Excited atoms-wall collisions and their manifestations in the fluorescence excitation line shapes

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Since the invention of the extremely thin cell which sustains prolonged action of hot and dense alkali vapours, a number of spectroscopic problems have been solved with its aid. As the width of the cell is comparable to, or smaller than, the wavelength of the actual atomic transition, the Doppler width of the fluorescence light is reduced due to the cage effect. Stimulated by recent measurements of the fluorescent excitation line shapes in the extremely thin cell we studied the dependence of these line shapes on the cell thickness.

1. Introduction

Rarefied vapours are known to possess spatial dispersion. This well established optical concept in the case of rarefied vapours is due to the free flight of the atoms. Cojan [1] was the first to realize important consequences of this motion for atomic line shapes recorded in reflection. Contrary to what follows from conventional dispersion theory that ignores the spatial dispersion, the reflectivity of a boundary between a transparent dielectric medium and a rarefied atomic vapour does not follow the odd anomalous dispersion profile broadened due to the Doppler effect. Instead, a narrow even profile was observed. The width of the selective reflection line was equal to the square root of the product of the Doppler width and the natural width of the actual transition. The theory developed in [1] linked these features to the transient polarization of the atom that leaves the reflecting surface. While the atoms that arrive at the reflecting surface are on their free flight with a fixed velocity, the atoms that leave the reflecting surface may be either scattered or thermally desorbed from the surface. Even if an atom was just elastically scattered and preserved the polarization that it had before the collision, its polarization does not correspond to the detuning of the incident field because after the collision the Doppler shift, simultaneously with the normal component of the atom’s velocity, has changed sign. In the case of inelastic collisions, as well as in the case of desorption after prolonged dwelling on the surface, the polarization of the atom most probably goes to zero. Hence, in these latter cases also the atomic polarization is far from being the same as it should be in the steady state, the state assumed in conventional dispersion theory. The ideas presented in [1] were further developed much later by Schuurmans [2-4]. Nonlinear effects in selective reflection were first considered in [5], further developed in [6], and observed experimentally [7,8]. The theory of nonlinear selective reflection was developed also at arbitrary incidence angle [9] and for the pump-probe scheme [10].

Another approach to sub-Doppler spectroscopic techniques in gaseous media was suggested by Romer and Dicke [11]. In this work a half wavelength-thick cell was employed to restrict the atomic
motion in one direction while the diameter of the cell was large compared to the wavelength. In a pillbox shaped copper cell with the distance between the inner walls of 6.2 mm the TE_{11} mode was exited. The spectral width of the inversion transition in ammonia at 24 GHz was found to be 18 kHz, much smaller than the Doppler width that is equal to 73 kHz. It was argued that this narrowing is due to the almost homogeneous distribution of the field inside the half wavelength-thick cell. The theory that describes the periodic dependence of the spectral line shapes on the cell thickness was developed in [12]. It was shown that the homogeneity of the field inside the cell is not a necessary condition for spectral narrowing. Instead, spectral narrowing takes place and manifests itself most spectacularly in the case where the rear boundary of the cell does not reflect light at all. Thus, the theory was applicable best of all in the optical domain although the optical cells with the distance between the inner walls in the nanometer range did not exist at that time. First experiments with the cells of 10 μm and thicker [13,14] were interpreted with the transients due to the optical pumping [15]. The field starts to flourish [17-20], only after the advent of the extremely thin cell [16], which sustains prolonged action of hot and dense alkali vapours. Due to space limits we can mention here only the most recent research based on the spectroscopy of extremely narrow slices of atomic vapour [21-23].

In this contribution we are going to address the peculiarities of one of the most popular techniques in the spectroscopy of extremely thin vapour layer, namely, the fluorescence excitation line shapes.

2. Basic equations.

Despite of the obvious linear dependence of the intensity of the fluorescence on the excitation intensity when the intensity of the excitation is small enough, to describe this process one needs to employ the density matrix equation that includes not only polarization but also the populations of the levels involved. Disregarding the degeneracy of the energy levels of the real world atoms one can describe the excitation dynamics within the framework of a two-level model. In this case one has to solve the set of equations for non-diagonal element of the density matrix $\rho_{21}$

$$V \frac{d\rho_{21}}{dx} + [\gamma_2 - i(\Omega - kV)]\rho_{21} = i \frac{dE}{2\hbar}$$

(1)

and the population difference $D = \rho_{11} - \rho_{22} = 1 - 2\rho_{22}$

$$V \frac{dD}{dx} + \gamma_1(D - 1) = -\frac{2dE}{\hbar} \text{Im}(\rho_{21})_r.$$  

(2)

In both equations it is assumed that the equilibrium value of the population difference is unity and as we are going to proceed in the framework of perturbation theory, this equilibrium value enters also the right hand side of Eq. (1). The meaning of other symbols are as follows: $x$ is the coordinate of the atom, $V$ is the projection of the atomic velocity on the $x$ axis, $\Omega$ is the laser field detuning relative to the atomic transition frequency, $d$ is the transition dipole moment, $E$ is the amplitude of the laser field, $\gamma_1$ and $\gamma_2$ are the relaxation constants of the population and the polarization, respectively, $k=2\pi/\lambda$ is the wave vector, thus $kV$ is the Doppler shift of the moving atom.

In what follows we will describe the simplest case when the inequality $\gamma_1 << \gamma_2$ holds. In this case the steady state solution of Eq. (1)

$$\rho_{21} = \frac{i dE}{2\hbar} \frac{1}{\gamma_2 - i(\Omega - kV)}$$

(3)
may be substituted into Eq. (2). On the other hand, the steady state solution of Eq. (2) that reads as

\[ \widetilde{D} = \left| \frac{dE}{\hbar} \right|^2 \frac{\gamma_2/\gamma_1}{\gamma_2^2 + (\Omega - kV)^2} \]  

(4)
does not satisfy the boundary condition: the atoms that leave both boundaries at \( x=0 \) and \( x=L \), where \( L \) is the atomic layer thickness, should be in their ground states. To satisfy the boundary conditions one has to consider the transient solutions of Eq. (2) as well. The particular solutions of Eq. (2) that satisfies these conditions are different for atoms moving in opposite directions. For \( V>0 \) the solution of Eq. (2), which satisfies the boundary condition \( D=1 \) at \( x=0 \) reads as

\[ D = 1 - \widetilde{D}[1 - \exp(-\gamma_1 x/V)] \]  

(5)

while for \( V<0 \), the solution that satisfies the same boundary condition \( D=1 \) at \( x=L \)

\[ D = 1 - \widetilde{D}[1 - \exp(-\gamma_1 (x-L)/V)] \]  

(6)

should be used to calculate the upper state population \( \rho_{22} = (1 - D)/2 \). To get the fluorescence excitation spectrum \( S(\Omega, L) \), we integrate the population of the upper state over the atomic layer thickness \( L \) and the velocity distribution

\[ f(V) = \frac{1}{V_T \sqrt{\pi}} \exp \left[ -\left( \frac{V}{V_T} \right)^2 \right] \]  

(7)

where \( V_T \) is the most probable velocity in the three-dimensional Maxwell velocity distribution. The result of the integration

\[ S(\Omega, L) = \frac{\gamma_2}{2\gamma_1} \left( \frac{dE}{\hbar} \right)^2 \left\{ L \int_{-\infty}^{\infty} f(V)dV \right\} \frac{1}{\gamma_1} \left[ 1 - \exp \left( -\gamma_1 L/V \right) \right] \frac{1}{\gamma_2^2 + (\Omega - kV)^2} + \frac{1}{\gamma_2^2 + (\Omega + kV)^2} Vf(V)dV \]  

(8)

may be conveniently represented in terms of the dimensionless parameters \( \Gamma_{1,2} = \gamma_{1,2}/kV_T \), \( \Delta = \Omega/kV_T \) and \( \phi = kL = 2\pi L/\lambda \)

\[ S(\Delta, \phi) = \frac{\phi}{\Gamma_2} \exp(-\gamma_2^2)dy - \frac{1}{\Gamma_1} \left[ 1 - \exp \left( -\frac{\Gamma_1 \phi}{y} \right) \right] \frac{1}{\Gamma_1^2 + (\Delta - y)^2} + \frac{1}{\Gamma_1^2 + (\Delta + y)^2} y \exp(-y^2)dy \]  

(9)

Fig. 1 plots the fluorescence excitation spectra for the following set of parameters: \( \Gamma_1=0.01 \), \( \Gamma_2=0.1 \), \(-3<\Delta<3 \). Thus both relaxation constants are much smaller than the Doppler width \( kV_T \), while the
condition for validity of Eq. (3) is satisfied. The values of $\varphi$ are chosen in such a way that the atomic layer thicknesses $L$ vary from $\lambda/8$ to $5\lambda$. The outermost curve corresponds to the thick vapour layer.

Figure 1. Fluorescence excitation spectra of a narrow slice of atomic vapours.

3. Conclusion.
The above consideration shows that the fluorescence excitation line narrows as the vapour layer becomes thinner. This narrowing takes place even in the case when the polarization adiabatically follows after the level populations. Contrary to other effects observed in extremely thin layers, a fluorescence excitation line narrows monotonically. At the same time the absolute value of the fluorescence depends nonlinearly on the layer thickness. At the smallest thickness this dependence is almost quadratic, while for larger thicknesses it approaches a linear dependence. For a limited range of thicknesses this dependence may be well approximated by a power function with a noninteger exponent between 1 and 2 as it was observed in the experiment [24, 25].

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