Collisional Depolarization of Fluorescence in the Impact and Quasistatic Limit

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Collisional Depolarization of fluorescence radiation has been treated by considering the impact and the quasistatic limit of the general theory of redistribution. The result shows that a variation of the degree of polarization within the fluorescence spectrum is to be expected.

1. Introduction

In a preceding paper [1] it has been argued on the basis of quasistatic theory that the polarization state of fluorescence excited by polarized light should be frequency dependent. On the other hand it has been shown by Nienhuis [2] that for weak collisions no frequency dependence arises, except for special situations (multiplett mixing, influence of the Doppler effect). However, it appears that it is essential to take into account also the effect of strong collisions in order to obtain the predicted frequency dependence. Note that the distinction between weak and strong collision contributions is not relevant as frequency goes; the reason is that the line core is determined by both weak and strong collisions, whereas in the wings the latter dominate.

In this paper we want to show how our result follows from the general theory of redistribution treated by Omont et al. [3], if we consider both the impact and the quasistatic limit of this theory.

2. Polarization Dependent Frequency Distribution

In the case of broad-band excitation, to which we restrict ourselves here, the frequency distribution of the collision induced fluorescence radiation (neglecting the Doppler effect) is described by the following function:

$$F(\omega) = 2\,\mathrm{Re}\,\langle \int \mathrm{d}\tau' \int \mathrm{d}\tau\, e^{-i\omega\tau}\, \mathrm{Tr}\, \varrho_{\mathrm{e}}(\tau') \, (\boldsymbol{\mu}_{\mathrm{eg}}\,\boldsymbol{e})_{\tau'\to\tau'+\tau}\, (\boldsymbol{\mu}_{\mathrm{ge}}\,\boldsymbol{e}^*)\,\rangle_{\mathrm{av}} \qquad (1)$$

where ω and $\boldsymbol{e}$ are respectively the frequency and the polarization vector of the fluorescence radiation, and where $\boldsymbol{\mu}_{\mathrm{eg}}$ etc. are matrix elements of the dipole operator between the ground and the excited state. The quantity $\varrho_{\mathrm{e}}(\tau')$ describes the time evolution of the density matrix of the excited state in the interval $0 \to \tau'$. Similarly $(\boldsymbol{\mu}_{\mathrm{eg}}\cdot\boldsymbol{e})_{\tau'\to\tau'+\tau}$ indicates the time evolution of the product $\boldsymbol{\mu}_{\mathrm{eg}}\cdot\boldsymbol{e}$ during the interval $\tau'\to\tau'+\tau$. These quantities can be expressed by means of the time evolution operator $T(\tau)$ as follows:

$$\varrho_{\mathrm{e}}(\tau') = T(\tau')\,\varrho_0\,T^{\dagger}(\tau'), \qquad (2\text{ a, b})$$
$$(\boldsymbol{\mu}_{\mathrm{eg}}\cdot\boldsymbol{e})_{\tau'\to\tau'+\tau} = T^{\dagger}(\tau'+\tau,\tau')\boldsymbol{\mu}_{\mathrm{eg}}\cdot\boldsymbol{e}\,T(\tau'+\tau,\tau').$$

The trace in (1) is taken over all internal states of the radiating atom, whereas the average is over all initial positions and velocities of the perturbers. The intervals τ' and τ correspond respectively to the relaxation and the reemission process.

The expression (1) may be derived as a special case from the redistribution function [3] by integrating over all frequencies of the exciting radiation (see also [4]).

Note that in the more general case where the excitation is not broad-band the simple picture of well separated excitation, relaxation and reemission intervals no longer holds.

Impact Limit

In the impact limit, which has been treated in [3], the function $F(\omega)$ can be easily evaluated by considering that collisions are uncorrelated. According to this assumption the average in (1) can be factorized:

$$F(\omega) = 2\,\mathrm{Re} \int \mathrm{d}\tau\, e^{-i\omega\tau}\, \mathrm{Tr}\,\langle \int \mathrm{d}\tau'\, \varrho_{\mathrm{e}}(\tau')\,\rangle \, \langle\, (\boldsymbol{\mu}_{\mathrm{eg}}\,\boldsymbol{e})_{\tau'\to\tau'+\tau}\,(\boldsymbol{\mu}_{\mathrm{ge}}\,\boldsymbol{e}^*)\,\rangle\,. \qquad (3)$$

The brackets now indicate ensemble averages over all collisions in the corresponding time intervals. For

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the first bracket we write

$$\varrho = \langle \int \mathrm{d}\tau' \, \varrho_{\mathrm{e}}(\tau') \rangle \, .$$

This quantity has been calculated in [1] for the special case of a $J=1$ level excited by linearly polarized light. The second bracket can be written as [5]

$$\langle \boldsymbol{\mu}_{\mathrm{eg}} \cdot \boldsymbol{e} \rangle_{\tau' \to \tau' + \tau} (\boldsymbol{\mu}_{\mathrm{ge}} \cdot \boldsymbol{e}^*) = e^{-\Gamma_{\mathrm{c}} \tau} (\boldsymbol{\mu}_{\mathrm{eg}} \cdot \boldsymbol{e}) (\boldsymbol{\mu}_{\mathrm{ge}} \cdot \boldsymbol{e}^*) \, ,$$

independent of τ'.

Expression (2) is thus given by:

$$F(\omega) = (\boldsymbol{\mu}_{\mathrm{eg}} \cdot \boldsymbol{e}) (\boldsymbol{\mu}_{\mathrm{ge}} \cdot \boldsymbol{e}^*) \times f(\omega) \tag{4}$$

where $f(\omega)$ is the Lorentz profile:

$$f(\omega) = 2 \, \mathrm{Re} \int \mathrm{d}\tau \, \exp\{-(i\,\omega + \Gamma_{\mathrm{c}})\tau\} \, .$$

In the distribution as given by (4) the polarization properties are contained in the first factor, which is frequency independent. If we define a polarization degree P by considering for instance the two directions z and x of the polarization vector and write

$$P = (F_z - F_x)/(F_z + F_x) \, , \tag{5}$$

the frequency factor $f(\omega)$ drops out. As predictable, the absence of correlations in the impact limit leads to a frequency independent polarization degree.

Quasistatic Limit

This case has to be considered in the far wings of the line. In order to derive this limit from Eq. (1) we first note that the ensemble average over initial positions of perturbers in phase space does not change if it is taken at different instants. This implies, however, that there is no reaction of internal transitions in the radiating atom on the perturber motion; such assumptions are generally made in quasi-classical line-broadening theory [5] (e. g. straight path approximation).

Thus, if in Eq. (1) the average is taken at instant τ', expression (2 b) becomes independent of τ' and we may write

$$F(\omega) = 2 \, \mathrm{Re} \langle \int \mathrm{d}\tau \, e^{-i\omega\tau} \, \mathrm{Tr} \, [\int \mathrm{d}\tau' \, \varrho_{\mathrm{e}}(\tau')] \\ (\boldsymbol{\mu}_{\mathrm{eg}} \cdot \boldsymbol{e})_\tau (\boldsymbol{\mu}_{\mathrm{ge}} \cdot \boldsymbol{e}^*) \rangle_{\mathrm{av}} \, . \tag{6}$$

We now consider the quasistatic wings. We then may assume that at the end of interval τ' there is a strong collision situation; by this we mean, that the perturber is so close to the radiating atom that the latter is in a definite magnetic substate with respect to the internuclear axis. Now, if the integral $\int \mathrm{d}\tau' \, \varrho_{\mathrm{e}}(\tau')$ is taken over all possible instants τ' where this happens, the result will be the unit matrix, since on the long run all orientations with respect to the internuclear axis become equally probable. As the unit matrix is invariant under rotations we may thus write

$$\int \mathrm{d}\tau' \, \varrho(\tau') = 1 \quad (\text{unit matrix}) \, . \tag{7}$$

After substituting this into (6) we obtain a distribution function which we consider in the quasistatic limit. As has been shown in [1] this leads to the expression:

$$F(\omega) \sim \sum_{M_{\mathrm{e}} M_{\mathrm{g}}} |(\boldsymbol{\mu}\,\boldsymbol{e})_{M_{\mathrm{e}} M_{\mathrm{g}}}|^2 \int \mathrm{d}R \, R^2 \, \delta[\omega - \omega_{M_{\mathrm{e}} M_{\mathrm{g}}}(R)] \, . \tag{8}$$

M_{g} and M_{e} designate magnetic substates of the ground and excited state with respect to the internuclear axis. $\omega_{M_{\mathrm{e}} M_{\mathrm{g}}}$ equals $\hbar^{-1}$ times the difference of potentials associated with each pair of M_{g} and M_{e}. It can be shown that the quantity.

$$|(\boldsymbol{\mu}\,\boldsymbol{e})_{M_{\mathrm{e}} M_{\mathrm{g}}}|^2$$

averaged over all orientations of the internuclear axis with respect to a space-fixed axis is independent of $\boldsymbol{e}$. Thus the distribution $F(\omega)$ is polarization independent. From this it follows that in the far wings the radiation is completely depolarized.

On the other hand, the polarization degree (5) in the impact limit is in general different from zero. For instance, in the special case $J_{\mathrm{e}} = 1 \; J_{\mathrm{g}} = 0$ it has the value

$$P = (\varrho_{00} - \varrho_{11})/(\varrho_{00} + \varrho_{11})$$

where $\varrho_{00} \neq \varrho_{11}$ are given in [1].

Remembering that the impact limit describes the line core and the quasistatic limit the line wings one may conclude that the polarization degree should decrease when moving from the center into the wings. However, in order to obtain the law of variation of the polarization degree with frequency one would have to solve Eq. (1) completely which will be the object of further investigations.

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