Spectroscopy of Atomic Vapors in Nanometer Cells: Dicke Narrowing and Beyond

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Abstract. Sub-Doppler spectroscopy of gaseous media confined in thin pillbox-shaped cells was pioneered by R.H. Dicke. In the past, this idea attracted much less attention compared to “Dicke narrowing” in buffer gas where the atoms or molecules perform a diffusive motion instead of being bounced back and forth between the walls of the cell in a completely predetermined nature. The situation is going to be changed as atomic spectroscopy becoming an essential part of mobile devices for civil and military applications that require tiny spectroscopic cells. In the pillbox shaped cells, the role of the fast moving atoms is diminished, while the slowly moving atoms contribute most to the absorption as well as to the fluorescence. The role of the slowly moving atoms and their transient polarization in selective reflection spectroscopy was highlighted by J.L. Cojan. By merging these two approaches we have developed a theoretical description of optical reflection from and transmission through the narrow slice of atomic vapours.

1. Two different Dicke narrowing mechanisms
More than fifty years ago R.H. Dicke proposed two methods of the Doppler width suppression. Both methods rely on the fact that the extent of the Doppler broadening depends on the phase difference between the atomic oscillator and the external field rather than on the instantaneous value of the atomic velocity. Hence, the Doppler width may be diminished in a room temperature vapor cell provided the spatial shifts of the atoms are restricted. In the first, most prominent method, this is accomplished by the gas phase collisions [1]. In the second method, which, in the past, attracted much less attention, the atoms are placed in a narrow pillbox-shaped cell [2]. Thus, the atom-wall collisions serve to restrict the atomic motion. Both methods, to be used in high-resolution spectroscopy, have to resolve the problem of collisional broadening that can surpass the Doppler width and compromise an attempt to enhance the resolution.

1.1. Dicke narrowing due to collisions with buffer gas atoms
In a cell with rarefied vapours the mean free path of atoms or molecules is much larger than the wavelength of electromagnetic radiation corresponding to the transition in question. In this case Doppler broadening dominates. In denser samples, the mean free path is shortened and the Doppler width is diminished. To avoid collisional broadening, which is very effective in the case of collisions between the same atoms, buffer gases may be employed. The method works perfectly if the internal state of the radiating particle and the phase of its polarization are preserved in the course of the collision event. There is a vast literature on this subject.
1.2. Dicke narrowing in a pillbox

The main idea of [2] is that in a pillbox shaped cell the slowly moving atoms contribute most to the absorption as well as to the fluorescence simply because they spend more time in their free flights between the walls. In this case preservation of the internal state of the radiating particle is less important, while the distance between the cell walls gains crucial importance. Dealing with the microwave region, R.H. Dicke employed a standing wave in a cell one half wavelength thick. This particular choice of the width guarantees that all atoms experience the field oscillations of the same phase.

2. Cojan sub-Doppler reflection spectroscopy

The role of the slowly moving atoms and their transient polarization in the presence of only one boundary was highlighted by J.L. Cojan [3]. His theory of the sub-Doppler spectral line shapes in reflection was further developed in [4]. An essential part of the theoretical description consists in the statement that the atoms that move out of the boundary between the transparent solid material and the vapor itself are not in the steady state. In optical domain the atomic polarization is completely destroyed after the atom-wall collision. Even more, in most cases the atoms that leave the surface are in their ground state [5]. As the polarization of these atoms is zero at the surface, there is no reason to expect that their contribution to the reflectivity of the boundary is equal to the contribution of the atoms with the steady state polarization. A somewhat surprising result is that the atoms that leave the surface with the velocity $v$ make just the same contribution to the reflection spectrum as the atoms that are approaching the surface with the velocity $-v$. Hence, integration over the velocity distribution runs from minus infinity to zero rather than from minus infinity to plus infinity. Such integration is known to lead to the sharp Doppler-free features in the reflection spectra. More details may be found in [6-8].

Narrow sub-Doppler resonances in selective reflection were successfully employed to study collisional broadening of atomic spectral lines otherwise hidden under much larger Doppler width [9].

From the point of view of the electrodynamics of continuous media, sub-Doppler features in the selective reflection spectra are due to the spatial dispersion of a Doppler-broadened gas. As the Doppler broadening dominates, it means that the free path of the atoms exceeds the wavelength. Hence, the dielectric response of the gas is highly nonlocal. Macroscopic electrodynamics fails in this case and needs additional boundary conditions that may be supplied only by the microscopic theory. Nevertheless, when the microscopic theory is developed the results may be cast in the form of the admittance of the gas boundary. This value may be used in the ordinary Fresnel formulas of macroscopic electrodynamics as a substitute of the refractive index.

3. Nonlinear effects in selective reflection

The study of nonlinear effects in the selective reflection was started with an ordinary saturation effect in a two level system [10]. It was shown that the contribution of the departing atoms is not equal to the contribution of the arriving atoms in this case. The saturation intensities for both contributions differ as well. Nevertheless, the sub-Doppler features remain in the nonlinear reflection spectra. Nonlinear selective reflection from an atomic vapor at arbitrary incidence angle was studied in [11]. Nonlinear effects in selective reflection were employed to induce the self-diffraction of light on the boundary of resonance vapours [12]. Then, the nonlinear effects in selective reflection were studied in a pump-probe scheme experimentally [13] and theoretically in a two-level system [14] and in a three-level system [15].

4. Line-shape modification via optical coating of the interface

The shape of the spectral lines obtained in selective reflection at the boundary of a rarefied gaseous medium is usually dominated by the real part of its admittance. The situation may be changed by the optical coating of the transparent dielectric material that confines the gas. The task here is somewhat different from the ordinary antireflection coating. As the gas is rarefied, diminishing of the reflectivity of the bare dielectric material will lead to a very weak reflection proportional to the square of the gas
density. If, on the contrary, one want to enhance reflectivity proportional to the imaginary part of the surface admittance the coating thickness and its refractive index should be chosen properly. The exact formulas for one and two layer coatings are given in [16].

An important consequence of this consideration is that the spatial inhomogeneity of gas phase in the close proximity of the surface may lead to the mixing of real and imaginary parts of the surface admittance of the gas and the corresponding distortion of the line shapes.

5. van der Waals interaction of excited atoms with solid surfaces
As the shapes of the lines recorded in selective reflection are narrow and sensitive to the surface conditions they were successfully employed to study the van der Waals interactions of the excited atoms with the solid surfaces [17]. Even more intriguing, selective reflection spectroscopy provides with the evidence of van der Waals repulsion of the excited state atoms when there is a resonance between the atomic transitions and the internal excitations of the solid surface [18].

6. Reflection from and transmission through the narrow slice of atomic vapors
By merging the ideas of Dicke and Cojan we have developed a theoretical description of optical reflection from and transmission through the narrow slice of atomic vapors [19]. Contrary to the microwave regime, the standing wave approximation was not used assuming an antireflection coating to be applied on the rear wall of the cell. A manifold of line shapes was obtained depending on the width of the cell. An unusual interference between transient polarizations with the period doubled compared to familiar Fabri-Perot resonances is shown to lead to four fold enhancement of the reflection amplitude as well as switching between the even and odd spectral line shapes.

7. Invention of the Extremely Thin Cell
It was not until the invention of an Extremely Thin Cell by D. Sarkisyan [20] that the observation of these effects becomes possible in the optical domain. Since that time the field is flourishing with a number of linear and nonlinear optical effects observed in the ETC in different laboratories [21,22].

An additional feature of ETC is a possibility to explore the atom-wall interaction. Although important information has been obtained from the position and distortion of the central part of the spectral line [23], far wings provide information on the interaction at still smaller distances from the solid surface.

8. Applications
The atomic resonances are indispensable in the role of the absolute frequency reference in mobile devices for civil and military applications. Hence, the need for the tiny spectroscopic cells mount on the chip will grow [24].

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References
[1] Dicke R.H. 1953 The effect of collisions upon the Doppler width of spectral lines Phys. Rev. 89 472-3
[2] Romer R. H. and Dicke R.H. 1955 New technique for high-resolution microwave spectroscopy Phys. Rev. 99 532-6
[3] Cojan J.L. 1954 Contribution a l'etude de la reflection selective sur les vapeurs de mercure de la radiation de resonance du mercure Ann. Phys. (Paris) 9 385-440
[4] Schuurmans M.F.H. 1976 Spectral narrowing of selective reflection J. Phys. (Paris) 37 469-85
[5] Przhibelskii S.G. and Khromov V.V. 2000 Exchange between Translational and Electronic Energies of Atoms in Their Impacts with a Surface Optics and Spectros. 88 17-21
[6] Burgmans A.L.J., Woerdman J.P. 1976 Selective reflection from sodium vapor at low densities
1976 *J. Phys. (Paris)* 37 677-81

[7] Burgmans A.L.J., Schuurmans M.F.H. and Bölger B. 1977 Transient behavior of optically excited vapor atoms near a solid interface as observed in evanescent wave emission. *Phys.Rev.* 16 2002-7

[8] Schuurmans M.F.H. 1980 The fluorescence of atoms near a glass surface *Contemp. Phys.* 21 463-82

[9] Akul'shin A.M., Velichanskii V.L., Zibrov A.S., Nikitin V.V., Sautenkov V.V., Yurkin E.K. and Senkov N.V. 1982 Collisional broadening of intra-Doppler resonances of selective reflection on the D$_2$ line of cesium *JETP Letters* 36 303-7

[10] Vartanyan T.A. 1985 Resonant reflection of intense optical radiation from a low-density gaseous medium *Sov. Phys. JETP* 61 674-7

[11] Nienhuis G., Schuller F. and Ducloy M. 1988 Nonlinear selective reflection from an atomic vapor at arbitrary incidence angle, *Phys.Rev.* A 38 5197-205

[12] Akulshin A.M., Velichanskii V.L., Vartanyan T.A., Gamidov R.G., Sautenkov V.A. and Filimonov S.I. 1989 Self-diffraction of resonance radiation on a selective gas mirror *Opt. Spectrosc.* (USSR) 66 423-4

[13] Velichanskii L., Gamidov R.G., Pak G.T. and Sautenkov V.A. 1990 Nonlinear selective reflection of bichromatic light from interface between transparent dielectric and resonant gas *JETP Letters* 52 136-40

[14] Schuller F., Nienhuis G. and Ducloy M. 1991 Selective reflection from an atomic vapor in a pump-probe scheme *Phys.Rev.* A 43 443-54

[15] Schuller F., Gorceix O. and Ducloy M. 1993 Nonlinear selective reflection in cascade three-level atomic systems *Phys.Rev.* A 47 519-28

[16] Vartanyan T. A. and Träger F. 1994 Line shape of resonances recorded in selective reflection: influence of an antireflection coating *Opt. Commun.* 110 315-20

[17] Oria M., Chevrollier M., Bloch D., Fichet M. and Ducloy M. 1991 Spectral observation of surface-induced van der Waals attraction on atomic vapor *Europhys. Lett.* 14 527-32

[18] Fichet M., Schuller F., Bloch D. and Ducloy M. 1995 van der Waals interactions between excited-state atoms and dispersive dielectric surfaces *Phys. Rev.* A 51, 1553-64

[19] Vartanyan T.A. and Lin D.L. 1995 Enhanced selective reflection from a thin layer of a dilute gaseous medium *Phys. Rev.* A 51 1959-64

[20] Sarkisyan D., Bloch D., Papoyan A., Ducloy M. 2001 *Opt. Comm.* 200 201-8

[21] Cartaleva S., Saltiel S., Sargsyan A., Sarkisyan D, Slavov D., Todorov P. and Vaseva K. 2009 Sub-Doppler spectroscopy of cesium vapor layers with nanometric and micrometric thickness *JOSA* B 26 1999-2006

[22] Naumov A.N., Podshivalov A.A., Drabovich K.N., Miles R.B. and Zheltikov A.M. 2001 Theory of Doppler-free spectroscopy with $\lambda$-thick vapor cells *Phys. Lett.* A 289, 207

[23] Laliotis A. et al. 2007 Testing the distance-dependence of the van de Waals interaction between an atom and a surface through spectroscopy in a vapor nanocell *Proc. SPIE* 6604, 660406-1 - 11

[24] Hasegawa M., Chutani R.K., Gorecki C., Boudot R., Dziuban P., Giordano V., Clatot S., Mauri L. 2011 Microfabrication of cesium vapor cells with buffer gas for MEMS atomic clocks *Sensors and Actuators* A 167 594-601