Time-Dependent Phenomena Associated with the Resonant Scattering of Light by Perturbed Atoms*

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We report theoretical studies of the resonant scattering of light by perturbed atoms under conditions where the amplitude of the incident electric field varies with time. Adiabatic perturbations are simulated by a randomly fluctuating term in the energy separation between the resonant levels; lifetime effects are accounted for by adding a small imaginary term to the separation. Assuming linearity, we derive a general expression giving the intensity of the scattered light as a function of time. Explicit calculations are carried out in the motional narrowing limit for a variety of cases. Interference and inhomogeneous broadening are assessed. A brief analysis is made of recent scattering experiments involving Cr^{3+} in Al_2O_3. Incoherence in the source and the motion of the target atoms are also considered.

I. INTRODUCTION

In a recent series of publications,[1–3] the author has developed a theory of the resonant scattering of light by perturbed atoms. The main purpose of these papers was to show how the dynamics of the perturbation was reflected in the frequency spectrum of the scattered light. This was accomplished by calculating the differential cross section for photon scattering in the presence of the perturbations. The cross section, first obtained by Kramers and Heisenberg,[4] characterizes the scattering of a monochromatic beam of constant amplitude. In the present paper, we will focus on a somewhat different problem, the calculation of the scattered intensity in situations where the amplitude of the incident beam varies with time. Our purpose is to discuss in some detail the connection between the time dependence of the intensity of the scattered light, the intrinsic properties of the scatterer, and the amplitude of the incident field. Our analysis is intermediate between a formal study applying to all possible cases and a report of detailed numerical calculations pertaining to a particular system. We have made a point of displaying some of our results in full detail in order to facilitate possible comparison with experiment. The stimulus for this investigation comes in part from recent studies of the resonant scattering of light by Cr^{3+} ions in Al_2O_3 where a pulsed ruby laser was used as a source.[5]

In Sec. II, we will outline a semiclassical calculation of the scattered intensity for an arbitrary time-dependent incident amplitude. The resulting expression is then evaluated in a variety of special cases. Interference and inhomogeneous broadening are discussed in Sec. IV, while the results reported in Ref. 5 are analyzed in Sec. V. In Sec. VI, we summarize our findings. Miscellaneous aspects of the calculations are relegated to the appendices. It should be noted that the discussion of some of the approximations we make is rather limited. A more detailed analysis is given in II.

II. THEORY

Our approach parallels in many respects the analysis of II. We begin by studying the scattering from a single stationary atom. As in II, we simulate the effects of adiabatic perturbations (i.e., those which do not involve transitions between atomic states) by a randomly fluctuating term in the atomic level splitting. Diabatic perturbations (i.e., lifetime effects) are included by adding an imaginary part to the level splitting at appropriate points in the calculation. As discussed in detail in II, the assumption of a Gaussian spectrum for the fluctuations leads to a model which is applicable to a broad range of experiments. In particular, the model when evaluated in the motional narrowing limit simulates the effects of phonons which are the dominant perturbations in the Cr^{3+} experiment mentioned in the Introduction.[6]

As was done previously, we treat the atom as an effective two-level system with the Hamiltonian (in the absence of the radiation field)

$$\mathcal{H}_0(t)=[\hbar\omega_0+\hbar\delta\omega_0(t)]S_z. \tag{2.1}$$

Here ω_0 is the atomic frequency, $\delta\omega_0(t)$ is the fluctuation, and S_z is the z component of the effective spin ($S=\frac{1}{2}$). The interaction with the radiation field is written

$$\mathcal{H}_1(t)=\tfrac{1}{2}\alpha[\mathcal{E}(t)S_+e^{-i\omega_1 t+\epsilon t}+\mathcal{E}(t)^*S_-e^{i\omega_1 t+\epsilon t}], \tag{2.2}$$

where α is a constant involving matrix elements of appropriate components of the dipole moment operator taken between the resonant levels, $\mathcal{E}(t)$ is the amplitude of the incident electric field (we assume electric-dipole scattering is dominant), ω_1 is the angular frequency of the electric field, $S_\pm=S_x\pm iS_y$, and ϵ is a small positive constant.

As was shown in detail in I, the scattering process

* Supported by the National Science Foundation.
[1] D. L. Huber, Phys. Rev. **158**, 843 (1967); hereafter referred to as I.
[2] D. L. Huber, Phys. Rev. **170**, 418 (1968); hereafter referred to as II.
[3] D. L. Huber, Phys. Rev. **178**, 93 (1969); hereafter referred to as III.
[4] H. A. Kramers and W. Heisenberg, Z. Physik **31**, 681 (1925).
[5] F. Barocchi, M. Mancini, R. Pratesi, and G. Toraldo di Francia, IEEE J. Quantum Electron. **QE-4**, 391 (1968).
[6] D. E. McCumber, Phys. Rev. **133**, A163 (1964).

occurs when the incident electric field induces a time-dependent electric-dipole moment in the system. The electric dipole then radiates giving rise to the scattered light. The induced dipole moment is determined by the operator S_- which obeys the equation

$$i\hbar\frac{d}{dt}S_-(t)=\hbar[\omega_0+\delta\omega_0(t)]S_-(t)-S_z(t)\alpha\mathcal{E}(t)e^{-i\omega_1 t+\epsilon t}. \tag{2.3}$$

At this point, it is convenient to assume that the electric field associated with the incident wave is sufficiently weak so that we may neglect its effect on the time dependence of $S_z(t)$ on the right-hand side of (4.2). When this is the case, the scattering process is linear in the sense that the induced moment is proportional to the amplitude of the field. Under steady-state conditions, linearity is maintained if there is negligible saturation in the scattering process. The condition that the saturation be negligible can be written[7]

$$\alpha^2\mathcal{E}^2/\hbar^2\gamma_L\Delta\omega_{\mathrm{H}}, \tag{2.4}$$

where $1/\gamma_L$ is the lifetime in the upper level and $\Delta\omega_H$ is the homogeneous linewidth. In a pulse experiment, the behavior is linear if the angle through which the effective spin is turned in the rotating frame is much less than unity. For resonance ($\omega_1=\omega_0$), this condition can be written[8]

$$\frac{1}{\hbar}\int_{-\infty}^{\infty}\alpha\mathcal{E}(t)dt\ll 1. \tag{2.5}$$

Denoting the part of the induced dipole-moment operator which gives rise to the resonant scattering by $P_{\mathrm{ind}}(t)$, we have

$$P_{\mathrm{ind}}(t)=\beta S_-^{\mathcal{E}}(t),$$

where β is a second constant involving matrix elements of the dipole-moment operator and $S_-^{\mathcal{E}}(t)$ is the solution of (2.3) which vanishes as $t\to-\infty$:

$$S_-^{\mathcal{E}}(t)=\frac{-\alpha}{i\hbar}S_z e^{-i\omega_1 t}\int_{-\infty}^{0}dx\left[\mathcal{E}(x+t)e^{i(\omega_0-\omega_1)x+\gamma_L x}\times\exp\left(i\int_t^{x+t}\delta\omega_0(\bar{t})d\bar{t}\right)\right], \tag{2.6}$$

where we have included the effects of a finite lifetime by replacing ω_0 with $\omega_0-i\gamma_L$.

Apart from constants, the intensity of light scattered in a given direction, averaged over a time interval $2\pi/\omega_1$, is given by $\langle|\ddot{P}_{\mathrm{ind}}|^2\rangle$, where the angular brackets denote an average over the fluctuations in $\delta\omega_0$. If we make the further assumption that $\mathcal{E}(t)$ and $\delta\omega_0(t)$ vary slowly in a time interval ω_1^{-1}, then the principal contribution to $\ddot{P}_{\mathrm{ind}}$ comes from the factor $e^{-i\omega_1 t}$. Denoting the intensity by $I(t)$, we have

$$I(t)=A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)e^{i(\omega_0-\omega_1)(x_1-x_2)}\times\exp[\gamma_L(x_1+x_2)]\left\langle\exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle, \tag{2.7}$$

where

$$A=\alpha^2\beta^2\omega_1^4/4\hbar^2. \tag{2.8}$$

In obtaining (2.7), we have implicity assumed that the random process giving use to the frequency fluctuations is stationary, i.e.,

$$\left\langle\exp\left(i\int_{x_2+t}^{x_1+t}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle=\left\langle\exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle. \tag{2.9}$$

In addition, we have supposed that the separation between the levels is sufficiently large so that in the absence of the light there is a negligible equilibrium population in the excited state.

Equation (2.7) is the principal result of this section. It displays the intensity of the scattered light as a double time integral over the amplitude of the incident field. It should be remembered that this intensity, which would be measured in a photon-counting experiment, has an angular dependence which arises from the matrix elements concealed in the general parameter A. A second point is that were $\delta\omega_0(t)$ equal to zero, $I(t)$ would take the simple form

$$I(t)=A\left|\int_{-\infty}^{0}dx_1\mathcal{E}(x_1+t)e^{i\omega_0 x_1+\gamma_L x_1}\right|^2. \tag{2.10}$$

In view of this, it is worthwhile to write $I(t)$ as the sum of two terms:

$$\begin{aligned}I(t)=&A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)e^{i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)}\left\langle\exp\left(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\left\langle\exp\left(i\int_{x_2}^{0}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\\&+A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)e^{i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)}\left[\left\langle\exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\right.\\&\left.-\left\langle\exp\left(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\left\langle\exp\left(i\int_{x_2}^{0}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\right], \qquad (2.11)\\=&\bar{I}(t)+\Delta I(t).\end{aligned}$$

[7] This equation is an adaptation of the familiar magnetic resonance condition $\gamma^2H_1^2T_1T_2\ll 1$ [A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. 3].

[8] S. L. McCall and E. L. Hahn, Phys. Rev. Letters **18**, 908 (1967), Eq. (3).

The first term in (2.11), $\bar{I}(t)$, is the intensity arising from the average value of the induced dipole moment $\langle P_{\rm ind}\rangle$, while the second term is the contribution of the fluctuations $\langle P_{\rm ind}{}^2\rangle-\langle P_{\rm ind}\rangle^2$.

At this point, it is convenient to specialize to the Gaussian model,[2] in which case

$$\left\langle \exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\tilde{t})d\tilde{t}\right)\right\rangle = \exp\left(-\frac{1}{2}\int_{x_2}^{x_1}dt_1\int_{x_2}^{x_1}dt_2\langle\delta\omega_0(t_1)\delta\omega_0(t_2)\rangle\right). \quad (2.12)$$

If we further assume that the correlation time τ_c characterizing the fluctuations in $\delta\omega_0$ is short compared with $|\omega_0-\omega_1|^{-1}$ and $\gamma_L{}^{-1}$ (although long compared with $\omega_1{}^{-1}$), we have the motional narrowing limit[2]

$$\langle\delta\omega_0(t_1)\delta\omega_0(t_2)\rangle = 2\Delta\omega_D\delta(t_1-t_2). \quad (2.13)$$

In this case, we obtain the result

$$\left\langle \exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\tilde{t})d\tilde{t}\right)\right\rangle = \exp(-\Delta\omega_D|x_1-x_2|], \quad (2.14)$$

where $\Delta\omega_D$ is on the order of $\langle\delta\omega_0{}^2\rangle\tau_c$. Equations (2.7), (2.11), and (2.14) are the basic equations in the analysis which follows.

III. SPECIAL CASES

In this section, we will evaluate the scattered intensity in the motional narrowing limit for various $\mathcal{E}(t)$. After combining (2.11) and (2.13), we have

$$\bar{I}(t) = A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}(x_2+t)\exp[i(\omega_0-\omega_1)\times(x_1-x_2)+(\gamma_L+\Delta\omega_D)(x_1+x_2)], \quad (3.1)$$

$$\Delta I(t) = A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}(x_2+t)\times\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\times\{\exp[-\Delta\omega_D|x_1-x_2|] -\exp[\Delta\omega_D(x_1+x_2)]\}, \quad (3.2)$$

assuming $\mathcal{E}(t)$ is real. From these equations, it is evident that $\Delta\omega_D$ and γ_L contribute in the same way to $\bar{I}(t)$ but in rather different ways to $\Delta I(t)$. This result is anticipated in previous studies[1,2] where it was found that in coherent scattering only the total linewidth $(\Delta\omega_D+\gamma_L)$ entered, whereas the incoherent scattering depended also on the ratio $\Delta\omega_D/\gamma_L$.

We now consider a number of special cases.

A. $\mathcal{E}(t)=\mathcal{E}_0$(const)

$$\frac{\bar{I}(t)}{A\mathcal{E}_0{}^2} = [(\omega_1-\omega_0)^2+(\gamma_L+\Delta\omega_D)^2]^{-1}, \quad (3.3)$$

$$\frac{\Delta I(t)}{A\mathcal{E}_0{}^2} = \frac{\Delta\omega_D/\gamma_L}{(\omega_1-\omega_0{}^2)+(\gamma_L+\Delta\omega_D)^2}. \quad (3.4)$$

These results have a simple physical interpretation.[2] The first equation is the intensity associated with phase coherent scattering while the second is the intensity arising from the fluorescence. It is apparent that the second term differs from the first by the factor $\Delta\omega_D/\gamma_L$, the same factor which characterizes the ratio of fluorescent to coherent cross sections.[2]

B. $\mathcal{E}(t)=\mathcal{E}_0{}^{\lambda t}$ for $t\leqslant 0$; $\mathcal{E}(t)=\mathcal{E}_0$ for $t>0$

When $t<0$,

$$\bar{I}(t)/A\mathcal{E}_0{}^2 = e^{2\lambda t}/[(\omega_0-\omega_1)^2+(\gamma_L+\lambda+\Delta\omega_D)^2], \quad (3.5)$$

$$\frac{\Delta I(t)}{A\mathcal{E}_0{}^2} = \frac{e^{2\lambda t}[\Delta\omega_D/(\gamma_L+\lambda)]}{(\omega_0-\omega_1)^2+(\gamma_L+\lambda+\Delta\omega_D)^2}. \quad (3.6)$$

When $t>0$, since the expressions are rather lengthy, we give only $I(t)$. The expression for $\bar{I}(t)$ can be obtained from $I(t)$ by first setting $\Delta\omega_D$ equal to zero and then replacing γ_L by $\gamma_L+\Delta\omega_D$; $\Delta I(t)$ is then given by the difference $I(t)-\bar{I}(t)$.

$$\frac{I(t)}{A\mathcal{E}_0{}^2} = e^{-2\gamma_L t}\frac{\gamma_L+\lambda+\Delta\omega_D}{\gamma_L+\lambda}\frac{1}{(\omega_0-\omega_1)^2+(\gamma_L+\lambda+\Delta\omega_D)^2} +2\,\mathrm{Re}\left\{\frac{\exp[-\gamma_L t-\Delta\omega_D t+i(\omega_0-\omega_1)t]}{[\gamma_L-\Delta\omega_D+i(\omega_0-\omega_1)]}\frac{\{1-\exp[-\gamma_L t+\Delta\omega_D t-i(\omega_0-\omega_1)t]\}}{[\gamma_L+\lambda+\Delta\omega_D-i(\omega_0-\omega_1)]}\right\} +\frac{\gamma_L+\Delta\omega_D}{\gamma_L}\frac{1}{(\gamma_L+\Delta\omega_D)^2+(\omega_0-\omega_1)^2}+e^{-2\gamma_L t}\frac{\gamma_L-\Delta\omega_D}{\gamma_L}\frac{1}{(\gamma_L-\Delta\omega_D)^2+(\omega_0-\omega_1)^2} -2e^{-\gamma_L t-\Delta\omega_D t}\,\mathrm{Re}\left\{\frac{e^{i(\omega_0-\omega_1)t}}{[\gamma_L+\Delta\omega_D-i(\omega_0-\omega_1)]}[\gamma_L-\Delta\omega_D+i(\omega_0-\omega_1)]^{-1}\right\}, \quad (3.7)$$

where Re means the real part of the expression in curly brackets.

It is apparent that the change in the time dependence of the amplitude introduces transients in the intensity. Some of these die off in a time $(\delta\omega_D+\gamma_L)^{-1}$ while others persist for a time $\gamma_L{}^{-1}$. As t approaches infinity, however,

we find

$$\frac{I(t)}{A\mathcal{E}_0^2} \sim \frac{\gamma_L+\Delta\omega_D}{\gamma_L}\frac{1}{(\omega_0-\omega_1)^2+(\gamma_L+\Delta\omega_D)^2}, \tag{3.8}$$

in agreement with (3.3) and (3.4). The rapidly decaying transients arise from changes in the coherent component of the induced moment, while those occurring over an interval γ_L^{-1} are associated with changes in the intensity of the fluorescence.

C. $E(t)=\mathcal{E}_0$ for $t<0$; $E(t)=\mathcal{E}_0 e^{-\lambda t}$ for $t>0$

Where $t<0$,

$$\bar{I}(t)/A\mathcal{E}_0^2=[(\omega_0-\omega_1)^2+(\gamma_L+\Delta\omega_D)^2]^{-1}, \tag{3.9}$$

$$\frac{\Delta I(t)}{A\mathcal{E}_0^2} = \frac{\Delta\omega_D/\gamma_L}{(\omega_0-\omega_1)^2+(\gamma_L+\Delta\omega_D)^2}. \tag{3.10}$$

Equations (3.9) and (3.10) are, of course, the same as (3.3) and (3.4).

Where $t>0$, since the expressions for $I(t)$ and $\Delta I(t)$ are also rather complicated, we again display only $I(t)$.

$$\begin{aligned}\frac{I(t)}{A\mathcal{E}_0^2} &= e^{-2\gamma_L t}\frac{\gamma_L+\Delta\omega_D}{\gamma_L}\frac{1}{(\omega_0-\omega_1)^2+(\gamma_L+\Delta\omega_D)^2}\\
&\quad -2\lambda e^{-\gamma_L t-\lambda t-\Delta\omega_D t}\,\mathrm{Re}\left\{\frac{e^{i(\omega_0-\omega_1)t}[\gamma_L+\Delta\omega_D-i(\omega_0-\omega_1)]^{-1}}{[\gamma_L-\lambda-\Delta\omega_D+i(\omega_0-\omega_1)][\gamma_L-\lambda+\Delta\omega_D-i(\omega_0-\omega_1)]}\right\}\\
&\quad +e^{-2\lambda t}\frac{\gamma_L-\lambda+\Delta\omega_D}{\gamma_L-\lambda}\frac{1}{(\gamma_L-\lambda+\Delta\omega_D)^2+(\omega_0-\omega_1)^2}+e^{-2\gamma_L t}\frac{\gamma_L-\lambda-\Delta\omega_D}{\gamma_L-\lambda}\\
&\quad \times[(\omega_0-\omega_1)^2+(\gamma_L-\lambda-\Delta\omega_D)^2]^{-1}-2e^{-2\gamma_L t}[(\omega_0-\omega_1)^2\\
&\quad +(\gamma_L-\lambda-\Delta\omega_D)(\gamma_L+\Delta\omega_D)][(\gamma_L-\lambda-\Delta\omega_D)^2+(\omega_0-\omega_1)^2]^{-1}[(\gamma_L+\Delta\omega_D)^2+(\omega_0-\omega_1)^2]^{-1}.\end{aligned} \tag{3.11}$$

It is to be noted that $I(t)$ has transients similar to those displayed in Eq. (3.7). However, as t approaches infinity,

$$I(t)\sim 0, \tag{3.12}$$

as is to be expected, since the incident amplitude has become exponentially small. The intensity in the limit as λ becomes very large assumes the simple form

$$\frac{I(t)}{A\mathcal{E}_0^2} = \frac{\gamma_L+\Delta\omega_D}{\gamma_L}\frac{e^{-2\gamma_L t}}{(\omega_0-\omega_1)^2+(\gamma_L+\Delta\omega_D)^2}, \tag{3.13}$$

indicating an exponential decay in the absence of the incident light with a rate characteristic of the lifetime of the excited state.

D. $\mathcal{E}(t)=\mathcal{E}_0 e^{-\lambda|t|}$ (Symmetric Pulse)

For $t<0$, $\bar{I}(t)$ and $\Delta I(t)$ are given by Eqs. (3.5) and (3.6), respectively.

When $t>0$, we again display only $I(t)$.

$$\begin{aligned}\frac{I(t)}{A\mathcal{E}_0^2} &= \gamma_L^{-1}\,\mathrm{Re}\left\{\exp[-t(\gamma_L+\Delta\omega_D+\lambda+i(\omega_0-\omega_1))]\left(\frac{1}{\gamma+\Delta\omega_D+\lambda+i(\omega_0-\omega_1)}+\frac{1}{\gamma_L-\lambda-\Delta\omega_D-i(\omega_0-\omega_1)}\right)\right\}\\
&\quad -(\gamma_L-\lambda)^{-1}\,\mathrm{Re}\left\{\exp[-t(\gamma_L+\lambda+\Delta\omega_D+i(\omega_0-\omega_1))]\left(\frac{1}{\gamma_L-\lambda-\Delta\omega_D-i(\omega_0-\omega_1)}+\frac{1}{\gamma_L-\lambda+\Delta\omega_D+i(\omega_0-\omega_1)}\right)\right\}\\
&\quad -\frac{\lambda e^{-2\gamma_L t}(\gamma_L+\Delta\omega_D+\lambda)}{\gamma_L(\gamma_L+\lambda)[(\omega_0-\omega_1)^2+(\gamma_L+\lambda+\Delta\omega_D)^2]}+\frac{\lambda e^{-2\gamma_L t}(\gamma_L-\lambda-\Delta\omega_D)}{(\gamma_L-\lambda)\gamma_L[(\omega_0-\omega_1)^2+(\gamma_L-\lambda-\Delta\omega_D)^2]}\\
&\quad +e^{-2\lambda t}\frac{\gamma_L-\lambda+\Delta\omega_D}{\gamma_L-\lambda}\frac{1}{(\omega_0-\omega_1)^2+(\gamma_L-\lambda+\Delta\omega_D)^2}.\end{aligned} \tag{3.14}$$

In Sec. V, we will make use of (3.14) when $\Delta\omega_D \gg \lambda \gg \gamma_L$. In this limit, we have

$$I(t)/A\mathcal{E}_0^2 = (\Delta\omega_D/\lambda)[(\omega_1-\omega_0)^2+(\Delta\omega_D)^2]^{-1} \times(2e^{-2\gamma_L t}-e^{-2\lambda t}). \quad (3.15)$$

Equations (3.5), (3.6), and (3.15) show that the intensity of the scattered light at time t depends on the integral of the incident intensity (i.e., the number of photons absorbed) over the interval $[-\infty, t]$, a result which is characteristic of a fluorescent process. We obtain this behavior because, when $\Delta\omega_D \gg \gamma_L$, the strong fluctuations in the atomic frequency completely destroy the coherence between the incoming and outgoing fields.

The purpose of this section has been to apply the general equations derived in the preceding section to a variety of simple cases. In connection with this, two points need to be stressed. First, we have calculated the scattering only in the motional narrowing limit, and second, we have considered only single-atom scattering. Phenomena associated with scattering from an ensemble of atoms will be discussed in Sec. IV.

IV. INTERFERENCE AND IMHOMOGENEOUS BROADENING

In this section, we will examine effects which come into play when one is considering scattering from an ensemble of atoms. We first discuss interference. We assume that the atoms are located in a region whose dimensions are large compared with the wavelength of the light. As was shown in III, if the atoms are randomly distributed within this region, interference effects vanish for other than forward scattering. The resulting cross section then becomes the sum of the cross sections of the component atoms. What we wish to consider here are effects arising from departures from a fully random distribution.

If we designate the position of the jth atom by $\mathbf{r}_j$ and the difference between the wave vectors of the incoming and outgoing photons by $\Delta\mathbf{k}$ then the intensity of light scattered from an ensemble of identical atoms I_{tot} becomes

$$I_{\text{tot}} = A\Bigg\{\sum_{i,j} e^{i\Delta\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]$$
$$\times\Big\langle\exp\Big(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle\Big\langle\exp\Big(i\int_{x_2}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle+\sum_j\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)$$
$$\times\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\Big[\Big\langle\exp\Big(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle$$
$$-\Big\langle\exp\Big(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle\Big\langle\exp\Big(i\int_{x_2}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle\Big]\Bigg\}. \quad (4.1)$$

In (4.1), we have made the assumptions (1) that the amplitude of the electric field is the same at all sites and (2) that the frequency fluctuations at the different sites are independent of one another. In order to proceed further, we divide the region where the atoms are located into cells of volume Λ^3, where Λ is the wavelength of the light.[9] If the volume of the system is denoted by V, then the total intensity can be written

$$I_{\text{tot}}(t) = \frac{AV}{\Lambda^3}(\langle n_\Lambda^2\rangle-\langle n_\Lambda\rangle^2)\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]$$
$$\times\Big\langle\exp\Big(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle\Big\langle\exp\Big(i\int_{x_2}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle+\frac{AV}{\Lambda^3}\langle n_\Lambda\rangle\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)$$
$$\times\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\Big[\Big\langle\exp\Big(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle$$
$$-\Big\langle\exp\Big(-i\int_{x_1}^{0}\delta\omega_0(\bar{t})d\bar{t}\Big)\Big\rangle\Big\langle\exp\Big(i\int_{x_2}^{0}\delta\omega_0(\bar{t})dt\Big)\Big\rangle\Big], \quad (4.2)$$

where $\langle n_\Lambda\rangle$ is the mean number of atoms in the cell and $\langle n_\Lambda^2\rangle-\langle n_\Lambda\rangle^2$ is the dispersion in n_Λ. For a completely

[9] W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1955), Chap. 21.

random distribution, $\langle n_\Lambda^2\rangle-\langle n_\Lambda\rangle^2=\langle n_\Lambda\rangle$, so that

$$I_{\rm tot}(t)=\frac{AV\langle n_\Lambda\rangle}{\Lambda^3}\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\times\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\times\left\langle\exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle. \quad (4.3)$$

On the other hand, if there is clustering or a regular distribution (i.e., a lattice), interference effects will be present, and the total intensity is no longer the sum of the intensities contributed by the different atoms.[10]

The second point concerns the effects of inhomogeneities which give rise to a distribution in resonant frequencies. In order to analyze this effect, we will assume that the spatial distribution is sufficiently random so that $I_{\rm tot}$ has a form similar to (4.3), except that we must also average over ω_0. If $\mathcal{P}(\omega_0)d\omega_0$ is the probability that the resonance frequency lies between ω_0 and $\omega_0+d_{\omega_0}$, then

$$I_{\rm tot}(t)=N\int_{-\infty}^{\infty}\mathcal{P}(\omega_0)d\omega_0\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\times\exp[i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\times\left\langle\exp\left(i\int_{x_L}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle, \quad (4.4)$$

where N is the number of resonant scatterers. If $\mathcal{P}(\omega_0)$ is a Lorentzian, $(\delta/\pi)[(\omega_0-\bar{\omega}_0)^2+\delta^2]^{-1}$, this equation takes a particularly simple form when we assume a Gaussian spectrum for $\delta\omega_0$ and pass to the motional narrowing limit:

$$I_{\rm tot}(t)=N\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\times\exp[i(\bar{\omega}_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)]\times\exp[-(\Delta\omega_D+\delta)|x_1-x_2|]. \quad (4.5)$$

Under these conditions, the effects of inhomogeneities can be accounted for by replacing $\Delta\omega_D$ with $\Delta\omega_D+\delta$ where δ is a measure of the width in the distribution of resonant frequencies. It should be noted that this is the case only for the integrated (over frequency) intensity. The effect of a distribution in resonant frequencies on the frequency dependence of the differential cross section is rather more complicated as can be seen, for example, by averaging the right-hand side of Eq. (2.11) of II over $\mathcal{P}(\omega_0)$.

[10] Interference and other phenomena associated with light scattering in condensed media are discussed in detail by I. L. Fabelinskii [*Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968)].

V. ANALYSIS OF EXPERIMENTAL STUDIES

In this section, we will discuss recent resonant scattering experiments reported by Barocchi *et al.*[5] These investigators studied the scattering of light by Cr^{3+} ions in Al_2O_3. The source was a pulsed ruby laser, and the transitions were between the $^4A_2$ ground state and the ^2E excited state. By making use of the temperature-dependent shift of the resonant levels, they were able to tune the target to the incident frequency. When this happened, there was an enhancement of the scattered light.

The experiments were performed on a sample of Al_2O_3 doped with 0.05% Cr^{3+}. The duration of the laser pulse was on the order of 10^{-8} sec, and the scattered light was detected at right angles with respect to the incident beam. By taking advantage of the aforementioned thermal shift, they obtained a resonance in the neighborhood of 240°K. At temperatures above 77°K, homogeneous broadening arising from the Raman scattering of phonons is the dominant linewidth mechanism.[11] At 240°K, the value for the linewidth reported by McCumber and Sturge is 1.8×10^{12} sec^{-1}.[11]

The remaining parameter needed for the comparison between experiment and theory is γ_L, the lifetime in the upper level. Some care must be exercised here, since the ^2E level of Cr^{3+} is split by trigonal perturbations and spin orbit coupling into a pair of doublets $2\bar{A}(^2E)$ and $\bar{E}(^2E)$ separated by 29 cm^{-1}.[12] In the Barocchi experiment, the scattering comes mainly from the $\bar{E}$ level. The lifetime in the $\bar{E}$ level is determined by two processes, radiative transitions to the ground state, which occur at the rate 0.3×10^3 sec^{-1}, and nonradiative phonon-assisted transitions to the $2\bar{A}$ level. At 240°K, the phonon-assisted transition is by far the dominant process. A lower limit on this transition rate can be obtained by evaluating the one-phonon contribution. Using data reported by Geschwind *et al.*,[13] we find $\gamma_{\rm NR}$ (one phonon)$\approx10^9$ sec^{-1}. Since multiphonon processes are important at high temperatures, the actual value of the nonradiative transition rate may be one or two orders of magnitude greater than the one-phonon value, although still less than $\Delta\omega_D$.

The question then arises in making the comparison between experiment and the theory outlined in Secs. III and IV if one uses the radiative transition rate or the nonradiative rate for γ_L. We argue that the radiative rate is to be used in comparing the intensities of the coherent and incoherent scattering. The reason is that once the ion has undergone a phonon-assisted transition from $\bar{E}$ to $2\bar{A}$, it is far more likely that it will return to the $\bar{E}$ state by the inverse process than undergo a radiative transition to the ground state. As a consequence,

[11] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).

[12] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

[13] S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn, Phys. Rev. **137**, A1087 (1965).

while the phonons serve to keep the populations of the $2\bar{A}$ and $\bar{E}$ levels in thermal equilibrium, it is only the radiative transitions which depopulate the upper level in the sense implied in Secs. II and III.

This argument can be stated in somewhat more mathematical terms. If we assume that the incident amplitude is constant in time then the incoherent and coherent intensities are in the ratio $\Delta\omega_D/\gamma_L$. If we replace γ_L by $\gamma_R+\gamma_{NR}$ (R and NR denote radiative and nonradiative, respectively), we must also include the contribution to the fluorescence from $\bar{E}$ which follows phonon assisted transitions from $\bar{E}$ to $2\bar{A}$ and back to $\bar{E}$. If we make use of the fact that the radiative transition rates from $\bar{E}$ and $2\bar{A}$ to the ground state are about the same and further, and that at high temperatures ($kT\gg 29$ cm^{-1}) the phonon-assisted transition rate from $\bar{E}$ to $2\bar{A}$ is comparable to the rate for the inverse process $2\bar{A}$ to $\bar{E}$, we find that the ratio $\mathcal{R}$ of the incoherent to coherent intensities can be written as an infinite series:

$$\mathcal{R}=[\Delta\omega_D/(\gamma_R+\gamma_{NR})]\{1+[\gamma_{NR}/(\gamma_R+\gamma_{NR})]^2 +[\gamma_{NR}/(\gamma_R+\gamma_{NR})]^4+\cdots\} \quad (5.1)$$
$$=[\Delta\omega_D/(\gamma_R+\gamma_{NR})]\{1-[\gamma_{NR}/(\gamma_R+\gamma_{NR})]^2\}^{-1}.$$

In this equation, $[\gamma_{NR}/(\gamma_{NR}+\gamma_R)]^2$ is the probability that the ion undergoes at least one nonradiative transition from E to $2\bar{A}$ and back to $\bar{E}$ before undergoing radiative decay. When $\gamma_{NR}\gg\gamma_R$, the ratio becomes

$$\mathcal{R}=\Delta\omega_D/2\gamma_R, \quad (5.2)$$

as anticipated from the preceding discussion. The factor of two indicates that only half the fluorescent transitions originate in the $\bar{E}$ state; the remainder come from $2\bar{A}$.

On the basis of the discussion given above, the intensity of light scattered by a single atom in the Barocchi experiment should have the time dependence shown in Eq. (3.15) for $t\gtrsim 0$. The values of γ_L, λ, and $\Delta\omega_D$ that apply are 10^3, 10^8, and 10^{12} sec^{-1}, respectively. The important point here is that the intensity decays as $\exp(-2\gamma_L t)$ after the incident light has been shut off [$\exp(-2\lambda t)\ll 1$]. As long as $2\gamma_L t\lesssim 1$, the intensity of the fluorescence is within a factor of 2 of the total intensity at $t=0$. This happens because the phonons completely destroy the coherence of the scattering process, as is indicated by the fact that $\mathcal{R}\approx 10^9$. Consequently, the scattered light is incoherent and emerges over a time comparable with the lifetime of the excited state. In the experiments reported in Ref. 5, no attempt was made to monitor the intensity as a function of time. However the possibility of making such measurements is being explored.[14]

It is important to note that the analysis we have made has been based on the assumption that the distribution of atoms which are resonant with the light is completely random and that the scattering process is linear. If scattering comes primarily from clusters of atoms ($\langle n_\Lambda^2\rangle-\langle n_\Lambda\rangle^2\gg\langle n_\Lambda\rangle$), then the coherent component will be enhanced in the manner predicted by Eq. (4.2). Linearity will be assured if the experiments are carried out at very low intensities.

[14] F. Barocchi (private communication).

VI. SUMMARY

In the preceding sections, we have outlined a calculation of the intensity of the light which is resonantly scattered by an ensemble of atoms. We have separated the single-atom contribution into its coherent and incoherent parts and have examined the effects of interference and a distribution of resonant frequencies.

There are, however, several aspects of the theory which deserve further comment. First, we have approximated the resonant atom by a two-level system. This does not appear to be a serious defect as long as $I(t)$ is interpreted as the intensity in a small band of frequencies centered about the resonance frequency. This is required so that photons emitted in fluroescence from other levels are not counted. Second, we have assumed that the scattering atoms are stationary. In Appendix A, we discuss the modifications that must be made when they are in random motion. Finally, if the equations of Secs. III and IV are to be of use, the incident amplitude must vary in a regular (and known) way with time. This, of course, presupposes a coherent source such as provided by a laser. In Appendix B, we extend our analysis to allow for fluctuations in $\mathcal{E}(t)$.

It is apparent, from the analysis in Sec. III, that scattering measurements carried out with time-dependent sources permit one to determine in principle unique values for both $\Delta\omega_D$ and γ_L, whereas steady-state absorption measurements yield only the sum $\Delta\omega_D+\gamma_L$. Information about the intrinsic properties of the scatterer is always valuable. However, we feel that the interaction of a scattering system with a radiation field is an interesting problem in its own right. It is our hope that further experimental studies of this problem will be undertaken with scatterers whose intrinsic properties are well understood.

APPENDIX A

The purpose of this appendix is to modify Eq. (2.7) to allow for random motion of the target atoms. If $\mathbf{r}(t)$, taken to be a classical variable, denotes the position of the atom at time t, then we have

$$P_{\rm ind}(t)=i\alpha\beta\hbar^{-1}S_z e^{-i\omega_1 t}e^{-i\mathbf{k}_2\cdot\mathbf{r}(t)} \times\exp\left[-i\left(\omega_0 t+\int_{-\infty}^{t}\delta\omega_0(\bar{t})d\bar{t}\right)\right] \times\int_{-\infty}^{t}dt'\exp\left[i\left(\omega_0 t'+\int_{-\infty}^{t'}\delta\omega_0(\bar{t})d\bar{t}\right)\right]e^{i\mathbf{k}_1\cdot\mathbf{r}(t')}, \quad (A1)$$

where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave vectors of the incoming and outgoing photons, respectively. With (A1), we obtain the equation

$$I(t)=A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\times e^{i(\omega_0-\omega_1)(x_1-x_2)+\gamma_L(x_1+x_2)}\left\langle\exp\left(i\int_{x_2}^{x_1}\delta\omega_0(\bar{t})d\bar{t}\right)\right\rangle\times\left\langle\exp\left(i\mathbf{k}_1\cdot\int_{x_2}^{x_1}\mathbf{v}(\bar{t})d\bar{t}\right)\right\rangle, \quad \text{(A2)}$$

where $\mathbf{v}(t)[=\dot{\mathbf{r}}(t)]$ is the velocity of the particle. In obtaining (A2), we have made the assumption that we could separate the averaging over the fluctuations in $\delta\omega_0$, which arise from collisions between atoms, from the average over the velocities, a point which is discussed in detail in III. If we treat kinematic effects in the Gaussian approximation[3] and collisions in the impact limit,[3] we have

$$I(t)=A\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)e^{i(\omega_0-\omega_1)(x_1-x_2)}\times e^{i\Delta_c(x_1-x_2)}e^{\gamma_L(x_1+x_2)-\gamma_c|x_1-x_2|}\times\exp\left(-\frac{1}{2}\int_{x_2}^{x_1}dt_1\int_{x_2}^{x_1}dt_2\langle\mathbf{k}_1\cdot\mathbf{v}(t_1)\mathbf{k}_1\cdot\mathbf{v}(t_2)\rangle_v\right), \quad \text{(A3)}$$

where Δ_c is the shift in resonance frequency and γ_c is the collision width.

In the case of an ideal gas, the velocity autocorrelation function $\langle\mathbf{k}_1\cdot\mathbf{v}(t_1)\mathbf{k}_1\cdot\mathbf{v}(t_2)\rangle_v$ has the simple form $k_1^2(KT/m)$, where K is Boltzmann's constant, T is the temperature, and m is the mass of the atom. The final exponential factor in (A3) can be written $\exp[-(KT/2m)(x_1-x_2)^2]$.

APPENDIX B

In this appendix, we indicate the modifications in (2.7) that are necessary when the amplitude fluctuates in a random way with time. When this is the case, we replace the product $\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)$ by the correlation function $\langle\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\rangle_\varepsilon$, where the brackets symbolize a statistical average over the fluctuations which are assumed to have a time scale which is long compared with ω_1^{-1}. For example, a possible functional form for the correlation function might be

$$\langle\mathcal{E}(x_1+t)\mathcal{E}^*(x_2+t)\rangle_\varepsilon=S(t)e^{-\phi|x_1-x_2|}, \quad \text{(B1)}$$

where $S(t)$ is a slowly varying envelope function and ϕ^{-1} is a measure of the time over which the electric field remains correlated. It is worth pointing out that, if the correlation function has the form displayed in (B1), the ϕ dependence of the intensity in the motional narrowing limit is determined by the sum $\phi+\Delta\omega_D$. Thus, if $\Delta\omega_D\gg\phi$, the fluctuations in $\mathcal{E}$ may be neglected.