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NOMENCLATURE, SYMBOLS, UNITS, AND THEIR USAGE IN SPECTROCHEMICAL ANALYSIS—XVII. LASER-BASED MOLECULAR SPECTROMETRY FOR CHEMICAL ANALYSIS: ABSORPTION

(IUPAC Recommendations 1999)

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Nomenclature, symbols, units, and their usage in spectrochemical analysis—XVII. Laser-based molecular spectrometry of chemical analysis: Absorption (IUPAC Recommendations 1999)

CONTENTS

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Abstract: 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 spectroscopy.

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 recommendations 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 analytical 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 dispersion and isolation of radiation.

Part X (*Pure Appl. Chem.* **60**, 1461–1472 (1988)) deals with sample preparation for analytical 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 atomization.

Part XIII (*Pure Appl. Chem.* **64**, 261–264 (1992)) deals with terms related to chemical vapour generation.

Part XIV (*Pure Appl. Chem.* **70**, 517–526 (1998)) deals with a general notation for laser-based atomic spectroscopy.

Part XV (*Pure Appl. Chem.* **67**, 1913–1928 (1995)) introduces the fundamental aspects for laser-based molecular spectroscopy for chemical analysis.

Part XVI (*Pure Appl. Chem.* **69**, 1435–1449 (1997)) presents nomenclature for laser-based molecular spectrometry for chemical analysis methods involving luminescence.

Part XVIII (*Pure Appl. Chem.* **69**, 1451–1468 (1997)) presents nomenclature for laser-based molecular spectrometry for chemical analysis methods involving Raman spectroscopy.

This document, Part XVII of this series, deals with the fundamentals and applications of laser absorption spectroscopy used in laser-based molecular spectroscopy for chemical analysis. It has four main sections: fundamentals of laser absorption spectroscopy, Doppler-limited spectroscopy, sub-Doppler laser spectroscopy, and time-resolved laser spectroscopy [1].

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

This document does not cover laser-induced effects causing luminescence, which are covered in Part XVI, or scattering processes, which are covered in Part XVIII. Some relevant common terms have already been defined in Part XVI and are not redefined here. References to earlier documents in this series are given in square brackets.

2 FUNDAMENTALS

In absorption spectroscopy, especially, *tunable lasers* [see VII, XV] 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 their feasibility in different spectral regions and their *sensitivity* [see II].

2.1 Interactions between radiation and matter

2.1.1 Oscillation model

According to the classical model of the *refractive index* [see I, IX], 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 a resonance frequency:

$$\hat{n} = n - \mathrm{i}k \tag{1}$$

where n is the real refractive index and the imaginary part k is the *absorption index*, which can be related to the *absorption coefficient*. The dependence of the refractive index on frequency (wavelength) is called the *dispersion curve*. The *Kramers–Kronig* relations combine absorption and dispersion by use of the complex refractive index $\hat{n}$. The *transition moment* [2] can be calculated by use of the time-dependent Schrödinger equation and the wavefunctions of the ground and excited states. The Einstein transition probabilities [see XV] correlate to this transition moment.

2.1.2 Nonlinear absorption

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

2.1.3 Reflection and refraction

According to the *Fresnel equations*, the reflected and refracted radiant powers are influenced by the complex refractive indices of matter adjacent to an interface, 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 about the medium's absorption spectrum. For exact irradiance or radiant power measurements, *reflections* at all interfaces have to be taken into account. The effects of chirality will be dealt with in a future document.

2.2 Laser characteristics and absorption spectra

2.2.1 Linewidth

Both the linewidths of the laser radiation [see XV, 2.6.2] and the *absorption spectrum* of the sample are important in absorption spectrometry.

Due to Heisenberg's uncertainty principle, the energy uncertainties of the upper and lower energy levels of a transition at *central transition frequency* ν_0 produce a line of finite width. The function of the intensity in the vicinity of ν_0 is called the *line profile*. The frequency interval between the two frequencies at which the intensity is half the maximum is the *full width at half-maximum* (FWHM), called more briefly *linewidth* or *half-width*. The regions outside this *kernel* are the *line wings* (see Fig. 1). The line profile of a *damped oscillator* is given by a *Lorentzian profile* [see XVI] whose width corresponds to the *natural linewidth* $\delta\nu$.

$$\delta\nu = \frac{A_{ij}}{2\pi} = \frac{1}{2\pi\tau_{\mathrm{rad}}} \tag{2}$$

or

$$\delta\omega = A_{ij} = \frac{1}{\tau_{\mathrm{rad}}} \tag{3}$$

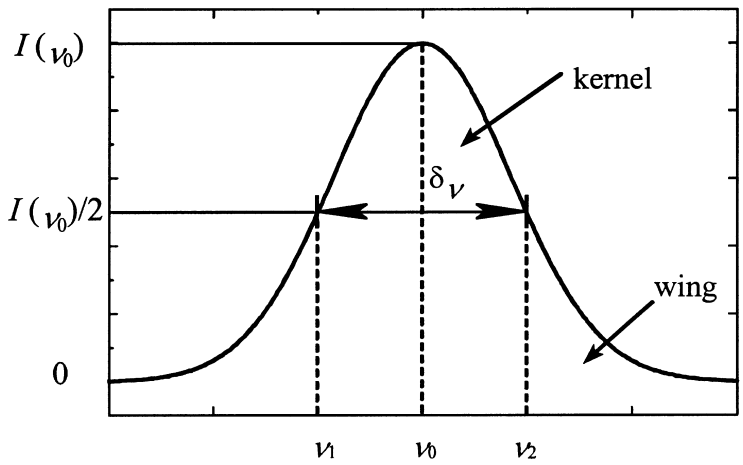

Fig. 1 Line profile: *natural linewidth* $\delta\nu$, kernel, and wings of a spectral line.

The natural linewidth correlates the *Einstein transition probability* A_{ij} of spontaneous emission to the *radiative lifetime* τ_{rad} of a molecular level [see XV]. If the lower state is also an excited state, both of the uncertainties contribute to the linewidth.

2.2.1.1 Spectral resolution. The *resolving power* [see I, IX] is defined by

$$R = \left|\frac{\lambda}{\Delta\lambda}\right| = \left|\frac{\nu}{\Delta\nu}\right| \tag{4}$$

(where λ is the wavelength, see Fig. 2) giving the minimal separation of closely spaced lines. According to the *Rayleigh criterion* (for diffraction-limited optical systems), this condition is fulfilled if the central diffraction maximum of one line coincides with the first minimum of the other line (see Fig. 2). This coincidence is indicated for a Lorentzian line when the dip between the maxima drops to $8/\pi^2 \approx 0.8$ of $I_{\max}$.

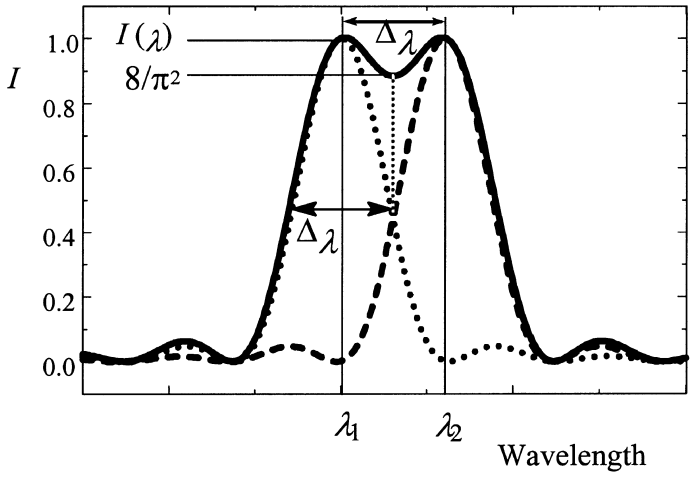

Fig. 2 Rayleigh criterion.

2.2.1.2 Line profiles. The Doppler effect broadens the natural line profile (see Lorentzian profile in Fig. 3) due to the thermal motion of the absorbing or emitting species. This Doppler-broadened spectral line exhibits a *Gaussian profile*, which exceeds the natural linewidth by approximately two orders of magnitude at standard conditions of temperature and pressure [see XVI].

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]).

2.2.1.3 Broadening of lines. The Lorentzian profile is given by *homogeneous broadening* [see XVI], 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 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 of 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 (Section 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 *polarization* 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 fluctuations. 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.

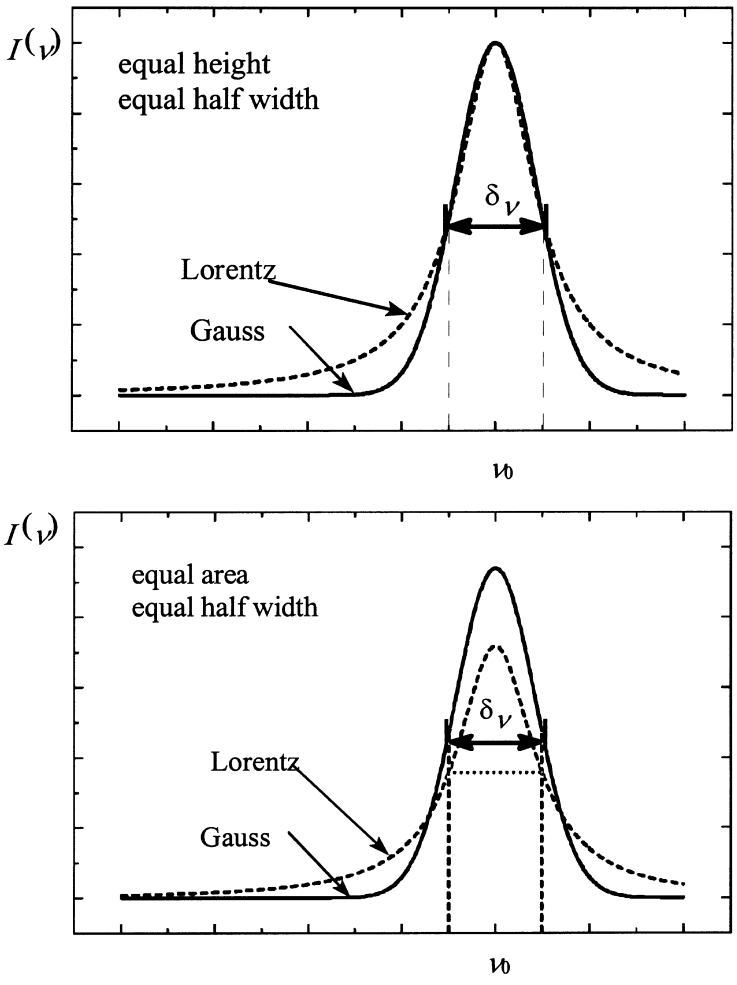

Fig. 3 Lorentzian and Gaussian line profile: (top) equal heights: (bottom) equal areas.

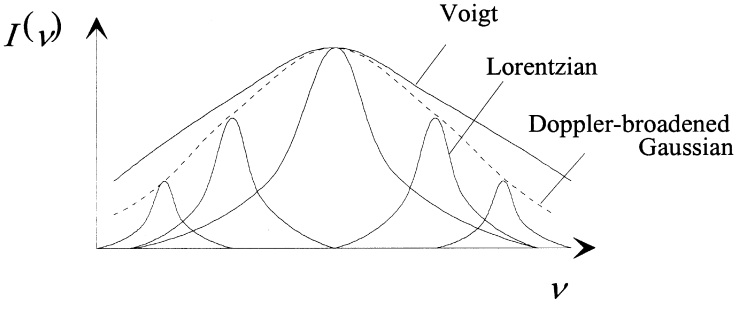

Fig. 4 Voigt line profile.

Intensity stabilization is achieved 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 appropriately altered using feedback techniques.

2.2.3.2 Wavelength fluctuations. For extreme wavelength stability only *single-mode lasers* can be used. In most multimode 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 contributions 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, the intensity and other laser properties of the light source influence the limits of detection and limits of determination of a sample. For details on the definitions and usage of these terms, see Chapter 18.4 of [3].

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 linewidth itself might be smaller.

In the case of small absorption coefficients, a small difference of two large quantities has to be determined. This problem can be minimized as follows. (i) By frequency modulation, tuning the laser through the absorption spectrum. The difference in the transmitted intensities for two frequencies is detected with a *phase-sensitive detector* (lock-in), synchronized to the modulation frequency *f*. This restricts the frequency response to a narrow interval at *f*. This method is superior to intensity modulation. (ii) Directly monitoring the intensity absorbed rather than relying on the difference measurement. A further approach is *intracavity absorption*, placing the sample inside the resonator (Section 3.1.3).

3.1.1 Fluorescence excitation spectroscopy

In *fluorescence excitation spectroscopy*, by 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 transferred to thermal energy, which gives rise to temperature and pressure changes. In *photoacoustic spectroscopy*, periodic modulations of the laser beam produce pressure variations which can be detected by a microphone or other transducer.

3.1.3 Intracavity absorption

The detection sensitivity is increased many-fold if the sample is placed inside the cavity and *intracavity absorption* is used. Several effects can give rise to such amplification.

Q-factor amplification [see V, 6.2.3; XV, 5.3] can be obtained via 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 the ratio of the free spectral range $\delta\nu$ of an interference filter or interferometer to the theoretical half-width $\Delta\nu$ given by

$$F^* = \frac{\delta\nu}{\Delta\nu} = \frac{\pi\sqrt{\rho}}{1-\rho} \tag{5}$$

which is determined by the reflectivity ρ and determines the resolving power R of an interferometer [see IX and XV].

If the internal loss of the cavity is low, large enhancement factors are achieved for absorptive samples in the 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 the laser output. Mode competition and mode-coupling phenomena cause *mode oscillations*. One of the oscillating modes is tuned across the absorption spectrum into resonance, changing the laser frequency.

3.1.4 Ionization spectroscopy

Absorption of photons by molecular transitions can be monitored by *ionization spectroscopy*, detecting ions or electrons produced by *photoionization* (by radiation), by *collision-induced ionization* (thermally), or by *field ionization* (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 the determination of rotational constants, 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 moments via the *Stark shift*. The quality of the determined molecular parameters is limited by the accuracy of the electric field measurement.

3.1.6 Double resonance methods

Optical–optical double resonance can be achieved by stepwise excitation caused by simultaneous interaction of two optical fields. This concept can be varied by combining photons of frequencies of different spectral ranges such as *optical–radiofrequency*, *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 a bandwidth smaller than the desired spectral resolution. The laser frequency fluctuations have to be smaller than the natural linewidth $\delta\nu$, 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

Molecules, produced by vaporization in an oven, pass through a small hole A and, at a distance d, through a second aperture B (diameter $b \ll d$) in a free pass forming a *molecular beam* with a flux density approximately constant across the beam diameter.

The collimated molecular beam is crossed perpendicularly with a monochromatic probe laser. The Doppler width is reduced by 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.

Molecules can be internally cooled by free expansion of a gas into a vacuum (*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*.

The molecular beam and the 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

In *saturation spectroscopy*, optical pumping with a monochromatic tunable laser selectively saturates an

inhomogeneously broadened molecular transition. A 'hole' is burned into the population distribution of the absorbing state (*hole burning*). In Fig. 5, the population distributions of the lower (i) and upper (k) states are given with the effect of this hole burning.

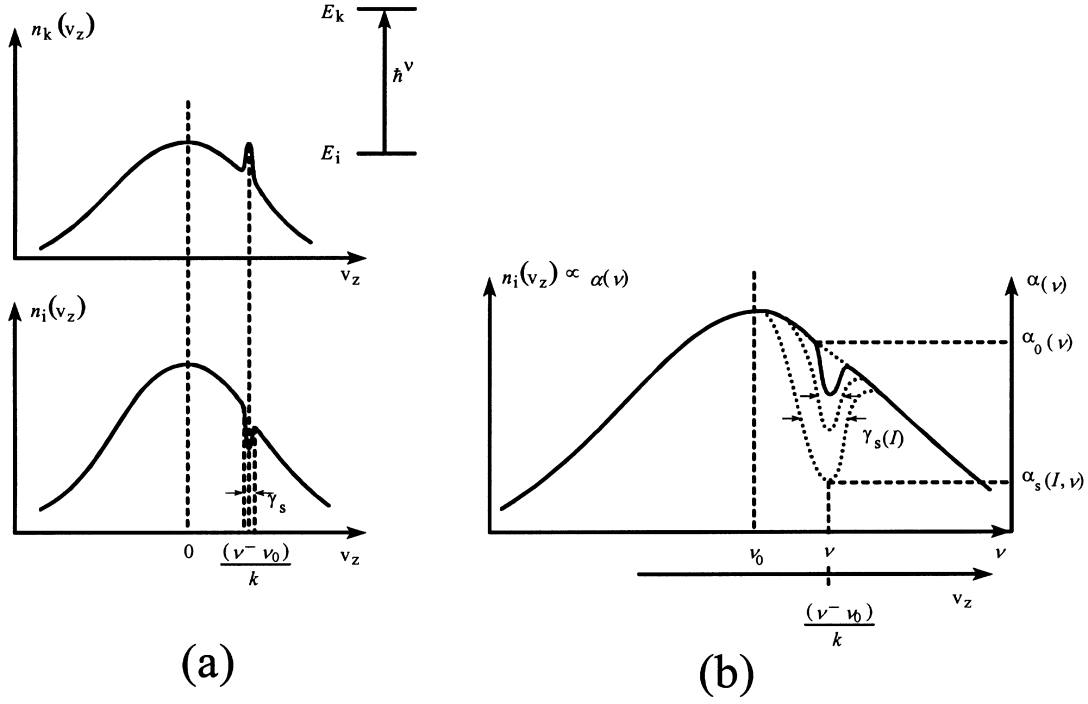

Fig. 5 (a) Population distribution of lower and upper state influenced by saturation and (b) increase of the Bennet hole with saturation intensity.

Using the *saturation parameter* at the centre of the absorption line

$$S_0 = 2S/\pi\gamma \tag{6}$$

where γ is the linewidth, one can define a ratio

$$S = B_{ik}\rho_{ik}(\nu)/P_R \tag{7}$$

of the depletion absorption rate $B_{ik}\rho_{ik}(\omega)$ to the sum P_R of all relaxation processes refilling level i. B_{ik} represents the Einstein stimulated absorption transition probability [see XV] for the transition $i \rightarrow k$ and ρ is the energy density of the radiant field. Given a normalized homogeneous line profile of a molecular transition with linewidth

$$\gamma_s = \gamma \cdot \sqrt{1 + S_0} (\gamma = \gamma_n + \gamma_c) \tag{8}$$

where γ_n is the natural linewidth, γ_c is the collisional broadening linewidth, and saturation broadening by strong fields, γ_s is very much smaller than the *Doppler width* if the interaction time of the molecules with the radiation is longer than the spontaneous lifetime and pressure as well as saturation broadening can be neglected at small laser intensities. This *homogeneous linewidth* represents the spectral width γ_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 burned into the population distribution. They merge together at $\nu = \nu_0$. When both waves interact with the same molecules (see Fig. 6), they are exposed to twice the intensity, forming a small dip in the centre ('*Lamb dip*').

3.2.2.1 Doppler-free saturation spectroscopy. Closely spaced absorption lines (see Fig. 7) are completely masked in the case of Doppler-limited absorption spectroscopy. However, their Lamb dips can be resolved in *Doppler-free saturation spectroscopy*.

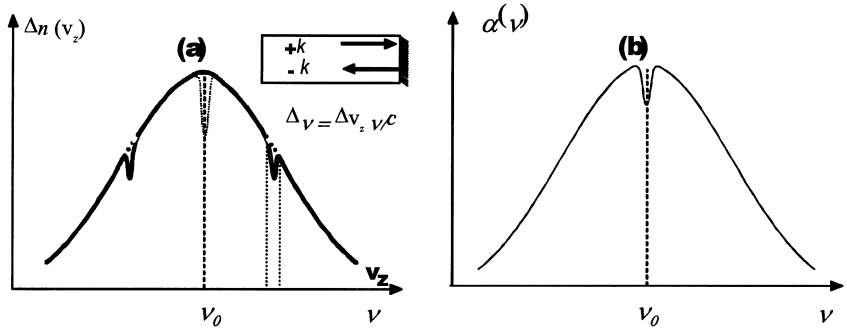

Fig. 6 Bennet hole (a) and Lamb dip (b) of two counterpropagating waves $+k$ and $-k$ at a Doppler-broadened absorption line; population distribution $\Delta n(v_z)$ and absorption coefficient $\alpha(\nu)$ are dependent on the frequency and velocity component v_z of the molecules.

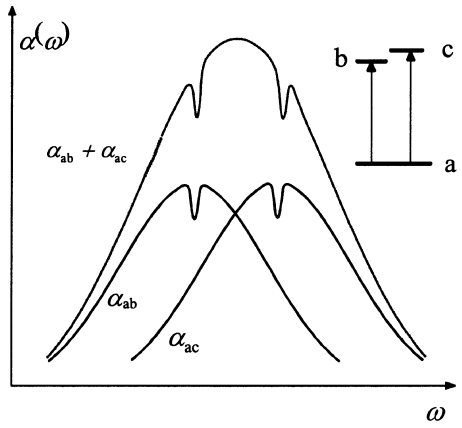

Fig. 7 Overlapping transitions located within Doppler profiles resolved by their Lamb dips.

3.2.2.2 Lamb-dip stabilization. The Lamb dip in a laser output can be used to lock the frequency to the centre of the gain profile and stabilize the wavelength by third derivative feedback to a lock-in amplifier as a reference. This method is called *Lamb-dip stabilization*.

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 nonlinear for such *coupled transitions*.

3.2.3 Polarization spectroscopy

Polarization spectroscopy is a sensitive Doppler-free technique that results mainly from the change in the refractive index induced by the polarized pump radiation, which produces a nonequal saturation and, in consequence, a nonuniform population of the sublevels. The results are small differences in amplitude and phase. The 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 apparatus allows the simultaneous observation of saturated absorption and dispersion. Measurement of the probe beam intensity for parallel and perpendicular polarizations at different positions of the analyser makes it possible to separate the dichroic 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 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 centres of two different molecular transitions and their outputs are superimposed and detected on a nonlinear detector.

3.2.6 Multiphoton spectroscopy

In *multiphoton spectroscopy*, the 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 Larmor 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 lifetime 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, using either a Pockels cells or an ultrasonic modulator, excites the molecular level. The modulated fluorescence intensity observed perpendicularly to the incident light is phase shifted with respect to the incident light. This phase shift depends on the lifetime. Nonexponential 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* technique. 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 or *pump and probe techniques* are used.

REFERENCES

1 W. Demtröder. *Laser Spectroscopy: Basic Concepts and Instrumentation*, 2nd enlarged edn. Springer Verlag, Berlin, Heidelberg, New York (1996).

2 I. Mills, T. Cvitas, K. Homann, K. Kallay, K. Kuchitsu. *Quantities, Units and Symbols in Physical Chemistry*, 2nd edn. Blackwell Science, Oxford (1993).

3 J. Inczedy, T. Lengyel, A. M. Ure. *Compendium of Analytical Nomenclature Definitive Rules 1997*, 3rd edn. Blackwell Science, Oxford (1998).

6 INDEX OF TERMS