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Nonlinear Laser Spectroscopy

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With 193 Figures

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Prof. VLADILEN S. LETOKHOV
Institute of Spectroscopy, Academy of Sciences USSR, Akademogorodok,
SU - 142092 Moskow / USSR

Prof. VENIAMIN P. CHEBOTAYEV
Institute of Semiconductor Physics,
Siberian Branch of the Academy of Sciences of USSR
SU - 630090 Novosibirsk / USSR

Dr. DAVID L. MACADAM
68 Hammond Street, Rochester, NY 14615/USA

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Preface

The laser as a source of coherent optical radiation has made it possible to investigate nonlinear interaction of optical radiation with atoms and molecules. Its availability has given rise to new research fields, such as nonlinear optics, laser spectroscopy, laser photochemistry, that lie at the boundary between quantum electronics and physical optics, optical spectroscopy and photochemistry, respectively. The use of coherent optical radiation in each of these fields has led to the discovery of qualitatively new effects and possibilities; in particular, some rather subtle effects of interaction between highly monochromatic light and atoms and molecules, in optical spectroscopy, have formed the bases for certain methods of so-called *nonlinear, laser Doppler-free spectroscopy*. These methods have made it possible to increase the resolution of spectroscopic studies from between 10^5 and 10^6, limited by Doppler line broadening up, to about 10^{11}; at present some laboratories are developing new techniques that have even higher resolution. The discovery and elaboration of the methods of nonlinear laser spectroscopy have resulted largely from contributions by scientists from many countries, in particular from the USA (Massachusetts Institute of Technology, Stanford University, National Bureau of Standards in Boulder, Harvard University, etc.), the USSR (P.N. Levedev Institute of Physics, Institute of Semiconductor Physics in Novosibirsk, Institute of Spectroscopy, etc.), France (University of Paris, Ecole Normal Superiere), Germany (University of Heidelberg), Japan (Tokyo University). Their contributions are used as the basis of our book, in which we have tried to describe as fully as possible, and systematically, the present statue of this area of research. In so doing, we used the publications of many scientists and of our own. In some places, our personal interests seem to be rather strong, and we have disturbed the proportions to some extent by centering emphasis on the research work carried out at the laboratories in the Institute of Spectroscopy and the Institute of Semiconductor Physics of the USSR Academy of Sciences. Unfortunately, we could not deal with some aspects of the subject. We live about 4000 km apart; let that be some excuse for us in this joint project. When preparing the English version of this book, we used the Russian publication of our book *Principles*

of Nonlinear Laser Spectroscopy published in the Soviet Union by the Nauka (Science) in the summer of 1975. However, in doing so we considered it necessary to change both its form and content. Instead of the six chapters in the Russian edition this book consists of ten chapters, and it is much larger. So, the book is essentially new; we have changed even its title, a little. We have worked out the plan of this book together and discussed the contents of each chapter, so that the whole book could be coordinated. But we had to finish some chapters separately. Chapters from 1 to 4 and 10 were written by V.S. Letokhov and those from 5 to 9 by V.P. Chebotayev.

This monograph is the first attempt to generalize and analyze from a common standpoint this quickly developing area in laser spectroscopy. Recently Springer-Verlag has published the monograph *High-Resolution Laser Spectroscopy* (Volume 13 of its *Topics in Applied Physics* series) to which we have also made a contribution. That has some points in common with our present monograph, in which all of the topics are given more detailed and wider consideration, which should be of use, not only to scientists specialized in this field but also to students and post-graduates as well as to specialists in associated fields of research.

When preparing the English version, we took into consideration, of course, the results of the investigations carried out from 1974 to 1975 and also comments we received after publication of the Russian book. In this connection, we would like to express our deep appreciation to Prof. E.B. Alexandrov, Prof. S.G. Rautian, Dr. B.D. Pavlik for their remarks. Thanks are also due to Dr. E.V. Baklanov and Dr. E.A. Titov who greatly assisted in writing some new chapters for the English publication. We want to express our thanks to Prof. A.L. Schawlow and Dr. H. Lotsch who initiated the publication of our book in English.

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Professor V.S. Letokhov
Moscow, Podolskii rayon,
Akademgorodok, Institute of
Spectroscopy Akademy of
Sciences USSR

Professor V.P. Chebotayev
Novosibirsk, Akademgorodok
Institute of Semiconductor
Physics Siberian Branch of
Academy of Sciences USSR

Main Notations

"a"	index denoting an amplifying medium
a	diameter of a light beam
a_k	probability amplitude for Kth level (Schrödinger picture)
a(w)	homogeneous line shape normalized to the maximum unit
A_{21}	Einstein A coefficient of $2 \to 1$ transition
A	weight of particle in atomic units
"b"	index denoting an absorbing medium
C(t)	cosine (in phase) component of polarization
c	speed of light
c.c.	abbreviation for "complex conjugate"
d	distance between two light beams
e	electron charge
$\underline{e}$	vector of light-field polarization
E	instantaneous strength of the field electric component
E_i	energy of ith quantum level
$\mathcal{E}$	slowly varying amplitude (envelope) of the running light wave
$\mathcal{E}_{st}$	slowly varying amplitude of the standing light wave
$\mathcal{E}_o$	amplitude of the weak probe wave
f = a,b	index denoting a medium type
f_p	factor of resonance broadening due to saturation
g_f	coefficient in parameter of saturation G_f ($G_f = g_f \cdot P$)
$G = gP = \left(\frac{P_{12}\mathcal{E}}{\hbar}\right)^2 \frac{1}{\gamma\Gamma}$	degree of saturation or parameter of saturation
$G_f = g_f P$	degree of saturation of amplifying (f = a) or absorbing (f = b) medium
$\hbar$	Planck's constant/2π
h	relative amplitude of dip
K,$\underline{K}$	wave vector of a light wave
K	Boltzmann's constant
l_f(f = a,b)	length of the resonance medium
L	cavity length
$L(x) = (1 + x^2)^{-1}$	lorentzian contour

M atom or molecule mass

N_o density of particles in a gas

N_i density of particles on i level

N_i^o initial density of particles on i level (without saturation)

$n_i(\underline{v}) = N_i W(\underline{v})$ velocity distribution of particles on i level

$n(v) = n_1(v) - n_2(v)$ velocity distribution of difference of populations of levels

$\underline{n}$ unit vector in direction of light wave or observation

$n(\omega), n_f$ index of refraction of medium at the frequency ω

$P = \frac{c}{8\pi\hbar\omega} E^2$ density of photon flow of a light wave (in photon/cm^2 s)

$\underline{P}(t,\underline{r})$ polarization of a resonance medium

$P_{12} = P = \underline{P}_{12}\underline{e}$ projection of matrix element of transition dipole moment

P gas pressure

Q_i rate of particle excitation for i level

Q quality factor of the mode cavity

$q_i(J) = q_i$ relative population of the rotational sublevel J of vibrational i level

r curvature radius of a light wave

S factor of frequency pulling (autostabilization)

$S(t)$ in quadrature component of polarization

$S(\omega)$ shape of the Doppler contour

T temperature, Kelvin

$u = (\frac{2kT}{M})^{1/2}$ velocity of particles in a gas

$\underline{v}$ particle velocity

$v = v_z = \underline{vn}$ projection of particle velocity onto the direction of a light wave

v_o average velocity of particle

v_r particle-velocity component perpendicular to the direction of a light wave (radial component of velocity)

$v_{res} = c\frac{\nu - \nu_o}{\nu_o} = c\frac{\omega - \omega_o}{\omega_o}$ resonant projection of particle velocity

V absolute velocity of atom or molecule

$V = \frac{pE}{2\hbar}$, $V_{12} = \frac{P_{12}E}{2\hbar}$ energy interaction between atom and field in frequency units

$W(v)$ distribution of particle velocities

W_{ik} integral probability of transition $i \to k$

w rate of induced transitions between levels

$\alpha(\omega) = \kappa_a(\omega)$ coefficient of resonant amplification per unit length

$\alpha_{eff} = \kappa_a - \kappa_b = \alpha(\omega) - \kappa(\omega)$ coefficient of effective resonant amplification per unit length

$\beta = \frac{\kappa_{bo} g_b}{\kappa_{ao} g_a} = \frac{\kappa_{bo} G_b}{\kappa_{ao} G_a}$ parameter in theory of a gas laser with nonlinear absorption

Γ, Γ_f homogeneous half-width of line at half-height (rad/s)

$\tilde{\Gamma}$ parameter of collisional broadening of spectral line ($\Delta\omega_{coll} = 2\tilde{\Gamma}p$, p - gas pressure)

$\Gamma_B = \Gamma\sqrt{1+G}$ half-width of the Bennett hole

γ_i rate of radiation decay of population of i level

$\gamma_{coll}^{(i)}$ rate of collisional relaxation of population of i level

$\tilde{\gamma}_i = \gamma_i + \gamma_{coll}^{(i)}$ total rate of relaxation of population of i level

$\gamma = 2\left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)^{-1}$ parameter, the reciprocal of the total lifetime of a particle at two transition levels

$\tilde{\gamma} = 2\left(\frac{1}{\tilde{\gamma}_1} + \frac{1}{\tilde{\gamma}_2}\right)^{-1}$ parameter γ, with collisions taken into account

$\gamma' = \frac{1}{2}(\gamma_1 - \gamma_2)$

$\gamma_{12} = \frac{1}{2}(\gamma_1 + \gamma_2)$

γ_o coefficient of linear nonresonance losses per unit length

$\gamma_{rad} = \gamma_1 + \gamma_2$ radiation width of the transition at half-height (rad/s)

$\Delta = \omega_1 - \omega_2$ frequency difference of two fields

$\Delta = \frac{c}{2L}$ frequency interval between axial modes

$\Delta_o = \omega_a - \omega_b$ frequency detuning of line centers of amplifying and absorbing transitions

$\Delta\omega = 2\pi\Delta\nu$ width of resonance dip at half-height

$\Delta\omega_c$ cavity bandwidth

$\Delta\omega_{coll} = 2\pi\Delta\nu_{coll} = 2\tilde{\Gamma}p$ collisional broadening

$\Delta\omega_D = 2\pi\Delta\nu_D = 2\omega_o(2\ln 2\frac{kT}{M})^{1/2}$ Doppler width

$\Delta\omega_{tr} = 2\pi\Delta\nu_{tr}$ transit time width of line

$\Delta\omega_{res}$ width of resonance power peak

$\Delta\omega_{sp}$ resonance broadening due to sphericity of a light wave

$\Delta\omega_g = 2\pi\Delta\nu_g$ geometrical broadening of resonance due to nonparallelism of light waves

$\delta = \frac{\Omega}{\Gamma} = \frac{\omega - \omega_o}{\Gamma}$ dimensionless detuning of the field frequency ω about the transition frequency ω_o

$\delta\omega_f (f = a,b)$ width of mode instability region in a ring laser (width of competing resonance)

θ angle between two plane light waves

$\kappa(\omega) = \kappa_b(\omega)$ coefficient of resonance absorption, per unit length

$\kappa_o(\omega) = \kappa_{bo}(\omega)$ coefficient of absorption of a weak field, per unit length

$\kappa_a(\omega) = \alpha(\omega)$ coefficient of resonance amplification, per unit length

$\kappa_{ao}(\omega) = \alpha_o(\omega)$ coefficient of amplification of a weak field, per unit length

Λ length of particle free path

λ length of a light wave

ν_o frequency of quantum transition between two levels (in Hz)

$\rho = \frac{\gamma}{\Gamma}$ parameter of coherent interaction of light field and gas ($\rho = 1$, coherent interaction; $\rho = 0$, incoherent interaction)

ρ_{ii} diagonal matrix element which is proportional to the ith level population

$\rho_{ij} (i \neq j)$ off-diagonal matrix elements that are proportional to polarization

$\sigma(\underline{v},\omega)$ cross section of radiation transition between levels of a particle with its velocity $\underline{v}$ in the wave field with the frequency ω

σ_o cross section of particle transition between levels in the maximum

τ_{coll} average time between collisions of particles

$\tau_i = \frac{1}{\gamma_i}$ lifetime of i level

τ_{tr} particle transit time with an average velocity through a light beam

τ_v relaxation time of population of a vibrational level

τ_r relaxation time of population of a rotational sublevel

ϕ_o angle of atomic beam

ϕ light-wave phase

ϕ_{dif} diffraction angle

$\chi = \chi' - i\chi''$, χ_f polarizability of a medium

$\psi(\underline{r},t)$ Schrödinger wave function

$\Omega = \omega - \omega_o$ detuning of field frequency ω about the transition frequency ω_o

$\tilde{\Omega} = [\Omega^2 + (2V)^2]^{1/2}$

$\omega = 2\pi\nu$ field frequency

$\omega_o = 2\pi\nu_o$ frequency of quantum transition between levels

ω_c resonant frequency of a mode cavity

$\omega' = \omega - \underline{k}\underline{v}$

$\omega_f (f = a,b)$ central frequency of amplifying ($f = a$) or absorbing ($f = b$) medium

Contents

1. Introduction

1.1 Doppler Broadening of Optical Spectral Lines

The basic part of our knowledge of the structure of matter at the atomic-molecular level has been obtained from optical spectroscopy. But as our knowledge of the atomic and molecular structure becomes deeper, the limit of the potentialities of optical spectroscopy, conditioned by the line broadening of emission and absorption spectra of a substance, becomes essential. The biggest spectral-line broadening caused by particle interaction in a condensed medium or a dense gas can be eliminated by observing spectral lines of a low-pressure gas. Yet we cannot accomplish in this way the ultimate goal, which is to produce spectral lines whose widths are dictated by the properties of quantum transitions of individual particles. The thermal broadening of spectral lines due to the Doppler effect is responsible for this.

A moving particle (an atom or a molecule) emits or absorbs radiation that is not exactly at the quantum-transition frequency $\omega_0 = \omega_{21}$ between two energy levels E_1 and E_2, which is determined by the Bohr quantization condition,

$$\hbar\omega_0 = E_2 - E_1 , \tag{1.1}$$

where $\hbar$ is Planck's constant, but at a frequency somewhat shifted by the Doppler effect (Fig.1.1a). The spectral line of a single particle $a(\omega)$ is shifted by a value that depends on the projection of the particle velocity $\underline{v}$ on the direction of observation $\underline{n}$,

$$a_{\underline{v}}(\omega) = a\left(\omega - \underline{n}\frac{\underline{v}}{c}\omega\right) . \tag{1.2}$$

In a gas, the particles move in all possible directions; that is why the Doppler shift differs for each particle. At thermal equilibrium, all directions are equiprobable; that is, the velocity distribution of the particles is isotropic. Therefore, the projection of the particle velocity on any direction ($v = \underline{n}\underline{v}$) is given by the Maxwell distribution,

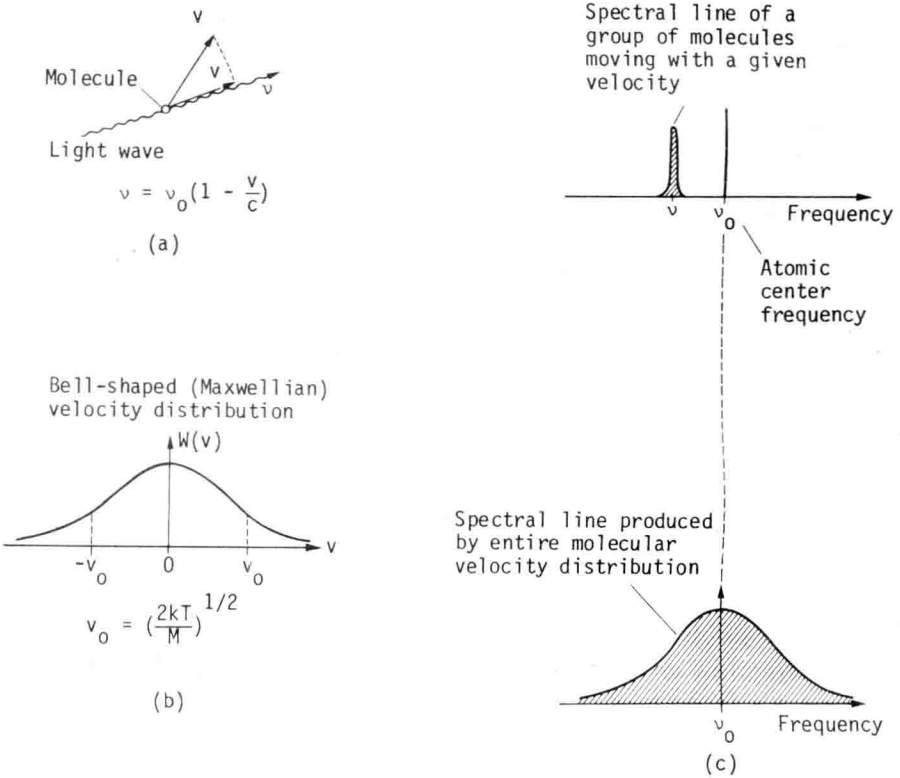

Fig.1.1a-c Influence of the Doppler effect on the shape of a spectral line: (a) Doppler shift due to a molecule moving with velocity $\underline{v}$. The Doppler effect shifts the emission frequency from ν_0 to ν; (b) Thermal distribution of particle velocities; (c) Corresponding spectral lines. The upper curve is the response of particles moving with velocity $\underline{v}$ as in (a). The lower curve is the response due to atoms over the entire thermal distributions

$$W(v) = \frac{1}{\sqrt{\pi}u} \exp[-(v/u)^2] \quad , \quad u = \left(\frac{2kT}{M}\right)^{1/2} \quad , \tag{1.3}$$

which has the symmetrical form of the Gauss curve (Fig.1.1b). As a result, the spectral line of the assembly of particles has a symmetrical profile with its center at the quantum-transition frequency ω_0 (Fig.1.1c).

In a simple case, when the broadening caused by the Doppler effect and that caused by particle collisions are statistically independent, the spectral-line shape of the whole set of particles $S(\omega)$ is defined by the line-shape convolution of an individual particle with the Doppler-shift distribution, that is, by the distribution of the projections of the atomic velocity on the observation direction,

$$S(\omega) = \int a_{\underline{v}}(\omega) W(\underline{v}) d(\underline{v}\underline{n}) \ . \qquad (1.4)$$

In the case of thermal equilibrium, when the velocity distribution of the particles is maxwellian, given by (1.3), the total half-height broadening of spectral line due to the Doppler effect $\Delta\omega_D$ is given by

$$\Delta\omega_D = \frac{2\omega_o}{c}\left(2 \ln 2 \frac{kT}{M}\right)^{1/2} = 7.163 \cdot 10^{-7} \sqrt{\frac{T}{A}}\, \omega_o \ , \qquad (1.5)$$

where M and A denote the mass and atomic weight of a particle, and T is the temperature K. Figure 1.2 shows the dependence of the relative Doppler broadening on the atomic weight of a particle at various temperatures. For atoms and molecules with atomic weight $A \approx 100$ at normal temperature, the Doppler width $\Delta\omega_D \approx 10^{-6}\ \omega_o$.

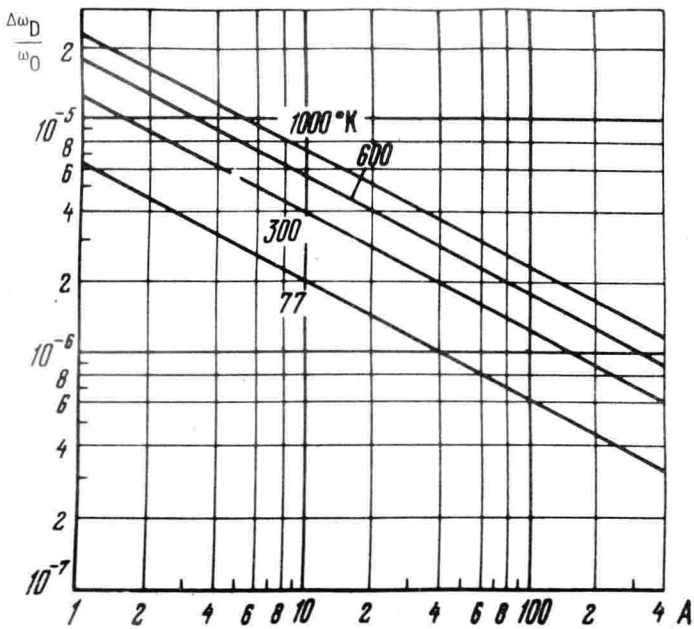

Fig.1.2 Relative value of the Doppler line width for particles with atomic weight A (in at. units) at different temperatures

If an atom or a molecule have several transitions so close that, because of Doppler broadening, their spectral lines overlap, conventional methods of linear optical spectroscopy cannot resolve their structure. High-resolution experiments sometimes indicate, however, that the spectral line under observation is too wide to be explained by only thermal motion of the particles.