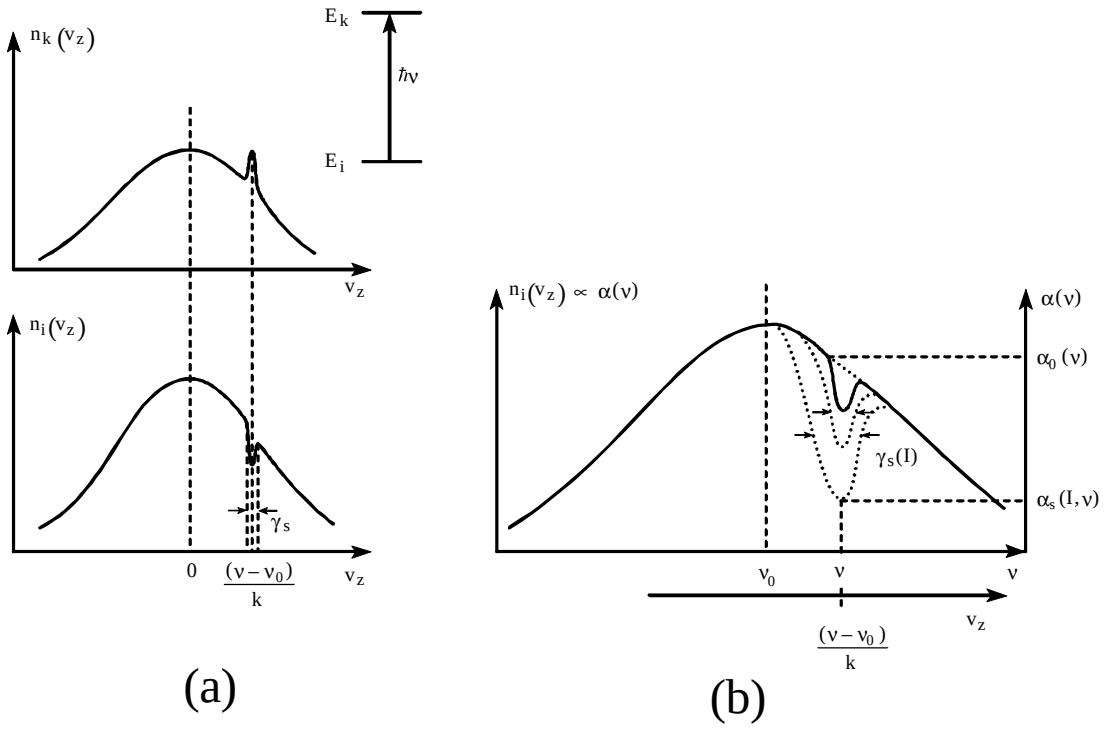


Fig. 6: (a) Population distribution of lower and upper state influenced by saturation and (b) increase of the Bennet hole with saturation intensity.

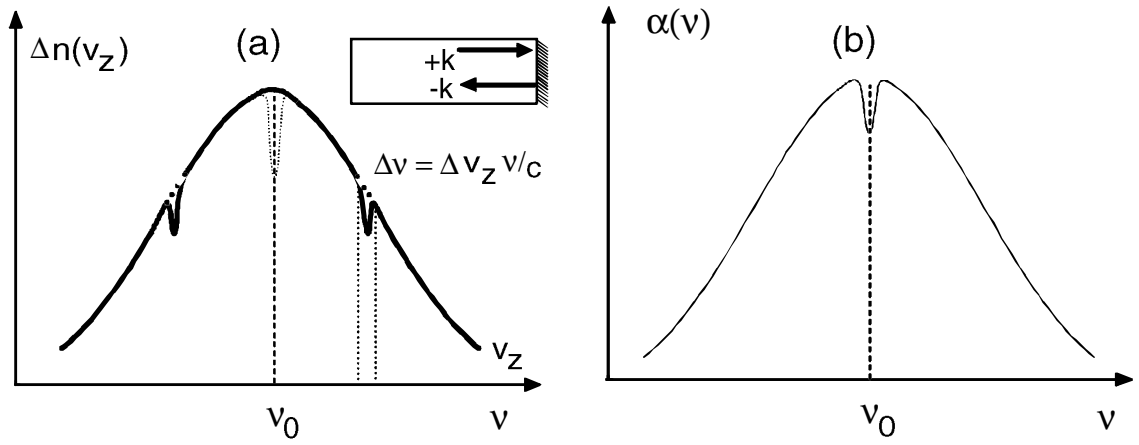


Fig. 7: Bennet hole (a) and Lamb dip (b) of two counterpropagating waves +k and -k at a Doppler-broadened absorption line; population distribution $\Delta n(v_z)$ and absorption coefficient $\alpha(\nu)$ in dependence on frequency and velocity component v_z of molecules.

3.2.2.1 Doppler free saturation spectroscopy

Closely spaced absorption lines (see Fig. 8) are completely masked in the case of Doppler-limited spectroscopy. However, their Lamb dips can be resolved.

3.2.2.2 Lamp dip stabilisation

The Lamb dip in a laser output can be used to lock the frequency to the center of the gain profile and stabilise wavelength by third derivative fed back to a lock-in amplifier as a reference.

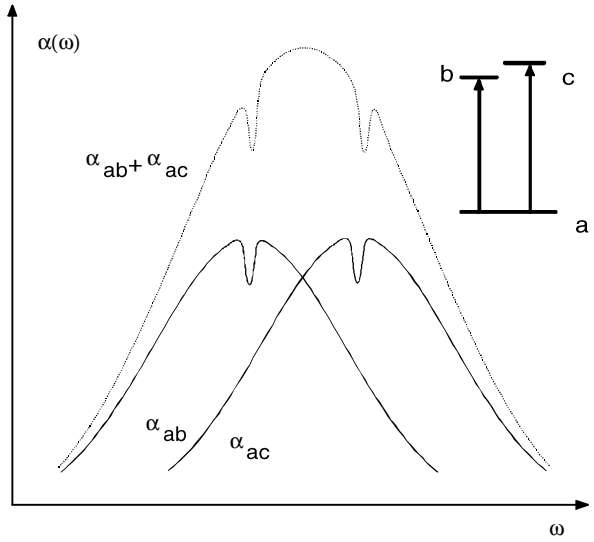


Fig. 8: Within Doppler profiles overlapping transitions resolved by their Lamb dips.

3.2.2.3 Coupled transitions

Coupling phenomena exist for two laser fields at two frequencies interacting simultaneously with molecules at the same level. The interaction between the fields and the molecular system is non-linear.

3.2.3 Polarization spectroscopy

Polarization spectroscopy is a sensitive Doppler-free technique that results mainly from the change of the refractive index induced by the polarized pump radiation, which produces a non-equal saturation and in consequence a non-uniform population of the sublevels. The results are small differences in amplitude and phase. Line profile and magnitude of the polarization signals depend on the small differences in absorption coefficients and refractive indices.

Polarization labelling spectroscopy is based on a combination of polarization spectroscopy and optical double resonance. This technique is especially useful if the upper state is perturbed.

A slight variation of the experimental set-up allows the simultaneous observation of saturated absorption and dispersion. The measurement of the probe beam polarization for parallel and perpendicular polarizations supplies for different positions of the analyser to separate the dichroitic signal (anisotropic saturated absorption) and the birefringence signal (saturated dispersion).

3.2.4 Interference spectroscopy

Interference spectroscopy has higher sensitivity than polarization spectroscopy because of the use of detection of phase differences rather than amplitude differences. A pure dispersion line profile is obtained without distortion by a Lorentzian term.

3.2.5 Heterodyne spectroscopy

Heterodyne spectroscopy is a very accurate method to determine line splittings.Two independent lasers are stabilized onto the line centers of two different molecular transitions and their outputs are superimposed and detected on a nonlinear detector.

3.2.6 Multi photon spectroscopy

Simultaneous absorption of two photons from waves travelling in opposite directions produces a zero Doppler shift. All molecules absorb at the same sum frequency independent of their velocities.

3.2.6.1 Level crossing spectroscopy

An additional magnetic field acts as a Lorentz force on the oscillating electron, which causes the plane of oscillation to precess around the field direction with a Lamor angular frequency. In molecules the hyperfine splittings complicate the angular momentum coupling scheme. The shape of the Hanle signal depends on the orientation of the polarizer. If the Landé factor is known, level crossing spectroscopy supplies the effective life time of the excited level.

4 TIME RESOLVED LASER SPECTROSCOPY

4.1 Lifetime measurement methods

4.1.1 Phase shift

In the phase shift method, sinusoidally modulated incident light excites the molecular level using either a Pockels cell or an ultrasonic modulator. Fluorescence intensity observed perpendicularly to the incident light is phase shifted with respect to the incident light. This phase shift depends on the life time. Non-exponential decays need measurement at different modulation frequencies.

4.1.2 Pulse excitation

Pulse excitation using a pulsed or mode-locked laser (see [XV]) avoids problems with the influence of induced emission. The decay is monitored by boxcar or transient recorder techniques. Deviations from exponential decays can be seen directly.

4.1.3 Delayed coincidence

In the delayed coincidence method, short excitation pulses are kept so low in intensity that not more than one fluorescence photon is emitted per pulse, which is monitored by single photon counting techniques.

4.1.4 Time-of-flight

Molecular beams (sometimes accelerated by a voltage) are excited at a well-defined location and the subsequent fluorescence intensity is measured at a distance from the point of excitation in the time of flight method.

4.2 Transient absorption spectroscopy

The experimentally measured quantity in transient absorption spectroscopy is the change in absorbance at a given probe wavelength as a function of time following an excitation pulse. Fast transient absorption measurements of isotropic samples are generally dependent on the relative polarizations of the pump and probe pulses. Population and orientation information has to be separated. In the case of picosecond spectroscopy streak cameras are used.

5 LITERATURE

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2. Mill, I and Cvitas T, "Quantitites, Units and Symbols in Physical Chemistry, 2nd Ed." (Blackwell, UK, 1993)

6 INDEX OF TERMS