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Velocity selective optical pumping

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Résumé. — Le pompage optique par une source lumineuse peu intense (l'évolution des atomes a lieu dans un régime de pompage ; « rate equation regime ») et quasi monochromatique, peut introduire des corrélations entre les variables externes (vitesse) et les observables internes (population, orientation, alignement) des atomes. On donne un calcul de ces observables en fonction de la vitesse des atomes dans le cadre d'une description phénoménologique des effets des collisions. On calcule les profils des raies, obtenus en balayant la fréquence du laser au voisinage de la résonance optique des atomes. On discute également la combinaison de cette méthode avec des techniques de pompage en polarisation modulée ou de dépolarisation magnétique. On a ainsi accès à la dynamique de relaxation des vitesses du gaz à l'intérieur du profil Doppler.

Abstract. — We consider optical pumping with a quasi monochromatic tunable light beam, in the low intensity limit where a rate equation regime is obtained. The velocity selective optical pumping (V.S.O.P.) introduces a correlation between atomic velocity and internal variables in the ground (or metastable) state. The aim of this article is to evaluate these atomic observables (orientation, alignment, population) as a function of velocity, using a phenomenological description of the relaxation effect of collisions. The V.S.O.P. line shapes, obtained by scanning the pumping beam frequency and using a counterpropagating detection beam with the same frequency, are given in various circumstances. The combination of V.S.O.P. with modulated pumping, magnetic resonance, and level crossing methods is considered; the corresponding line shapes can provide useful information on the relaxation characteristics, such as collision rates and kernels.

1. Introduction. — The conventional broadband light sources generally used in optical pumping experiments provide signals that contain velocity averages over the Doppler profile of the atomic observables. It is nevertheless well known that optical pumping combined with magnetic resonance or level crossing techniques can give « Doppler free » spectroscopic information, i.e. measurements of atomic structures which are not resolved within the Doppler width of the optical transition. On the other hand, as far as one is concerned with relaxation phenomena, such as collisions transferring atoms between different velocity classes of the maxwellian distribution, no information is available in conventional optical pumping.

The aim of the present article is to consider the application of a single mode laser beam to optical pumping of an atomic gas. In general, a description of the interaction between an atom and a narrow band intense laser field includes various saturation effects and optical coherences. Here we shall put the emphasis on the monochromaticity rather than the intensity of the pumping light source, which we assume to be weak enough to avoid any saturation of the optical transition. In this low intensity limit optical coherence effects remain negligible and the atomic observables evolve according to the rate equation theory of optical pumping [1, 2]. New features are nevertheless introduced by the selection of a single group of atomic velocity in the pumping process. In other words, the quasi monochromatic light beam tends to introduce strong correlations between external variables (velocities) of the atoms and their internal variables (orientation, alignment, hyperfine population differences etc...) created by the optical pumping cycle. The use of a weak counterpropagating detection beam then allows the resolution of the velocity distribution of the optical pumping observable. Consequently, the velocity selective pumping allows a study of various relaxation phenomena induced by collisions: velocity changes, depolarization, exchange etc., that tend to restore the thermal equilibrium distribution of the pumped atoms.

Some previous studies have been concerned with particular aspects of optical pumping contributions in the low intensity limit of saturation spectroscopy.
experiments [3-6]. A few experiments on pure velocity selective optical pumping (V.S.O.P.) have recently been reported and a qualitative discussion of the recorded line profiles including collision effects has been given [7]. We intend to present some theoretical aspects on V.S.O.P. and a more quantitative description of the type of line shapes obtained in [7]. We study in particular the manifestations of collisions with depolarization in V.S.O.P. line shapes within a phenomenological model.

The combination of V.S.O.P. with various classical optical pumping techniques such as modulated pumping, magnetic resonance, and magnetic depolarization, is also considered in the present article. These techniques applied to V.S.O.P. are seen to introduce some specific features in the velocity-resolved observable distribution which are useful for the study of the characteristics of the collisional relaxation, e.g. collision rates, depolarization rates and kernel shapes. The V.S.O.P. allows the selection of well-defined observables in single electronic states, which simplifies the theoretical interpretation of collisional relaxation effects in the detected line profiles.

In section 2, the theory of optical pumping is applied to the case of a monochromatic pumping beam to describe the evolution of the velocity-correlated observable. Section 3 contains a phenomenological formulation of the effects of collisions and the evaluation of typical spectral line shapes. The application of various optical pumping methods in V.S.O.P. for a study of collision effects is discussed in section 4. Comments on experimental results are included in section 5, and the last section contains a discussion and concluding remarks.

2. The evolution of observables in V.S.O.P. —

The physical situation considered in this article is summarized in figure 1. A monochromatic light beam is incident on the sample cell for optical pumping in the atomic gas. The pumping beam is expanded to ensure homogeneous pumping conditions and to avoid a saturation of the optical transition. A counter-propagating narrow detection beam is used to probe the sample on the axis of the pumped volume. When the linewidth of the light is small compared with the atomic homogeneous linewidth $\Gamma_{eq}$, we can write the field $\mathbf{\epsilon}$ as a classical plane wave with polarization $\mathbf{e}_z$, angular frequency $\Omega$ and wave number $k$:

$$\mathbf{\epsilon}(r, t) = \mathbf{e}_z \exp[i(k \cdot r - \Omega t)] + c.c. \quad (1)$$

We consider the influence of the pumping light on the atomic system, which we describe by a ground (or metastable) state and an excited state with angular momenta $J_0$ and $J_e$, respectively (Fig. 2). The resonance frequency of the optical transition is $\Omega_0$, and a possible external magnetic field separates the Zeeman sublevels of the ground and excited states by the energies $h_0 g$ and $h_0 e$, respectively.

![Fig. 2. — Atomic two-level system with Zeeman multiplets in the ground and excited states. $J_e, J_g$ are the angular momenta and $h_0 g, h_0 e$ the Zeeman energies of the ground and excited states, respectively. $\Omega_0$ is the resonance angular frequency of the atomic transition.](image)

In optical pumping with classical discharge light sources, the correlation time of the interaction between atom and field is limited by the inverse spectral width of the incoming light, and is thus short enough for optical coherence effects to remain negligible. Hence the rate equation description of [1] is adequate, and the evolution of the atomic system is formulated in terms of absorption and spontaneous emission rate coefficients. The rate description has also been applied to optical pumping with free-running multi-mode laser fields, where the correlation time is still limited by the spectral width of the light [8-10].

A single-frequency laser field has a long coherence time and the optical coherences induced in the interaction with an atomic system must in general be taken into account. The time evolution of the system is then adequately described by Bloch type equations. However, as long as the monochromatic pumping field is weak enough, we can still obtain an « optical pumping regime » for monochromatic excitation. The necessary condition is:

$$| \mathbf{D} \cdot \mathbf{\epsilon} | \ll h \Gamma_{eq} \quad (2)$$
where the atomic dipole moment is denoted by \( \mathbf{D} \), the field strength by \( \mathbf{E} \), and \( \Gamma_{eg} \) is the homogeneous linewidth of the transition (determined by spontaneous emission or collisions). Condition (2) expresses the fact that the Rabi evolution of the atomic populations is vanishingly small in a time equal to the relaxation time of the induced optical coherence. Higher order effects of optical coherence are then negligible so that the rate theory remains adequate for a description of the influence of the light. Nevertheless, due to the supposed long relaxation time of the lower level of the optical transition, the pumping beam can still have strong effects on the population of the Zeeman sublevels, as in ordinary optical pumping.

Even if the monochromatic field does not introduce any new physical aspects into the description of the optical pumping cycle itself, it clearly gives rise to velocity selective effects. A velocity-dependent density matrix \( \rho(v) \) has to be attributed to the atoms of each velocity group in the gas to account for the correlation between internal variables and atomic velocities. In the absence of collisional coupling between different velocity groups, the optical pumping equations of [1, 8, 9] can be applied to each velocity group, in the case of monochromatic excitation.

### 2.1 Rate Equations

Let \( \rho_g(v) \) and \( \rho_e(v) \) be the density operators describing the atoms with velocity \( v \) in the Zeeman multiplets of the ground and excited levels. In the plane wave model of the field incident along the \( Z \) axis, we neglect the dependence on radial components and keep only the axial velocity component \( v_z = v \). When applying the rate equations of [9] to monochromatic pumping, it is consistent with (2) to ignore the effects of stimulated emission (we assume that \( F_{eg} \) is not much larger than the decay rate \( r \) of the excited state). We then have the optical pumping equations

\[
\frac{d}{dt} \rho_g(v, t) = -\frac{1}{2} \gamma_p(v) \left\{ B_g \rho_g(v, t) \right\} + i \Delta E(v) \left[ B_g \rho_e(v, t) \right] + \Gamma_0 \sum_{i=x,y,z} D_i \rho_e(v, t) D_i - i \mathcal{K}_g \rho_g(v, t) \tag{3a}
\]

\[
\frac{d}{dt} \rho_e(v, t) = \gamma_p(v) (\mathbf{e}_g \cdot \mathbf{D}) \rho_g(v, t) (\mathbf{e}_e \cdot \mathbf{D}) - \Gamma \rho_e(v, t) - i \mathcal{K}_e \rho_e(v, t) \tag{3b}
\]

where \( \Gamma = \Gamma_0 + \Gamma_e \); \( \Gamma_0 \) defines the rate of spontaneous emission from the excited state back to the ground or metastable state, and \( \Gamma_e \) is the rate of «escape» of atoms from the excited state due to other processes (collisions, spontaneous emission towards other levels, etc.). The operator \( B_g \) is given by

\[
B_g = (\mathbf{e}_e \cdot \mathbf{D}) \rho_e(v, t)
\]

where \( \rho_e(v, t) \) is the projection operator onto the excited state and \( \mathbf{D} \) is an operator of order one that contains only the angular part of the atomic dipole operator \( \mathbf{D} \). The velocity-dependent absorption rate \( \gamma_p(v) \) and the light shift \( \Delta E(v) \) are defined by the real and imaginary parts, respectively, of the expression

\[
\frac{1}{2} \gamma_p(v) + i \Delta E(v) =
\]

\[
i \frac{|\mathbf{E}|^2 |\Omega_{eg}|^2}{(2 J_e + 1) \hbar^2} (\Omega - \Omega_0 - \mathbf{k} \cdot \mathbf{v} + i \Gamma_{eg})^{-1}
\]

where \( \Omega_{eg} \) is the reduced matrix element:

\[
\Omega_{eg} = \langle J_e | \mathbf{D} | J_g \rangle
\]

(we assume that \( \omega_x, \omega_y \ll \Gamma \)).

The first two terms on the r.h.s. of (3a), containing the anticommutator and the commutator, respectively, describe the effects of absorption and light shifts in optical pumping [1]. Due to the velocity dependence in (5), the absorption is non-negligible only for a narrow velocity group inside the maxwellian distribution. The third term on the r.h.s. of (3a) expresses the transfer from the excited state back to the ground state by spontaneous emission. Due to the isotropy of spontaneous emission, only the density matrix components of \( \rho_e \) and \( \rho_g \) of the same multipolarity are coupled in the term proportional to \( \Gamma_0 \).

The first term on the r.h.s. of (3b) describes the effect of optical pumping from the ground state on the excited state, the second term the spontaneous decay of the excited state. The last terms in (3a) and (3b) containing \( \mathcal{K}_g \) and \( \mathcal{K}_e \) (the hamiltonians divided by \( \hbar \)), account for the effects of external magnetic fields. Equations (3) enable one to calculate the evolution of velocity correlated atomic observables under the influence of monochromatic optical pumping.

Physically, a relaxation of the pumped density matrix will take place, and constantly tend to restore the thermal equilibrium. When the atomic gas is dilute enough to allow neglecting the effect of collisions, the ground state density matrix \( \rho_g(v) \) is assumed to decay isotropically with a rate \( \gamma_0 \) towards the thermal equilibrium state \( \rho_g(v) \), due to escape from the pumping beam and collisions on the cell walls. Assuming \( \gamma_0 \ll \Gamma \), we have to add a relaxation term only to (3a):

\[
\frac{d}{dt} \rho_g(v, t)_{rel} = \gamma_0 [\rho_g(v) - \rho_g(v, t)]
\]
where the thermal equilibrium is described by

$$\rho_0(v) = (2J + 1)^{-1} N(v) \exp\left(-\left(\frac{v}{\Delta}\right)^2\right)$$

(8)

including the maxwellian distribution of width $\Delta$ :

$$N(v) = \frac{N_0}{\sqrt{\pi \Delta}} \exp\left[-\left(\frac{v}{\Delta}\right)^2\right]$$

(9)

with the atomic number density denoted by $N_0$.

To simplify, we consider the weak pumping limit where the intensity is low enough to satisfy $\gamma_p \ll \gamma_0$. This means that each absorption process takes place in a quasi-equilibrium distribution of atomic populations. To first order in the pumping intensity, we can then replace $\rho_p$ by $\rho_0$ in the absorption and light shift terms of (3). The commutator in the light shift term then vanishes, and as the commutator with $\mathcal{K}_q$ is negligible compared with $\Gamma$ in weak magnetic fields, we can write :

$$\frac{d}{dt} \rho_p(v, t) = \gamma_p(v, t) M \rho_0(v) +$$

$$+ \gamma_0[\rho_0(v) - \rho_p(v, t)]$$

(10)

where $M$ is defined as the pumping operator

$$M = \frac{\Gamma}{T} \left(\sum_{i=x,y,z} D_i(e_x \cdot D) P_i(e_x \cdot D) D_i - B_k\right)$$

(11)

and $P_k$ is the projection onto the ground state. The operator $M$ includes the pumping effect of « depopulation » by absorption, expressed by $B_k$, as well as the « repopulation » pumping due to transfer of anisotropy from the excited state to the ground state by spontaneous emission, which is expressed by the first term on the r.h.s. of (11). Because of the vector properties of the optical dipole $D$, only orientation or alignment (in addition to isotropic population transfer) can be produced by one optical pumping cycle starting from an isotropic initial state. In the first order approximation, we can therefore neglect the creation of higher order multipole components of $\rho_p$ as well as the coupling between the multipoles of different order.

At this stage, we assume $\mathcal{K}_q$ in (10) to include the effect of a static magnetic field only and we study the evolution of a longitudinal observable $\mathcal{A}$ (population, longitudinal orientation or alignment) of the ground state :

$$\mathcal{A} = \mathcal{A}_0, J_z, 3J_z J_z - J^2.$$  

(12)

The mean value $\langle \mathcal{A} \rangle$ of $\mathcal{A}$ depends on $v$ (correlations between internal and external variables) and we can use (10) to write the equation of motion (1) :

$$\frac{d}{dt} \langle \mathcal{A} \rangle(v, t) = \frac{\gamma_p}{\gamma_0} \langle \mathcal{A} \rangle_p N(t) \frac{(\Gamma_{sp})^2}{(\Omega - \Omega_0 - k)^2 + \Gamma_{sp}^2}$$

$$\left(\frac{1}{\gamma_0} + \frac{1}{\gamma_p}\right) + \frac{\gamma_{sp}}{\gamma_0} \langle \mathcal{A} \rangle(v, t) + \frac{\gamma_{sp}}{\gamma_0} \langle \mathcal{A} \rangle_0(t)$$

(13)

where the pumping rate is determined by

$$\gamma_p = 2|\mathcal{E}|^2|D_{es}|^2/(2J + 1) \Gamma_{se} R^2$$

(14a)

$$\langle \mathcal{A} \rangle_p = \text{Tr} \{ M \mathcal{A} \}/(2J + 1)$$

(14b)

and

$$\langle \mathcal{A} \rangle_0 = \begin{cases} 0 & \text{if } \mathcal{A} \text{ describes the orientation or alignment}, \\ N(v) & \text{if } \mathcal{A} \text{ describes the population} \end{cases}$$

(14c)

If $\Gamma_{se} = 0$, the operator $M$ is traceless, which means that the ground state population is conserved in the optical pumping cycle. The sign of the anisotropy observable $\langle \mathcal{A} \rangle_p$ may depend on $\Gamma_{se}/\Gamma_0$ (competition between absorption and repopulation effects if $J = J + 1$). Obviously the observables introduced also depend on the polarization of the pumping light. The stationary solution of (13) is easily obtained and shows that the optical pumping process maintains a population depletion, orientation or alignment of the atoms inside a narrow Doppler-shifted velocity group described by a lorentzian of width $2 \Gamma_{se}$. This width is not power broadened since we have ignored any saturation of the pumping, measured by the parameter $\gamma_{p}/\gamma_0$. The coupling to other velocity groups by collisional relaxation will be considered in section 3.

2.2 Detection. — By using the detection scheme of figure 1 and measuring the modification of intensity or polarization of the probe light, the observable distribution inside the Doppler-broadened line can be resolved. In analogy with saturation spectroscopy techniques, the monochromatic detection beam of frequency $\Omega_d$ probes the ground state observables in a single Doppler-shifted velocity group.

A general polarization matrix formulation of the absorption and dispersion signals in optical pumping and their relation to atomic observables has been given in [12]. The straightforward application of the formalism of [12] to a monochromatic beam is outlined in the Appendix. Any pumping or relaxation effect of the probe beam is neglected. For a weak detection field and when the Doppler width is much larger than the natural linewidth (Doppler limit) one can show [13] that, after integration over the atomic velocities, the terms arising from coherent interaction with the pump and probe beams are negligible.

The recorded signal will depend on the method of analysing the transmitted light. By an appropriate choice of polarizations in the pump and probe beams and by using modulation techniques, a well-defined observable of the atomic ground state can be experimentally isolated in the detection signal [7].

In general, two types of signals are detected : the

(1) A more general optical pumping equation for broadband excitation including the coupling between various multipole components of $\rho_p$ has been given in [11].
absorptive part of the probe field induced susceptibility gives a signal described by the integral
\[ S_A(\Omega_d) \propto \int_{-\infty}^{\infty} dv \frac{I_{eg}}{\left(\Omega_d - \Omega_0 + k \cdot v\right)^2 + (I_{eg})^2} \langle A \rangle(v) \]
whereas measuring the dispersive part yields the form
\[ S_D(\Omega_d) \propto \int_{-\infty}^{\infty} dv \frac{\Omega_d - \Omega_0 + k \cdot v}{\left(\Omega_d - \Omega_0 + k \cdot v\right)^2 + (I_{eg})^2} \langle A \rangle(v). \]

The absorption signal depends on the observable of a velocity group determined by the frequency \( \Omega_d \) of the probe light field; by tuning \( \Omega_d \) over the Doppler width, the velocity distribution \( \langle A \rangle(v) \) can be measured. In the following we will assume that the pump and probe beams originate from the same laser and consequently have the same frequency.

3. Relaxation by collisions. — 3.1 Collisional redistribution. — When a buffer gas is present in the sample cell or when the active gas pressure becomes non-negligible, collisions must be considered. Collisions are frequently treated as either « strong » thermalizing collisions, or « weak » collisions producing a velocity change that is small compared with the Doppler width, and resulting in a « diffusion like » transport in velocity space. The manifestations of velocity-changing collisions in saturated absorption spectroscopy have been investigated in detail by several authors (see e.g. [14, 15, 16]). We consider here some related aspects in a V.S.O.P. experiment.

An atom in the ground (or metastable) state which has been oriented or aligned by optical pumping has a long effective « lifetime » in the beam, ultimately determined by \( 1/\gamma_0 \). We assume the buffer gas pressure to be sufficiently high to give rise to several collisions between the active atom and the buffer gas atoms during \( 1/\gamma_0 \). Such a collision may change the velocity component of the atom without entirely destroying the anisotropy observable considered. Hence a transfer to different velocity groups may take place. By studying the redistribution of the ground state observable in the velocity space one may obtain information on the velocity-correlated collisional relaxation of the various atomic multipoles.

To simplify the approach we will assume the effects of a possible collisional coupling between different multipole components of \( \rho_A \) to be negligible [17]. Hence the collisional relaxation will be approximated by an isotropic process for each multipole. We also limit the study to collisions between active and perturber atoms.

We assume that the pressure is low enough to allow us to neglect collisions during the excited state lifetime \( 1/F \). The rate at which collisions change the axial velocity of ground state atoms from \( v \) to \( v' \) will be defined by the one-dimensional collision kernel \( P(v, v') \). The problem is reduced to one dimension by the rather simplistic assumption that the integration over transverse velocity components can be carried out independently in the equations of motion, leaving only the dependence on the axial component.

The rate of collisional transfer of the observable \( \langle A \rangle \) from the velocity group \( v \) to the group \( v' \) can now be phenomenologically described by the product kernel
\[ K(v, v') = P(v, v') \Xi(v, v') \] with
\[ \Xi(v, v') \leq 1 \]
where the « conservation kernel » \( \Xi(v, v') \) gives the relative amount of the observable \( \langle A \rangle \) that is conserved in the collision changing the velocity from \( v \) to \( v' \). The optical pumping equation (13) is then rewritten to include the velocity-changing collisions:
\[ \frac{d}{dt} \langle A \rangle(v, t) = \gamma_p(v) N(v) \langle A \rangle(v) - \gamma_f(v) \langle A \rangle(v, t) + \gamma_0 \langle A \rangle(0) + \int_{-\infty}^{\infty} dv' \langle A \rangle(v', t) K(v', v). \] (19)

The total velocity dependent relaxation rate \( \gamma_f(v) \) for the observable of a single group of atoms having the velocity \( v \) is
\[ \gamma_f(v) = \gamma_0 + \gamma_c(v) \] (20)
where \( \gamma_0 \) accounts for the isotropic decay of the observable by diffusion of atoms out of the beam, quenching on the cell walls etc., and \( \gamma_c(v) \) denotes the rate of transfer of atomic ground state population out of the velocity group \( v \) by collisions:
\[ \gamma_c(v) = \int_{-\infty}^{\infty} P(v, v') dv'. \] (21)

The last term in (19) describes the coupling with other velocity groups and leads to a redistribution of the pumped observable in the various velocity groups.

In this model, the total decay rate \( \gamma_f(v) \) at the velocity \( v \) is directly connected to the population and is thus the same for all atomic observables, whereas the kernel \( \Xi(v, v') \) depends on the particular observable \( A \) considered and contains the collisional depolarization effect on the ground state anisotropy. For the population \( A = 1 \), \( \Xi = 1 \) by definition. The population kernel \( P(v, v') \) can be assumed to satisfy the « balance » relation
\[ \int_{-\infty}^{\infty} dv' N(v') P(v', v) = \int_{-\infty}^{\infty} dv' N(v) P(v, v') = \gamma_c(v) N(v) \]
(22)
which allows the thermal equilibrium velocity distribution of atomic population to be unchanged by collisions. In general, however, there is no « detailed balance » in the collisional transfer of anisotropy between different velocities, owing to the effect of a partial depolarization in a collision.

Equations of the type (19) can be formally solved in the steady state by a standard iteration method (see e.g. the review article of [18]). This type of solution provides information on the general structure of the line shape including collision effects. Without specifying our kernel we solve the steady state distribution of \( \langle \mathcal{A} \rangle (v) \) from (19) by summing over all possible numbers of collisions:

\[
\langle \mathcal{A} \rangle (v) - \langle \mathcal{A} \rangle_0 (v) = \langle \mathcal{A} \rangle_p \frac{\gamma_0(v)}{\gamma_1(v)} N(v) + \sum_{n=1}^{\infty} F^{(n)}(v)
\]  

(23)

with

\[
F^{(n)}(v) = \frac{1}{\gamma_1(v)} \int_{-\infty}^{\infty} dv' \frac{\gamma_1(v')}{\gamma_1(v')} N(v') K^{(n)}(v', v)
\]  

(24)

\[
K^{(n)}(v, v) = \int_{-\infty}^{\infty} dv_1 K^{(n-1)}(v', v_1) \gamma_1^{-1}(v_1) K(v_1, v)
\]  

(25a)

\[
K^{(1)}(v', v) = K(v', v)
\]  

(25b)

The solution (23) consists of two parts; the first term on the r.h.s. is the narrow lorentzian distribution representing the directly pumped atoms that have not yet undergone a collision. The second term forms a broader distribution composed of the sum of the contributions of all possible numbers of successive collisions. The shape of the broader distribution depends on the characteristics of the kernel.

The function \( \gamma(v) \) depends on the multipole component considered and may give a kernel \( K(v', v) \) that has a narrower velocity spread than \( P(v', v) \). Consequently, the steady state velocity distributions (23) of the various multipole components may differ and are in general narrower than the corresponding profile of a collisionally redistributed « population hole ».

A few approximations are useful for simplifying the expressions. First, \( \gamma_c(v) \) can in general be considered as a slowly varying function of \( v \) and can be approximated by a constant \( \gamma_c \). Second, we can approximate \( \Xi(v', v) \) by introducing a « conservation parameter » defined by

\[
\zeta(v') = \gamma_c^{-1} \int_{-\infty}^{\infty} dv K(v', v)
\]  

(26)

which describes the average amount of the observable transferred to other classes when an atom with velocity \( v' \) undergoes a collision. Furthermore, the function \( \xi(v) \) can be taken to be slowly varying with \( v \), and we approximate (26) by a constant \( \xi \) evaluated at some appropriate \( v \). We thus have \( |\zeta| \ll 1 \). The relation (26) now defines the normalization of \( K(v', v) \); the shape of the kernel still has to be specified for each particular case.

We can also consider the evolution of the total velocity-integrated observable \( \langle \mathcal{A} \rangle \) (detection with a broadband source). Integrating (19) over velocities in the « Doppler limit » where \( I_{eq} \ll kA \), we have the equation of motion

\[
\frac{d}{dt} \langle \mathcal{A} \rangle = \frac{\pi I_{eq}}{k} \gamma_0 \langle \mathcal{A} \rangle_p N(v_0) - \gamma_0 + \gamma_c \langle \mathcal{A} \rangle_0 + \gamma_0 \langle \mathcal{A} \rangle_0
\]  

(27)

where \( v_0 = (\Omega - \Omega_0)/k \) defines the mean velocity of the atoms in resonance with the pump field. From (27) it is seen that the relaxation rate of the velocity averaged optical pumping observable is \( \gamma_0 + (1 - \zeta) \gamma_c \) (corresponding to \( 1/T_1 \) measured in classical optical pumping experiments).

3.2 Models and Line Shapes. — The solution (23) yields analytical expressions only for particular functional forms of \( K(v', v) \). We first consider the « strong » collision model, where each collision results in a complete re-thermalization of the atomic velocities. We write the collision kernel with a « thermal » width as:

\[
K(v', v) = \frac{\sqrt{\pi \Delta}}{\sqrt{\gamma_c}} e^{-\frac{(v/v_c)^2}{\Delta}}
\]  

(28)

which is independent of \( v' \). Using directly (19) and (27) to solve the steady state distribution we have (in the Doppler limit):

\[
\langle \mathcal{A} \rangle (v) - \langle \mathcal{A} \rangle_0 (v) = \frac{\gamma_0}{\gamma_1} \langle \mathcal{A} \rangle_p N(v) \left\{ \frac{(I_{eq})^2}{(\Omega - \Omega_0 - k\Delta)^2 + (I_{eq})^2} + \frac{\sqrt{\pi I_{eq}}}{kA} \xi \gamma_c \left[ -\frac{\Omega - \Omega_0}{kA} \right] \right\}
\]  

(29)
which describes the Doppler-shifted lorentzian peak superposed on a broad gaussian background due to the redistribution by thermalizing collisions (2).

For a more general description we may characterize $K(v', v)$ by two parameters: the conservation parameter $\xi$ and an appropriate kernel width $\delta$ describing the «velocity memory» and average velocity spread in the time $\gamma^{-1}$ for the observable considered. An analytically tractable model kernel for «weak» or «intermediate» collisions that has frequently been used in studies of collision effects in spectroscopy is the Keilson-Storer form \cite{19}, which we apply here as an example. This kernel is given by:

$$K(v', v) = \frac{\xi \gamma_e}{\sqrt{\pi} \delta} \exp\left[\frac{- (v - \frac{\alpha v}{\delta})^2}{\delta^2}\right].$$  \hspace{1cm} (31)

where the width is $\delta=(1-\alpha^2)^{1/2} A$. The parameter $\alpha$ describes the «memory» and the strength of the collision and depends on the perturber-active-atom mass ratio \cite{20}. Using (31) in (23)-(25) and assuming $\Gamma_{eq} \ll \delta$ (intermediate collisions) we find the velocity distribution

$$\langle \mathcal{A} \rangle(v) - \langle \mathcal{A} \rangle_0(v) = \frac{\tilde{T}_e}{\gamma_T} \langle \mathcal{A} \rangle_0 N(v_0) \left\{ \frac{\Gamma_{eq}^2}{(\Omega - \Omega_o - \epsilon_0)^2 + (\Gamma_{eq}^2)^2} + \sqrt{\pi} \frac{\Gamma_{eq}}{kA} \sum_{n=1}^{\infty} \left( \frac{\xi \gamma_e}{\gamma_T} \right)^n (1 - \alpha^{2n})^{-1/2} \exp\left[\frac{- (v - \frac{\alpha v}{\delta})^2}{(1 - \alpha^2) \Lambda^2}\right]\right\}.$$

The second term on the r.h.s. sums the contributions of the atoms that have undergone $n$ collisions after their interaction with the pump beam. It produces again a broad background distribution.

If the absorptive part of the anisotropy (e.g. the dichroism of the gas) is detected by the probe beam, the signal is calculated from (15). When the pump and probe beams have the same frequency, we then obtain, using (32):

$$S_{\mathcal{A}}(\Omega) \propto \frac{\tilde{T}_e}{\gamma_T} \langle \mathcal{A} \rangle_0 \exp\left[\frac{- (\Omega - \Omega_o)^2}{kA}\right] \left\{ \frac{\Gamma_{eq}^2}{(\Omega - \Omega_o)^2 + (\Gamma_{eq}^2)^2} + \sqrt{\pi} \frac{2 \Gamma_{eq}}{kA} \sum_{n=1}^{\infty} \left( \frac{\xi \gamma_e}{\gamma_T} \right)^n (1 - \alpha^{2n})^{-1/2} \exp\left[\frac{- (\Omega - \Omega_o)^2}{kA} \left(1 + \alpha^2\right)^{-1/2}\right]\right\}.$$

The lorentzian in (33) is produced by the atoms directly pumped and detected (atoms of zero axial velocity). This term represents a «Doppler-free» resonance of homogeneous width $2 \Gamma_{eq}$. The sum term reproduces the effect of the collisions. The shape analogous to (33) in saturation spectroscopy is known from studies of population transfer by collisions \cite{16}.

The parameters $(\xi \gamma_e/\gamma_T)$ and $\alpha$ in (33) can in principle be determined by fitting appropriate curves of the type (33) to measured line shapes (3). The variation of $\xi$ essentially influences the convergence of the series in (33) and hence the amplitude and area of the broad profile, while the width of the distribution depends on $\alpha$. Figures 3 and 4 give theoretical curves which show the influence of the values of the parameters $(\xi \gamma_e/\gamma_T)$ and $\alpha$ on the line profile.

4. Variants of velocity-selective pumping. — Various spectroscopic methods are available in classical optical pumping which involve the coupling of the atoms to external magnetic fields or modulated light. Some of these techniques can be exploited in a particular manner in V.S.O.P. to yield information on specific velocity-resolved features in the collisional relaxation of the observables. We will consider here the application of a few useful methods.

4.1 Modulated pumping. — The choice of modulation technique depends on whether the observable considered is the population or a multipole component of higher order. Modulating either the intensity or the polarization of the pumping produces a time dependence in $\tilde{T}_e$ or $\langle \mathcal{A} \rangle_p$, respectively. Let us consider a specific experiment of the type shown in figure 1, where orientation is created by a circularly polarized pumping beam.

\textsuperscript{(2)} It is seen from (29) that as long as

$$\frac{\tilde{T}_e}{\gamma_T} \left(1 + \sqrt{\pi} \frac{\Gamma_{eq}}{kA} \frac{\xi \gamma_e}{\gamma_o (1 - \xi) \gamma_T}\right) \ll 1$$

the first order calculation is valid for optical pumping with the effect of collisions included. For $\xi \ll 1$, condition (30) is reduced to $\tilde{T}_e \ll \gamma_T$.

\textsuperscript{(3)} We see also from (33) that when $\gamma_e \gg \gamma_o$, the line shape becomes independent of pressure.
Fig. 4. — Examples of V.S.O.P. line shapes with velocity-changing collisions described by a Keilson-Storer kernel for various values of the parameter \( \alpha \) defining the width of the kernel. Other parameters are \( \gamma_c/\gamma_T = 0.95 \), \( \Gamma_{vs}/k_d = 0.02 \) and the maximum number of collisions = 200.

If the pumping polarization is sinusoidally modulated between right (\( \sigma_+ \)) and left (\( \sigma_- \)) circular polarizations, we have:

\[
\langle J_Z \rangle_p(t) = \langle J_Z \rangle_p \cos \omega t.
\]

We look for a solution of (19) of the form

\[
\langle J_Z \rangle(v,t) = \langle J_Z \rangle(v) e^{i\omega t} + \text{c.c.}
\]

and find that \( \langle \tilde{J}_Z \rangle(v) \) evolves according to the equation

\[
\frac{d}{dt} \langle \tilde{J}_Z \rangle(v) = \gamma_T(v) N(v) \langle J_Z \rangle_p - (\gamma_T + i\omega) \langle \tilde{J}_Z \rangle(v) + \int_{-\infty}^{\infty} dv' \langle \tilde{J}_Z \rangle(v') K(v',v)
\]

which contains the complex relaxation rate \( \gamma_T + i\omega \) in the place of \( \gamma_T \). This leads to the complex steady-state solution:

\[
\langle \tilde{J}_Z \rangle(v) = \langle J_Z \rangle_p \cos \varphi e^{-i\omega} \left[ \frac{j_p(v)}{\gamma_T} N(v) + \sum_{n=1}^{\infty} \cos^n \varphi e^{-i\omega n} F^{(n)}(v) \right]
\]

where \( F^{(n)} \) is given by (24) and \( \varphi \) is defined by

\[
\tan \varphi = \frac{\omega}{\gamma_T}, \quad 0 \leq \varphi \leq \frac{\pi}{2}.
\]

In detecting the dichroism of the sample by a circularly polarized probe beam, the signal is obtained from (15).
The time-averaged in-phase signal will then depend on \( \text{Re} \{ \langle \hat{J}_Z \rangle (v) \} \) and we find after performing the velocity integration in (24) and (15) in the limit \( \Gamma_{eg} \ll \delta \), where \( \delta \) is the kernel width:

\[
S_0(\Omega, \omega) \propto \frac{\gamma_T^2}{\omega^2 + \gamma_T^2} \left[ \frac{(\Gamma_{eg})^2}{(\Omega - \Omega_0)^2 + (\Gamma_{eg})^2} + \frac{2 \pi \Gamma_{eg}}{k \gamma_T} \sum_{n=1}^{\infty} \cos^{n-1} \varphi \cos (n + 1) \varphi K^{(n)}(v_0, -v_0) \right] \times \exp \left[ -\left( \frac{\Omega - \Omega_0}{k \Delta} \right)^2 \right].
\]

An additional signal is directly available with this method: the signal appearing in quadrature with the pump modulation is proportional to \( \text{Im} \{ \langle \hat{J}_Z \rangle (v) \} \), which yields

\[
S_{e/2}(\Omega, \omega) \propto \frac{\gamma_T^2}{\omega^2 + \gamma_T^2} \left[ \frac{\omega}{\gamma_T} \frac{(\Gamma_{eg})^2}{(\Omega - \Omega_0)^2 + (\Gamma_{eg})^2} + \frac{2 \pi \Gamma_{eg}}{k \gamma_T} \sum_{n=1}^{\infty} \cos^{n-1} \varphi \sin (n + 1) \varphi K^{(n)}(v_0, -v_0) \right] \times \exp \left[ -\left( \frac{\Omega - \Omega_0}{k \Delta} \right)^2 \right].
\]

Forming the ratio of the heights of the lorentzian peaks only in the two signals we find

\[
\left( \frac{S_{e/2}}{S_0} \right)_{\text{peak}} = \frac{\omega}{\gamma_T}. \tag{41}
\]

We see that this method can be used to directly measure \( \gamma_T \) from the slope of (41) as a function of the modulation frequency \( \omega \).

At large values of \( \omega \), we have:

\[
\varphi \to \frac{\pi}{2}, \quad \cos \varphi \approx \frac{\gamma_T}{\omega}.
\]

Using (39) and (40) we then see that the term corresponding to \( n \) collisions decreases proportionally to \( \omega^{-(n+1)} \), in phase (or quadrature) with the pump modulation when \( n \) is odd (or even). The term \( n = 0 \) for example (no collision) is in quadrature and proportional to \( 1/\omega \); this gives the behaviour of the narrow pumping peak at large \( \omega \). The next contribution is the term \( n = 1 \) (one collision) which decreases as \( 1/\omega^2 \) and is in phase (actually having the opposite phase) with the pumping polarization modulation. More precisely, we have:

\[
S_0(\Omega, \omega) \xrightarrow{\gamma_T \to \infty} \frac{\gamma_T^2}{\omega^2 + \gamma_T^2} \left[ \frac{(\Gamma_{eg})^2}{(\Omega - \Omega_0)^2 + (\Gamma_{eg})^2} - \frac{2 \pi \Gamma_{eg}}{k \gamma_T} K(v_0, -v_0) \right] \exp \left[ -\left( \frac{\Omega - \Omega_0}{k \Delta} \right)^2 \right],
\]

which shows that the dominant contribution to the in-phase signal at large \( \omega \) gives direct access to the collision kernel. The terms corresponding to large values of \( n \), while decreasing rapidly, acquire the largest "phase lag"; consequently, they can appear in quadrature even at relatively low frequencies.

A more detailed discussion is possible if a precise model for the collision kernel is chosen. For example, a kernel of the Keilson-Storer type (31) has been used to calculate the curves shown in figure 5, using formulas (39) and (40) at various frequencies \( \omega \). For comparison, a complete thermalization kernel (28) has also been used, leading to the curves of figure 6. In both cases, the broad collision backgrounds decrease more rapidly with \( \omega \) than the narrow pumping peaks. This is because high values of \( n \) play a role when the conservation parameter \( \xi \) is close to unity. The backgrounds also change sign when \( \omega \) is high enough. An interesting feature is the difference between figures 5 and 6: in the first case, the background becomes narrower while decreasing; in the second case (no velocity memory), it does not change shape.

4.2 MAGNETIC DEPOLARIZATION. — We apply a static magnetic field \( B_y \) along the axis perpendicular to the beam (see Fig. 1). We now have to retain the commutator with \( \mathcal{H}_e \) in (10) and introduce the hamiltonian:

\[
\mathcal{H}_e = \omega_0 J_y \tag{43}
\]

where \( \omega_0 \) is the Larmor frequency. With circular polarization in the pumping, the appropriate observable is the transverse component

\[
\langle J_+ \rangle = \langle J_z + i J_x \rangle
\]

of the orientation. By keeping the commutator term and including collisional transfer, we find for \( \langle J_+ \rangle (v) \) from (19):

\[
\frac{d}{dv} \langle J_+ \rangle (v) = \gamma_p(v) N(v) \langle J_z \rangle_p - (\gamma_T + i \omega_0) \langle J_+ \rangle (v) + \int_{-\infty}^{\infty} dv' \langle J_+ \rangle (v') K(v', v) \tag{44}
\]
which is equivalent in form with (36) and gives the same type of solution (37). The detected quantity is

\[ \langle J_x \rangle = \text{Re} \{ \langle J_x' \rangle \}, \]

and the calculated signal is identical to the expression (39) with \( \omega \) replaced by \( \omega_m \). In the present case, it is the precession of the magnetic moments of the atoms around the static field and the simultaneous velocity diffusion that will result in the change of sign in the background signal. At high magnetic fields the background disappears, but it does not follow a simple lorentzian variation (on the contrary, the depolarization of the peak follows a lorentzian curve with the width \( \gamma_f \)). Also, the limit corresponding to (42) is valid.

The transverse field method is equivalent to the modulated pumping with a transformation to the rotating frame. The quadrature signal (40) is, however, not available with magnetic depolarization.

4.3 MAGNETIC RESONANCE. — We consider here the effect of magnetic resonance in a rotating rf field, which is an exactly soluble case. Pumping longitudinally with circular polarization we apply a weak constant magnetic field \( B_0 \) along the \( Z \) axis and the rf field \( B_1(t) \) rotating at the angular frequency \( \omega \) perpendicular to the static field. We then have to include the commutator with the following hamiltonian in (10):

\[ \mathcal{H}_g = \omega_0 J_\perp + \frac{1}{2} \omega_1 (J_+ e^{-i\omega t} + J_- e^{i\omega t}) \]  

(45)

where \( \omega_1 \) is the Larmor frequency corresponding to \( B_1 \). By transforming to the frame rotating with the field \( B_1(t) \), the hamiltonian (45) becomes independent of time:

\[ \mathcal{H}_{\text{eff}} = (\omega_0 - \omega) J_\perp + \omega_1 J_x . \]  

(46)

The form (46) allows us to define an effective magnetic field and to choose the direction of this field as the Oz quantization axis. In the representation where

---

Fig. 5. — V.S.O.P. line shapes in modulated pumping for various values of the modulation frequency \( \omega \). This figure illustrates the effect of « intermediate » collisions described by a Keilson-Storer kernel with \( \sigma = 0.8 \). (a) Signal in phase with the pumping modulation; (b) signal in quadrature with the modulation. Other parameters : \( \gamma_\perp / \gamma_f = 0.95 \), \( \Gamma_{ex} / kD = 0.02 \), maximum number of collisions = 200. The collision broadened background is narrowed with increasing \( \omega \) and the in-phase background changes sign.

Fig. 6. — V.S.O.P. line shapes in modulated pumping, illustrating the effect of a « strong » (but not completely depolarizing) collision kernel that gives complete thermalization of the atomic velocity (no « memory »). (a) In-phase signal; (b) quadrature signal. Parameters : \( \gamma_\perp / \gamma_f = 0.95 \), \( \Gamma_{ex} / kD = 0.02 \), maximum number of collisions = 200. In this case, when \( \omega \) increases, the background decreases without becoming narrower, which is a different behaviour from that of figure 5.
\( J_{\text{eff}} \) is diagonal (axes Oxyz), we find from (10) the equations for the orientation components with collisions included:

\[
\frac{d}{dt} \langle \vec{J}_z \rangle (v) = \gamma_p(v) N(v) \langle \vec{J}_z \rangle_p \cos \theta - \gamma_T \langle \vec{J}_z \rangle (v) + \int_{-\infty}^{\infty} dv' \langle \vec{J}_z \rangle (v') K(v', v)
\]

(47)

\[
\frac{d}{dt} \langle \vec{J}_+ \rangle (v) = \gamma_p(v) N(v) \langle \vec{J}_z \rangle_p \sin \theta - (\gamma_T - i\tilde{\omega}) \langle \vec{J}_+ \rangle (v) + \int_{-\infty}^{\infty} dv' \langle \vec{J}_+ \rangle (v') K(v', v)
\]

(48)

where \( \langle \vec{J}_+ \rangle = \langle \vec{J}_x + i\vec{J}_y \rangle \) and:

\[
\tan \theta = \frac{\omega_1}{\omega_0 - \omega}
\]

(49)

\[
\tilde{\omega} = [(\omega_0 - \omega)^2 + \omega_T^2]^{1/2}.
\]

(50)

The longitudinal orientation in the laboratory frame is then:

\[
\langle J_z \rangle (v) = \langle \vec{J}_z \rangle (v) \cos \theta + \langle \vec{J}_z \rangle (v) \sin \theta.
\]

(51)

From the steady state solutions of (47) and (48) we obtain:

\[
\langle J_z \rangle (v) = \langle J_z \rangle_p \left\{ \frac{\gamma_p(v)}{\gamma_T} N(v) \left[ 1 - \frac{\omega_1^2}{\gamma_T^2 + \omega_1^2 + (\omega_0 - \omega)^2} \right] + \sum_{n=1}^{\infty} \frac{\omega_1^2}{(\omega_0 - \omega)^2 + \omega_1^2} \cos^{n+1} \varphi_1 \cos(n+1) \varphi_1 \right\} F^{\omega_1}(v)
\]

(52)

with \( \varphi_1 \) given by

\[
\tan \varphi_1 = \frac{\tilde{\omega}}{\gamma_T}, \quad 0 \leq \varphi_1 \leq \frac{\pi}{2}.
\]

(53)

Close to the resonance \( \omega \approx \omega_0 \), the background distribution described by the sum in (52) is depolarized at much smaller values of \( \omega_1 \) than the peak (cf. subsections 4.1, 4.2). Also, the background has a sharper variation as a function of \( \omega_0 \) than the peak (5). At \( \omega = \omega_0 \), the solution (52) takes the same form as (37) with \( \omega_1 \) replaced by \( \omega_1 \). With this method, it is the « Rabi nutation » of \( J \) in combination with velocity diffusion that causes the narrowing behaviour and the reversed sign of the background with the corresponding limit form (42).

The three methods of modulated pumping, magnetic resonance, and magnetic depolarization, lead to essentially equivalent forms of the velocity-correlated orientation distribution and give similar information on collision effects. The modulated pumping has, however, the convenience of accurate determination of the modulation frequency and a direct measurement of the quadrature signal providing an additional method of determining the collision rate.

5. Experimental results. — A detailed verification of the theoretical results obtained in the preceding sections is not presented here. An extensive study should include the discussion of the effect of the gas pressure over a large range, and of the effect of the polarization modulation frequency for different atomic observables (population, orientation, alignment) and with different atomic levels leading to low or high values of the conservation parameter \( \xi \). Instead, we give in this article a much simpler discussion, which is nevertheless sufficient to check that the qualitative behaviour of the V.S.O.P. profiles can be well understood within the theoretical frame developed above.

In particular, we show that high values of the conservation parameter \( \xi \) can be observed for the atomic orientation, even for a \( L \neq 0 \) atomic level.

A short report of the experiments, which were performed by optically pumping the metastable \( ^3P_2 \) and \( ^3P_0 \) levels of Ne, has already been published [7]. A single mode dye laser, operating with a homemade « double Michelson » mode selector [22] and pressure scanning of the laser frequency, was used as the pumping source. The general configuration of the experiment was similar to that of figure 1. The sample cell contained a natural Ne pressure of 5 mtorr and a He pressure of 50 mtorr. The orientation of the \( ^3P_2 \) metastable state was created with the line \( \lambda = 640.2 \) nm (\( J_g = 2 \rightarrow J_e = 3 \)), with a polarization \( \sigma_+ \) modulated at the frequency \( \omega/2 \pi \). The modulation was obtained either with a rotating \( \lambda/4 \)-plate (for low frequencies) or with a transverse electro-optic crystal. A circular polarizer was inserted in the probe beam, which originated from the same laser as the pump. The signal
delivered by the detector of figure 1 contained a component modulated at frequency \( \omega/2\pi \), proportional to the circular dichroism of the gas. This signal was demodulated by a lock-in detector and recorded as a function of laser frequency, which provided the V.S.O.P. profiles.

Figure 7 shows such an experimental profile, obtained at a low modulation frequency \( \omega/2\pi \approx 400 \text{ Hz} \). Two narrow Doppler-free peaks are observed; the main peak corresponds to the resonance frequency of \( ^{20}\text{Ne} \), the smaller one to the less abundant isotope \( ^{22}\text{Ne} \) (about 10% in natural neon). In addition, broad background signals are seen: they correspond mainly to the effect of Ne-He collisions which are seen to preserve a large proportion of the atomic orientation of the \( ^3\text{P}_2 \) state (a rough estimate of \( 1 - \xi \) is given by the ratio between the areas under the Doppler-free peak and the broad background; here we obtain \( \xi \approx 0.95 \)).

Figures 8a and 8b show the experimental curves obtained with a higher polarization modulation frequency \( \omega/2\pi \approx 44 \text{ kHz} \). Such an experiment gives a direct access to the collision relaxation phenomena inside the Doppler profile. Comparison with figures 5 and 6 shows that the qualitative behaviour of the curves is in agreement with theory (note in particular the change of sign in the wings of the in-phase curve, as predicted by (39)). Actually a more careful examination shows that the backgrounds of the experimental curves become narrower at higher frequencies, in agreement with the curves of figure 5 rather than those of figure 6. This is an indication of a pronounced velocity memory effect in the collisions. Such a result is not surprising since most velocity changes occur during collisions between metastable Ne atoms and the much lighter He atoms.

Figure 9 shows a similar experimental curve obtained with alignment instead of orientation, at a low modulation frequency. By comparison with figure 7, one notes that the background is smaller and narrower for alignment than for orientation, indicating that a smaller proportion of the atomic observable is conserved during collisions (\( \xi \) is smaller for alignment than for orientation) (6).

For several reasons, we feel that it would not really be meaningful to attempt a quantitative comparison of these curves with the theory that we have developed above. It is for example clear that in a mixture of two gases the collision kernel should include at least two parts corresponding respectively to Ne-Ne or Ne-He collisions, with different widths and heights. Moreover, (6) Comparing the areas of the backgrounds (normalized with the peak areas) for the alignment and orientation signals, respectively, gives \( (1 - \xi^{(2)})/(1 - \xi^{(1)}) \approx 1.5 \). This rough estimate is in agreement with measurements in optical pumping [23].
even in pure Ne, the situation is not simple, as known from the results of M. Gorlicki, A. Peuriot and M. Dumont [24], who used a more elaborate experimental set-up (two independent pump and probe lasers, direct time resolution with electro-optic shutters). These authors have shown that the Ne-Ne collision kernel contains two different contributions of very different widths. Finally it is not clear to what extent the one dimension approximation for treating velocity changes in the theory of section 3.1 is valid.

Several variants of these experiments have already been reported [7] but we shall only mention a few here. The V.S.O.P. method was applied to the metastable $^3P_0$ state of $^{21}$Ne, using again He as a buffer gas. This is an interesting situation since the quasi perfect conservation of nuclear orientation during atomic collisions would completely destroy any correlation between internal and external variables of the atoms, and therefore wipe out any Doppler-free peak, if the effect of metastability exchange collisions were negligible. Simply speaking, the metastability exchange collisions with unpolarized ground state Ne atoms act as a relaxation process and restore the line shape of the form (23). In principle, the dependence of exchange cross-sections on velocity change could be studied in this way.

Also, in a V.S.O.P. experiment including the Hanle effect, performed in the oriented ground state of Na, the essential depolarization features in the line shape described by (39) were observed [25].

6. Discussion and conclusion. — This work has been concerned with the effects of collisional relaxation only in the first order limit of the pumping, and assuming an isotropic relaxation, which allowed one to neglect the coupling between different multipole components of the density matrix in (3).

The calculations have been restricted to the low pressure regime where collisions in the excited state can be neglected. The cross-section for velocity-changing collisions in the excited state may be larger than in the ground state (e.g. in S-P transitions). If the buffer gas pressure is high enough, velocity transfer in the excited state must be included as well as a possible collision broadening of the optical transition. This complicates somewhat the optical pumping equations (3) but the qualitative features of the velocity-selective pumping remain explainable by the same kind of theory. If the collisions remove most of the excited atoms from the resonant velocity group without complete depolarization, the resonant group of ground state atoms will mainly experience a « depopulation » pumping, while the « repopulation » pumping cycle may still be dominant for the background ensemble of atoms. For transitions having $J_e = J_g + 1$, this will produce a reversed sign of the peak relative to the background in the orientation signal, as was observed in [7].

It is evident that there exists a close relationship between the V.S.O.P. and the various well-known saturation spectroscopy techniques. We have, however, preferred to use the optical pumping terminology in our approach in order to emphasize the distinctions rather than the similarities with the previous methods. In the V.S.O.P. method, the non-equilibrium distribution of atomic populations is created inside a degenerate Zeeman multiplet instead of between separate electronic levels, and the phenomena subject to interest refer to the anisotropy of one atomic state and to the polarization of the light. Such a method is historically associated with the notion of optical pumping. We have discussed the low intensity limit (2) where optical coherence effects vanish and the evolution of the observables is entirely described by rate equations rather than by Bloch equations. Saturation spectroscopy signals may in some cases contain significant contributions from various observables due to optical pumping in addition to pure optical saturation effects [3, 4, 26]. With appropriate polarization modulation techniques, the V.S.O.P. enables one to extract pure and well-defined optical pumping observables in the signals. Finally, by combining the V.S.O.P. with external magnetic fields, a variety of phenomena can be produced involving Zeeman coherences, which are characteristic of classical optical pumping methods.

The application of V.S.O.P. requires that one of the electronic states be long-lived (a ground or metastable state); hence the characteristic relaxation times of the observables are in general much longer than in saturation spectroscopy. The long-lived states are convenient for studies of collisional relaxation in low pressures, and the theoretical treatment of scattering cross-sections is simplified as the atomic potential of only one electronic state is required. Diffusion characteristics and mean free paths can also be studied by applying V.S.O.P. for instance with separated pump and detection beams [6].

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Appendix. — Detection signals in V.S.O.P. — To describe the general detection signal for the observables in V.S.O.P. we can apply the polarization matrix formulation of [12] with appropriate modifications for velocity-selective pumping and detection. Let the counterpropagating detection field have the form

$$\mathbf{E}_d(Z, t) = \mathbf{E}_d \exp[-i(k_d Z + \Omega_d t)] + \text{c.c.} \quad (A.1)$$

with

$$\mathbf{E}_d = \mathbf{E}^x_d e_x + \mathbf{E}^y_d e_y \quad (A.2)$$

where the complex amplitudes $\mathbf{E}^{x,y}_d$ determine the state of polarization. We describe the field $\mathbf{E}_d$ by a state vector $|\mathbf{E}_d\rangle$ in a two-dimensional polariza-
tion state space \([12]\) and associate a hermitian polarization matrix \(\pi\) to the state of the field:

\[
\pi = | \mathbf{e}_a \rangle \langle \mathbf{e}_a |. \tag{A.3}
\]

The field intensity \(I_a\) is given by

\[
I_a = \text{Tr} \{ \pi \}. \tag{A.4}
\]

The signal is obtained by analysing the polarization matrix \(\pi_T\) of the transmitted light as a function of the matrix of the incident light \(\pi_i\) and the atomic density matrix \(\rho_p\). The change in the transmitted field is calculated to first order in the incident probe field as a solution proportional to \(\rho_p\) evolving under the influence of the pumping field (cf. section 2.2).

Let \(B\) represent a dyadic polarizability operator in the tensor product space of the atomic state space and the field polarization state space \([12, 27]\). The operator \(B\) is defined by its matrix elements:

\[
\langle J, m | B_{ij} | J', m' \rangle = \langle J, m | (\mathbf{e}_a^* \cdot \mathbf{D}) P_j(e_\nu, D) | J', m' \rangle
\]

where \(J, m\) are the angular momentum and the magnetic quantum number, respectively. For an optically thin sample we use the formalism of \([12]\) to write the total change in the polarization matrix of the monochromatic probe light transmitted through the sample:

\[
\pi_T(\Omega_a, t) - \pi_i = - \{ G_\lambda(\Omega_a, t), \pi_i \} - i\{ G_D(\Omega_a, t), \pi_i \}.
\]

The operators \(G_\lambda\) and \(iG_D\) are the hermitian and antihermitian parts, respectively, of the integral expression:

\[
G_\lambda(\Omega_a, t) + iG_D(\Omega_a, t) = \frac{1}{2} \frac{\Omega_a l}{\varepsilon_0 c} \frac{|\Omega_{eg}|^2}{2J_e + 1} \int_{-\infty}^{\infty} dv \frac{\text{Tr} \{ \rho_p(v, t) B \}}{\Omega_a - \Omega_0 + k_a v + \imath \Gamma_{eg}} \]

where \(l\) is the length of the sample cell. The equation (A.6) enables one to calculate the general signal in the monochromatic detection of atomic observables correlated to velocity. Only the anticommutator on the r.h.s. of (A.6) has a non-zero trace; this term describes the attenuation of the light intensity by absorption. The commutator in (A.6) describes the effect of dispersion due to virtual transitions. The observables detected in a measurement will depend on the polarization of the probe light and the method of analysing \(\pi_T\) (for a detailed discussion see [28]).

In a typical experiment (cf. Fig. 1) the polarization of the detection beam is modulated between the circular \(\sigma_+\) and \(\sigma_-\) states. With phase-sensitive detection of the intensity modulation in the transmitted probe light, the signal is described by

\[
S = \langle \mathbf{e}_+ | \pi_T | \mathbf{e}_+ \rangle - \langle \mathbf{e}_- | \pi_T | \mathbf{e}_- \rangle \tag{A.8}
\]

yielding the circular dichroism of the sample. Using the development into irreducible tensor operators for \(B_{ij}\) \([12]\) we find for the dichroism:

\[
\text{Tr} \{ \rho_p(v, t) (B_{++} - B_{--}) \} = \sqrt{2} \langle T^{(1)}_0 \rangle (v, t) = C^{(1)} \langle J_\lambda \rangle (v, t) \tag{A.9}
\]

where \(T^{(1)}_0\) is the standard tensor operator component and \(C^{(1)}\) is (see e.g. [29])

\[
C^{(1)} = \sqrt{2} \left[ J_G (J_G + 1) \right]^{-1/2}
\]

Using (A.6), (A.7) and (A.9) we obtain the signal (A.8) from

\[
S(\Omega_a) = C^{(1)} \frac{\Omega_a l}{\varepsilon_0 c} \frac{|\Omega_{eg}|^2}{2J_e + 1} \int_{-\infty}^{\infty} dv \frac{\Gamma_{eg}}{\Omega_a - \Omega_0 + k_a v + \imath \Gamma_{eg}} \langle J_\lambda \rangle (v). \tag{A.11}
\]

This measurement yields the atomic orientation in a narrow group of velocities determined by \(\Omega_a\) and having the spread \(2 \Gamma_{eg}/k_a\).

Corresponding expressions are readily obtained for signals containing the dispersive part of (A.6).
References