482 (1971) and the references quoted therein.

[8]J. Wilks, *The Properties of Liquid and Solid Helium* (Clarendon, Oxford, 1967), Chap. 6.

[9]R. P. Feynman and M. Cohen, Phys. Rev. 102, 1189 (1956).

[10]R. P. Feyman, Phys. Rev. 94, 262 (1954).

[11]The recent measurements show that the roton minimum is not symmetric about P_0, and the value of μ is different for the two different sides of the minimum, indicating a better qualitative agreement with the spectrum (3) with $V=0$ rather than the spectrum (2) with $V=0$. An intermediate value is given as $\mu=0.15$ m [R. A. Cowley and A. D. B. Woods, Can. J. Phys. 49, 177 (1971)].

[12]J. L. Yarnell, G. P. Arnold, P. J. Bendt, and E. C. Kerr, Phys. Rev. 113, 1379 (1959).

[13]A. L. Fetter, Phys. Rev. Letters 27, 986 (1971).

[14]A. D. B. Woods, Can. J. Phys. 39, 1082 (1961).

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Populating Excited States of Incoherent Atoms Using Coherent Light*

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This paper deals with the equations of motion of the density matrix of a two-level atom in the presence of an intense multimode radiation field characterizing a multimode laser. Using a simplified treatment of line broadening which does not include correlations between momentum-changing collisions and pressure-broadening collisions, we obtain expressions which show the effect of pressure, laser-pulse length, and intensity on the excitation. We obtain analytic expressions in limiting cases of the pressure which allow prediction of the degree of excitation from a given laser pulse. In our treatment the phase relaxation time of the atoms is assumed to be fast enough so that coherence effects among the atoms can be ignored. Treating the velocity of the atoms statistically, we solve for three cases: constant velocity, velocity changes that are fast compared to the excitation time but slow compared to the dephasing time, and velocity changes that are fast compared to all other processes. The three cases yield the same formal equation for the two-body process of absorption of photons by incoherent atoms; however, the cross sections differ and are calculated explicitly for each case. Also discussed are the range of laboratory conditions and the relationship between these laboratory conditions and the various cases considered to demonstrate that under most circumstances this simple photon-absorption picture is applicable, provided the cross section is calculated correctly.

I. INTRODUCTION

The development of truly tunable lasers that span the entire visible and near-infrared spectrum as well as the near ultraviolet[1,2] has opened a new range of atomic physics experiments. The feature that distinguishes many of these experiments is the ability to populate selectively and efficiently a single excited state.[3]

This paper clarifies the conditions under which traditional expressions for the absorption of incoherent light can be applied to laser excitation. We treat the interaction of a multimode output of a laser with an atomic gas, subject to the restriction that there are no cooperative effects such as superradiance arising from coherence of the atoms. In particular, we assume a high dephasing rate for the atomic energy levels so that the atoms can be considered incoherent. Such dephasing can be produced most easily by collisions. The range of dephasing rates for various experimental conditions and the applicability of our treatment to each range are discussed.

The aim of this paper is to give an insight into the influence of various experimental parameters on the interaction of high-intensity light with absorbing atoms. We adopt the customary approach of treating pressure broadening and Doppler broadening independently by assuming that the two collisional processes are uncorrelated. Recently treatments of line broadening have increased in sophistication, and various authors have included the correlations between these two processes.[4] This paper is not designed to deal with line broadening in such a way as to give highly accurate and detailed absorption profiles. Rather we are content with simpler theories giving a good approximation to the actual line shape. In this way we will

try to gain an insight into the effect of collisions and velocities on the absorption of light in the case where the radiation field is intense enough to strongly change the populations of the states. In particular we want to justify the use of absorption coefficients obtained from low-intensity absorption experiments or perturbation theory and also to see when hole burning can be ignored. Therefore in order to obtain usable expressions for the cross section for excitation in limiting cases and to gain a feeling for the effect of changes in pressure, laser power, and laser-pulse length, we restrict ourselves to this more easily visualized treatment of separating pressure broadening and Doppler broadening. The cross sections derived in this paper hold in the limiting cases for which they are obtained and should be useful in predicting the degree of excitation in optical-pumping experiments using laser excitation.

The three cases for which we derive analytic expressions are case 1, where no momentum-changing collisions occur, case 2 where momentum-changing collisions are much more frequent than the dephasing collisions which give rise to pressure broadening, and case 3 where dephasing collisions are much more frequent than momentum-changing collisions. We do not derive explicit expressions where both collision processes are of comparable frequency, which is the case where the correlation between the types of collisions is most likely to be important. Correlations are obviously unimportant in case 1 (no momentum-changing collisions). In addition, Smith, Cooper, Chappell, and Dillon[5] have shown that, if the average momentum transfer during the phase-shifting collisions is small, then the term involving the correlations can be ignored. This is our case 3, where the rate of dephasing is much faster than rate of momentum change. Experimentally either the no momentum-changing collision case or the case where dephasing collisions are most frequent is often achieved in optical spectroscopy, the high dephasing rate with low-momentum transfer often being achieved by using a light buffer gas such as helium to broaden the absorption spectra of heavy atoms. Case 2, where momentum transfer is much more frequent than dephasing, occurs most commonly in the microwave region when magnetic dipole transitions are involved or in infrared molecular transitions. This case is included here mainly for completeness.

In case 1 we treat each velocity subset separately, and the absorption cross section obtained has a Lorentzian profile. The excitation of the atomic system shows the effects of hole burning as would be expected. For cases 2 and 3 we assume a redistribution of velocities which is sufficiently fast to prevent hole burning and the absorption cross section is the same for all atoms. The absorption cross section has a narrowed profile with the limiting form of a Lorentzian in case 2 and has the familiar Voigt profile for case 3. The results are summarized at the end of Sec. III.

The approach of the paper is to solve the equation of motion for the atom in the presence of an electromagnetic radiation field with a phenomenological damping constant to represent dephasing due to collisions. The equation of motion is general with the effect of momentum-changing collisions being included by making the resonant frequency of the atom time dependent in the laboratory frame. A general solution of the equations would show hole burning which depended on the explicit variation of the resonance frequency with time. We solve the equations of motion in the limiting cases where there are no collisions and where momentum-changing collisions are frequent compared to the excitation time, and we obtain the conditions for which these limiting cases hold. The Doppler broadening with high collision rates is introduced by using a Brownian-motion treatment of collisions. This approach is strictly applicable for the case of a large number of collisions with a small-momentum transfer on each collision[6] and obviously most consistent with our case 3, where the dephasing rate is much faster than the momentum-transfer rate.

In all three of our limiting cases we show that the condition of a high dephasing rate is sufficient to reduce the equation of motion to the form

$$\frac{\partial}{\partial t} A(t) = -\sum_i 2\eta_i(t)\sigma_i A(t) - \frac{A(t)+1}{T_1'} \quad ,$$

where $A(t)$ is a measure of the excitation of the atoms, $\eta_i(t)$ is the photon flux at frequency ω_i, σ_i is the cross section, and T_1' is the decay time of the excited state. This is the rate equation for two-body collisions. The fact that the rate equation takes this form shows that the coherence properties of the exciting light have no effect. We determine the form of σ_i for several cases in terms of conventional atomic parameters such as oscillator strengths, velocity distributions, and collision rates.

The solutions to the equations of motion are summarized in Eq. (50) and the ensuing discussion. In Sec. IV we then discuss the typical value of the physical parameters affecting the absorption. For convenience, a glossary of the principal terms used in this paper are included in the Appendix.

II. BASIC TREATMENT OF ATOM-LIGHT INTERACTIONS

Physical Picture

The effect of a multimode laser output on the density matrix of an ensemble of two-level atoms

is calculated to obtain the change in population for the ensemble. Our approach is semiclassical with a classical electromagnetic field interacting with quantum-mechanical atoms. Both Doppler and collisional broadening are considered.

We consider separately two effects of collisional broadening. First, we treat broadening due to dephasing collisions. We assume that the phase of the atoms as given by the off-diagonal elements of the density matrix has a damping time T_2' as a result of these collisions. Throughout this paper T_2' is assumed short compared to the laser pumping time τ_p. In particular, we require T_2' to be sufficiently short to assure that the atoms are incoherent with respect to each other and to the radiation field. In this way we can neglect such coherent phenomena as superradiance[7,8] and self-induced transparency.[9] Second, we consider the effect on absorption of momentum-transfer collisions that shift the resonant frequency ω of the atoms in the laboratory frame. We assume these momentum-changing collisions are not correlated with the dephasing collisions in order to treat the two types of broadening independently. In addition, we assume that the velocity distribution of the atoms, which give rise to Doppler broadening, has a Gaussian shape.

Three ranges for the rate at which these momentum-transfer collisions occur are considered. The first is the case of no collisions occurring during the entire interaction. The other two cases include both the low rate of momentum transfer, which results in the absorption cross section having a Voigt profile, and the high rate of momentum transfer, where the velocity shifts may give rise to a Lorentzian shape. In both the second and third cases, however, the rate of momentum transfer is assumed faster than the laser-pumping rate $1/\tau_p$, where the laser-pumping time τ_p is the characteristic time required for the laser to equalize the populations of the excited and the ground states. Note that this time should not be confused with the actual laser-pulse length τ_0. In all three ranges the rate of the dephasing collisions is assumed to be high.

Equations of Motion

We write the exciting laser pulse as the sum of an arbitrary number of longitudinal modes at frequencies ω_i, where $i=1, 2, 3, \ldots$, with real amplitudes $E_i(t)$ and polarizations $\hat{\epsilon}_i$. The modes have a uniform spacing $\Delta\Omega$ and the laser has a total linewidth Ω. The electric field

$$\vec{\mathbf{E}}(z, t) = \tfrac{1}{2}\textstyle\sum_i E_i(t)\,\hat{\epsilon}_i\{\exp[i(-k_i z+\omega_i t)]+\text{c. c.}\} \tag{1}$$

is assumed uniform in the transverse directions across the gas being excited.[10] The laser is turned on at $t=0$. The term c. c. stands for the complex conjugate of the preceding term.

We now write the equation of motion for the 2×2 density matrix for an atom with resonant frequency ω in the laboratory frame as

$$\rho(t)=\begin{bmatrix} aa^* & ab^* \\ ba^* & bb^* \end{bmatrix}=\begin{bmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{bmatrix}, \tag{2}$$

where a and b stand for the time-dependent amplitudes of the two states $|\Psi_a\rangle$ and $|\Psi_b\rangle$, respectively, in the total wave function

$$|\Psi\rangle = a(t)|\Psi_a\rangle + b(t)|\Psi_b\rangle . \tag{3}$$

The equation of motion is

$$\frac{\partial}{\partial t}\rho(t)=(i\hbar)^{-1}[\mathcal{H}, \rho(t)], \tag{4}$$

where

$$\mathcal{H}=\begin{bmatrix} E_a & V(t) \\ V^*(t) & E_b \end{bmatrix}, \quad V(t)=\langle\Psi_a|-e\vec{\mathbf{r}}\cdot\vec{\mathbf{E}}(z, t)|\Psi_b\rangle , \tag{5}$$

with E_a and E_b the respective energies of the states $|\Psi_a\rangle$ and $|\Psi_b\rangle$, and $E_b-E_a=\hbar\omega$. Writing Eq. (4) out, and letting $[\rho_{bb}(t)-\rho_{aa}(t)]=\Delta\rho(t)$, we obtain

$$\frac{\partial}{\partial t}\rho_{ab}(t)=i\omega(t)\rho_{ab}(t)+(i\hbar)^{-1}V(t)\,\Delta\rho(t)-\frac{\rho_{ab}(t)}{T_2'}, \tag{6a}$$

$$\frac{\partial}{\partial t}\rho_{ba}(t)=\frac{\partial}{\partial t}\rho_{ab}^*(t), \tag{6b}$$

$$\frac{\partial}{\partial t}\Delta\rho(t)=2(i\hbar)^{-1}[V^*(t)\rho_{ab}(t)-V(t)\rho_{ba}(t)]-\frac{\Delta\rho(t)+1}{T_1'}, \tag{6c}$$

where in (6a) we have added the phenomenological damping term for the off-diagonal elements to account for the broadening due to dephasing collisions,[11] and in (6c) we have added a term characterized by time T_1' to account for the decay of the excited-state population due to collisions or radiative decay. Note that in (6a) the resonant frequency ω is considered a function of time as a result of the velocity-changing collisions. In the case of no collisions, $\omega(t)$ is a constant and is simply equal to the Doppler-shifted frequency of the atoms in the particular velocity subset under consideration.

The solution to Eq. (6a) is

$$\rho_{ab}(t)=[i\hbar\mu(t)]^{-1}\int_0^t dt'\,\mu(t')V(t')\Delta\rho(t'), \tag{7}$$

where

$$\mu(t')=\exp\left[\int_0^{t'}\left(\frac{1}{T_2'}-i\omega(t'')\right)dt''\right]. \tag{8}$$

Equation (6c) becomes

$$\frac{\partial}{\partial t}\Delta\rho(t)=-2\hbar^{-2}\Big(V(t)[\mu^*(t)]^{-1}$$

$$\times\int_0^t dt'\,\mu^*(t')\,V^*(t')\,\Delta\rho(t')+\text{c. c.}\Big)$$

$$-\frac{\Delta\rho(t)+1}{T_1'}\quad . \tag{9}$$

Now recall that

$$V(t)=\tfrac{1}{2}\textstyle\sum_i p_i E_i(t)\{\exp[i(-k_i z+\omega_i t)]+\text{c. c.}\}, \tag{10}$$

where

$$p_i=-e\langle\Psi_a|\vec{r}\cdot\hat{\epsilon}_i|\Psi_b\rangle\ , \tag{11}$$

so that for $z=0$ we get

$$\frac{\partial}{\partial t}\Delta\rho(t)=-\sum_{i,j}(2\hbar^2)^{-1}\Big\{p_i p_j^* E_i(t)\int_0^t dt' E_j(t')\,\Delta\rho(t')\times\exp\Big(-\frac{t-t'}{T_2'}\Big)\exp\Big[\int_0^t -i\Delta\omega_i(t'')dt''\Big]\times\exp\Big[\int_0^{t'} i\Delta\omega_j(t'')dt''\Big]+\text{c. c.}\Big\}-\frac{\Delta\rho(t)+1}{T_1'}\ , \tag{12}$$

where $\Delta\omega_i(t'')=\omega(t'')-\omega_i$. Note that terms like

$$\exp\{\textstyle\int_0^t i[\omega(t'')+\omega_i]dt''\}$$

have been dropped since they average to zero on the time scale we are interested in.

To evaluate the effect of the cross terms $i\neq j$ we write Eq. (12) as

$$\frac{\partial}{\partial t}\Delta\rho(t)=-\sum_{i,j}(2\hbar^2)^{-1}\Big[p_i p_j^* E_i(t)\int_0^t dt'\,E_j(t')\Delta\rho(t')\times\exp\Big(-\frac{t-t'}{T_2'}\Big)\exp\Big(i\int_t^{t'}\Delta\omega_j(t'')dt''\Big)\times\exp(i\omega_{ij}t)+\text{c. c.}\Big]-\frac{\Delta\rho(t)+1}{T_1'}\ , \tag{13}$$

where $\omega_{ij}=\omega_i-\omega_j$. The cross term $\exp(i\omega_{ij}t)$ will contribute only for times on the order of $(\omega_{ij})^{-1}$ that can at most be $(\Delta\Omega)^{-1}$, the inverse of the mode spacing. It can be seen from (13) that if $\Delta\rho$ and $E(t)$ can be considered constant over times $\sim(\Delta\Omega)^{-1}$ and if T_2' is short compared to the laser-pulse length, then the contribution of the cross terms will average to zero. Ignoring the cross terms means that we only consider the photon flux averaged over times $\sim(\Delta\Omega)^{-1}$, and not the distribution over shorter times. These considerations hold for both mode-locked and random-phase systems. We will only consider cases where cross terms can be dropped.

Dropping the cross terms, we can rewrite Eq. (13) as

$$\frac{\partial}{\partial t}\Delta\rho(t)=-\sum_i(2\hbar^2)^{-1}|p_i|^2E_i(t)\int_0^t dt'\,E_i(t')\Delta\rho(t')\times\exp\Big(-\frac{t-t'}{T_2'}\Big)\Big[\exp\Big(i\int_t^{t'}\Delta\omega_i(t'')dt''\Big)+\text{c.c}\Big]-\frac{\Delta\rho(t)+1}{T_1'}\ . \tag{14}$$

III. EFFECT OF MOMENTUM-TRANSFER COLLISIONS

In Eq. (14)

$$\Delta\omega_i(t'')=\omega(t'')-\omega_i=\Delta\omega_{0i}+\dot{z}(t'')c^{-1}\omega_0,$$

where $\Delta\omega_{0i}=\omega_0-\omega_i$ is the resonance term for an atom at rest, and

$$\dot{z}(t'')c^{-1}\omega_0=2\pi\lambda^{-1}\dot{z}(t'')$$

is the Doppler shift for an atom moving with velocity $\dot{z}(t'')$ and λ is the resonant wavelength in the atom's rest frame. To evaluate the term

$$\Delta\rho(t')\exp[i\textstyle\int_t^{t'}\Delta\omega_i(t'')dt''],$$

we restrict ourselves to the three previously mentioned cases. In the first we have no velocity-changing collisions during the entire interaction so that $\Delta\omega_i(t'')$ is a constant for atoms moving with a given velocity; in the second and third we require the rate of change of velocities be sufficiently fast to assure that the population distribution is essentially the same for all velocity subsets of the gas. Within this latter restriction, the second and third cases will be shown to distinguish between the fast and slow rates of change of velocities compared to the rate at which atoms change relative phase, which is given by $1/T_2'+(\dot{z}_0/c)\omega_0$, where $\dot{z}_0$ is the root mean square of the velocity distribution in the gas. The term $1/T_2'$ gives the rate of randomization of phase due to collisions, while $(\dot{z}_0/c)\omega_0$ gives the shift of phase between atoms due to Doppler-shifted resonance frequencies. For $(\dot{z}_0/c)\omega_0\gg 1/T_2'$, we will see that the second case corresponds to a mean free path between velocity-changing collisions, that is short compared to the wavelength for the transition while case three has a long mean free path compared to the wavelength.

Case 1: No Velocity-Changing Collisions

In this case all atoms maintain their velocity throughout the entire interaction so that the resonant frequency is a constant for atoms in a particular velocity subset. Equation (14) becomes

$$\frac{\partial}{\partial t}\Delta\rho(t)=-\sum_i\hbar^{-2}|p_i|^2E_i(t)\int_0^t dt'\,E_i(t')\Delta\rho(t')\times\exp\Big(-\frac{t-t'}{T_2'}\Big)\cos[(t-t')\Delta\omega_i]-\frac{\Delta\rho(t)+1}{T_1'}\ . \tag{15}$$

At this point we assume that both $E_i(t)$ and $\Delta\rho(t)$ are essentially constant over times $\sim T_2'$, so that the damping term $\exp[-(t-t')/T_2']$ dominates the integral, and we can wite Eq. (15) as

$$\frac{\partial}{\partial t}\Delta\rho(t) = -\sum_i \hbar^{-2}|p_i|^2 E_i^2(t)\Delta\rho(t)\int_0^t dt' \cos[(t-t')\Delta\omega_i] \times \exp\left(-\frac{t-t'}{T_2'}\right) - \frac{\Delta\rho(t)+1}{T_1'} \quad . \quad (16)$$

Evaluating the time integral, we get

$$\frac{\partial}{\partial t}\Delta\rho(t) = -\sum_i \hbar^{-2}|p_i|^2 E_i^2(t)\Delta\rho(t)\left[\left(\frac{T_2'\cos[(t-t')\Delta\omega_i]}{1+(\Delta\omega_i T_2')^2} - \frac{(T_2')^2\Delta\omega_i \sin[(t-t')\Delta\omega_i]}{1+(\Delta\omega_i T_2')^2}\right) \times \exp\left(-\frac{t-t'}{T_2'}\right)\right]_{t'=0}^{t'=t} - \frac{\Delta\rho(t)+1}{T_1'} \quad . \quad (17)$$

Now let us assume that $e^{-t/T_2'} \approx 0$ for all but a negligible portion of the time that the laser is on, which is to say that the phase relaxation time T_2' is short compared to the laser-pulse length τ_0. Then we have

$$\frac{\partial}{\partial t}\Delta\rho(t) = -\sum_i \hbar^{-2}|p_i|^2 E_i^2(t)\Delta\rho(t)\frac{T_2'}{1+(\Delta\omega_i T_2')^2} - \frac{\Delta\rho(t)+1}{T_1'} \quad . \quad (18)$$

We can write Eq. (18) in the form

$$\frac{\partial}{\partial t}\Delta\rho(t) = -\sum_i 2\eta_i(t)\sigma_i(\omega)\Delta\rho(t) - \frac{\Delta\rho(t)+1}{T_1'} \quad , \quad (19)$$

by making the following observations. The flux of photons of energy $\hbar\omega_i \approx \hbar\omega_0$ in the ith mode is given by

$$\eta_i(t) = c(8\pi\hbar\omega_0)^{-1}E_i^2(t) \text{ photons cm}^{-2}\text{sec}^{-1}, \quad (20)$$

where ω_0 is the resonant frequency of an atom at rest. For the absorption of a photon of frequency ω_i by the gas, we can associate an atomic cross section

$$\sigma_i(\omega) = 2\pi e^2 f(mc)^{-1}\frac{T_2'}{1+[(\omega-\omega_i)T_2']^2} \quad , \quad (21)$$

where $|p_i|^2$ is related to the absorption oscillator strength f by $f = 2m\omega_0|p_i|^2(\hbar e^2)^{-1}$.[12] The factor of 2 is included in (19) to retain the cross section for photon absorption. Noting that $\Delta\rho = (N_b - N_a)/(N_b + N_a)$, where N_b is the population of the upper state and N_a is the population of the lower state, and that

$$\frac{\partial\eta}{\partial t} = -\frac{\partial N_b}{\partial t} = \frac{\partial N_a}{\partial t} \quad ,$$

we see that

$$\frac{N\partial\Delta\rho}{\partial t} = -2\frac{\partial\eta}{\partial t} \quad ,$$

so that

$$\frac{\partial\eta}{\partial t} = \sum_i \eta_i(t)N\sigma_i(\omega)\Delta\rho(t) - \frac{N[\Delta\rho(t)+1]}{2T_1'} \quad ,$$

where $N = N_a + N_b$.

For the case of no momentum-changing collisions, note that the absorption cross section, for atoms with a given velocity, is Lorentzian in character. Thus, our final general solution for the case of no momentum-changing collisions is

$$\Delta\rho(t) = [\gamma(\omega,t)]^{-1}\left(\Delta\rho(0) - \frac{1}{T_1'}\int_0^t \gamma(\omega,t')\,dt'\right) \quad , \quad (22)$$

where

$$\gamma(\omega,t) = \exp\left(\frac{1}{T_1'}\int_0^t [\textstyle\sum_i 2\eta_i(t')\sigma_i(\omega)T_1' + 1]\,dt'\right) \quad , \quad (23)$$

and $\Delta\rho(0)$ is the population difference at $t = 0$. If the atoms are in the ground state at $t = 0$ then $\Delta\rho(0) = -1$. Recall that $\eta_i(t)$ is the number of photons $\text{cm}^{-2}\text{sec}^{-1}$ in the ith mode of the light given by (20), and $\sigma_i(\omega)$ is the absorption cross section given by (21). T_1' is the relaxation time of the excited-state population, which in the absence of collisional depopulation is the spontaneous lifetime. Notice that because the excitation (22) is a nonlinear function of the cross section, the average excitation is obtained by averaging Eq. (22) over velocities with a given laser intensity and not by averaging the cross section given by Eq. (21).

There are two limits for which the solution to Eq. (22) can easily be evaluated: (a) *constant laser intensity* and (b) *no excited-state decay*. In limit (a) we assume the laser is constant in time. This limit is applicable when the risetime of the laser pulse is much shorter than both the laser pulse length τ_0 and the laser pumping time τ_p. We have $\eta_i(t) = \eta_i$ and the solution [Eq. (22)] reduces to

$$\Delta\rho(t) = \{\Delta\rho(0) + [\textstyle\sum_i 2\eta_i\sigma_i(\omega)T_1' + 1]^{-1}\} \times \exp\left(-[\textstyle\sum_i 2\eta_i\sigma_i(\omega)T_1' + 1]\frac{t}{T_1'}\right) - [\textstyle\sum_i 2\eta_i\sigma_i(\omega)T_1' + 1]^{-1} \quad , \quad (24)$$

so that for long light pulses $\Delta\rho$ goes exponentially to

$$-[\textstyle\sum_i 2\eta_i\sigma_i(\omega)T_1' + 1]^{-1} \quad .$$

We can see that here the laser pumping time τ_p is on the order of

$$T_1'/[\textstyle\sum_i 2\eta_i\sigma_i(\omega)\,T_1' + 1] \quad .$$

Equation (24) shows that the excited-state decay time T_1' prevents the population from becoming totally equalized unless T_1' is very large, as in limit (b).

In limit (b) we assume $T_1' \to \infty$ or, effectively,

that T_1' is much longer than the laser-pulse length τ_0, in which case the solution given by Eq. (22) reduces to

$$\Delta\rho(t) = \Delta\rho(0)\exp[-\textstyle\sum_i 2\sigma_i(\omega)\int_0^t dt'\,\eta_i(t')]\,, \quad (25)$$

and the solution goes exponentially to $\Delta\rho = 0$, which is the case of equal populations in the ground and excited states. The integral $\int_0^t \eta_i(t')dt'$ is just the total number of photons in the ith mode to have passed through the unit area of the sample in a time t since the laser pulse was initiated.

Cases 2 and 3: Redistribution of Velocities

In order to proceed to the second and third cases we require that the rate of change of velocities be high enough to keep the populations of all the velocity subsets equal. (This restriction will be explained below.) First, it would be useful to summarize some of the properties of the velocity distribution in a gas. We assume that the velocity changes are determined by a Markoff process, that the velocity distribution is invariant with time, and that if t and s are two times, then $\dot{z}(t)$ and $\dot{z}(s)$ have a bivariate Gaussian distribution. We are letting the mean $\langle\dot{z}(t)\rangle$ equal zero and the variance $\langle[\dot{z}(t)]^2\rangle$ equal $\dot{z}_0^2$, where the symbol $\langle\ \rangle$ represents the average over the probability distribution or the ensemble average. Let $\chi(\tau)$ be the correlation function

$$\chi(\tau) = \langle\dot{z}(t+\tau)\,\dot{z}(t)\rangle/\dot{z}_0^2\,.$$

Under these very general assumptions Doob[13] has shown that the following properties of $\dot{z}(t)$ and $z(t)$ hold. The conditional probability density for $\dot{z}\,(t+\tau)$ given $\dot{z}(t)$ is

$$P[\dot{z}(t+\tau)\,|\,\dot{z}(t)] = (2\pi)^{-1/2}\dot{z}_0^{-1}(1-\chi^2)^{-1/2} \times \exp\left(-\frac{1}{2}\frac{[\dot{z}(t+\tau)-\chi\dot{z}(t)]^2}{[1-\chi^2]\dot{z}_0^2}\right)\,, \quad (26)$$

where $\chi = \chi(\tau) = e^{-\beta|\tau|}$, with $\beta > 0$. It is also true that

$$\langle[\dot{z}(t+\tau)-\dot{z}(t)]^2\rangle = 2\dot{z}_0^2(1-e^{-\beta|\tau|}) \quad (27)$$

and $z(t+\tau) - z(t)$ has a Gaussian distribution with a variance $\sigma^2(\tau)$ given by

$$\sigma^2(\tau) = \langle[z(t+\tau)-z(t)]^2\rangle = (2\dot{z}_0^2/\beta^2)[e^{-\beta|\tau|}-1+\beta|\,\tau\,|]. \quad (28)$$

The gas is characterized by two physical parameters, $\dot{z}_0$ which determines the velocity distribution and β which determines the correlation time or the time it takes an atom to randomize its velocity. The two least certain of our physical assumptions are that the scattering is a Markovian process and that $\dot{z}(t)$ and $\dot{z}(s)$ have a bivariate Gaussian distribution; both assumptions must be defended for any particular case. For a discussion of the effect of collisions on the moments of the velocity distribution, the reader is referred to treatments of Brownian motion by Doob[13] and others.[14] The effect of the detailed collision process on the spectral line shape has also been studied recently, with special reference to gas lasers.[15,16]

Let us now return to Eq. (14) and consider the equation of motion for the ensemble average of $\Delta\rho(t)$:

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle = -\sum_i(2\hbar^2)^{-1}|p_i|^2E_i(t) \times\int_0^t dt'\,E_i(t')\exp\left(-\frac{(t-t')}{T_2'}\right) \times\Big[\exp[i(t-t')\Delta\omega_{0i}] \times\left\langle\Delta\rho(t')\exp\left(i\int_t^{t'}\frac{2\pi\dot{z}(t'')}{\lambda}\,dt''\right)\right\rangle + \text{c. c.}\Big] - \frac{\langle\Delta\rho(t)\rangle+1}{T_1'}\,. \quad (29)$$

We now would like to assume that $\Delta\rho(t')$ is uncorrelated with

$$\exp\left(i\int_t^{t'}\frac{2\pi\dot{z}(t'')}{\lambda}\,dt''\right),$$

so that the average of their products may be separated into the product of their averages. The requirement for this assumption can be seen by noting that $1/\beta$ is the characteristic time for the velocities to randomize as given by (26). If $1/\beta$ is much less than the time needed to pump the atoms, then the diffusion time through the various velocity subsets will be negligible compared to the time for the light to change $\Delta\rho(t)$. Therefore $\Delta\rho(t)$ will be the same for all velocity subsets and hence uncorrelated with the exponential term, so that

$$\left\langle\Delta\rho(t')\exp\left(i\int_t^{t'}\frac{2\pi\dot{z}(t'')}{\lambda}\,dt''\right)\right\rangle = \langle\Delta\rho(t')\rangle\left\langle\exp\left(i\int_t^{t'}\frac{2\pi\dot{z}(t'')}{\lambda}\,dt''\right)\right\rangle. \quad (30)$$

The time for pumping the atoms, which we have referred to as the laser-pumping time τ_p, is on the order of $\Delta\rho(\partial\Delta\rho/\partial t)^{-1}$. Thus, for (30) to hold, the requirement is

$$\beta\tau_p = \beta\Delta\rho\left(\frac{\partial\Delta\rho}{\partial t}\right)^{-1} \gg 1. \quad (31)$$

We discuss typical values of this quantity in Sec. IV.

For now, we assume (31) is satisfied. Note that

$$\left\langle\exp\left(i\int_t^{t'}\frac{2\pi\dot{z}(t'')}{\lambda}\,dt''\right)\right\rangle = \left\langle\exp\left(i\frac{2\pi}{\lambda}[z(t')-z(t)]\right)\right\rangle$$

and recall that $[2\pi/\lambda][z(t')-z(t)]$ has a Gaussian distribution with a variance

$$[2\pi\lambda^{-1}\sigma(t-t')]^2 = 2(\Delta\omega_D)^2\beta^{-2}(e^{-\beta|t-t'|}-1+\beta|t-t'|),$$

where $\Delta\omega_D = 2\pi\lambda^{-1}\dot{z}_0$. By using the Gaussian distribution one can easily show that

$$\left\langle \exp\left(i\frac{2\pi}{\lambda}[z(t')-z(t)]\right)\right\rangle = \exp\{-\tfrac{1}{2}[2\pi\lambda^{-1}\sigma(t-t')]^2\}\,. \tag{32}$$

We can now consider (32) for the second and third cases.

High rate of velocity-changing collisions (*case* 2). Using (32) we find that in (29) the integrand is significant as long as

$$\exp[-(t-t')/T_2']$$

and

$$\exp\{-\tfrac{1}{2}[2\pi\lambda^{-1}\sigma(t-t')]^2\}$$

are significant. Using the expression for the variance given above we see that if $\beta^2 \gg 2(\Delta\omega_D)^2$ and $\beta T_2' \gg 1$, then for most of the range over which the integrand in (29) contributes, $(t-t')\beta \gg 1$. We can neglect $e^{-(t-t')\beta}-1$ compared to $(t-t')\beta$ and obtain

$$\left\langle \exp\left(i\frac{2\pi}{\lambda}[z(t')-z(t)]\right)\right\rangle = \exp[-(t-t')(\Delta\omega_D)^2\beta^{-1}]\,, \tag{33}$$

so that (29) becomes

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle = -\sum_i \hbar^{-2}|p_i|^2 E_i(t)\int_0^t dt'\,E_i(t')\langle\Delta\rho(t')\rangle \times\exp\left[-\left(\frac{1}{T_2'}+\frac{(\Delta\omega_D)^2}{\beta}\right)(t-t')\right] \times\cos[(t-t')\Delta\omega_{0i}] - \frac{\langle\Delta\rho(t)\rangle+1}{T_1'}\,. \tag{34}$$

In this case of a very high collision rate, the Doppler broadening leads to a Lorentzian line shape with a width $(\Delta\omega_D)^2/\beta \ll \Delta\omega_D$. This is the collisional narrowing of Doppler-broadened lines predicted by Dicke[17] and observed with microwaves by Wittke and Dicke[18] and in the infrared by Rank and Wiggins.[19] The requirement for collisional narrowing is seen to be $\beta \gg \Delta\omega_D + 1/T_2'$. This condition cannot usually be satisfied for electric dipole transitions as discussed in Sec. IV. The term $\Delta\omega_D$ gives the dephasing rate of atoms due to the difference in their Doppler-shifted resonance frequency, while $1/T_2'$ gives the dephasing rate due to collisions. The requirement for collisional narrowing is that the collision rate be much faster than the total dephasing rate of the atoms. We might also note that $\Delta\omega_D = (\dot{z}_0/c)\omega_0 = 2\pi(\dot{z}_0/\lambda)$ and that $\dot{z}_0/\beta$ is the mean free path of an atom. For $\Delta\omega_D \gg 1/T_2'$ the requirement for collisional narrowing is $\dot{z}_0/\beta \ll \lambda/2\pi$.

To solve (34) we proceed from (15) for the case of no momentum-changing collisions replacing $1/T_2'$ by $1/T_2'+[(\Delta\omega_D)^2/\beta]$, $\Delta\omega_i$ by $\Delta\omega_{0i}$, and $\Delta\rho(t)$ by $\langle\Delta\rho(t)\rangle$. Therefore our solution is

$$\langle\Delta\rho(t)\rangle = [\gamma(t)]^{-1}\left(\langle\Delta\rho(0)\rangle - \frac{1}{T_1'}\int_0^t \gamma(t')\,dt'\right), \tag{35}$$

where

$$\gamma(t) = \exp\left(\frac{1}{T_1'}\int_0^t [\sum_i 2\eta_i(t')\sigma_i T_1' + 1]\,dt'\right)\,, \tag{36}$$

and $\eta_i(t')$ is given by (20). The absorption cross section is now given by

$$\sigma_i = 2\pi e^2 f(mc)^{-1}\left(\frac{1}{T_2'}+\frac{(\Delta\omega_D)^2}{\beta}\right)^{-1} \times\left[1+\left(\frac{\Delta\omega_{0i}}{1/T_2'+(\Delta\omega_D)^2/\beta}\right)^2\right]^{-1}. \tag{37}$$

The two limits (a) *constant laser intensity* and (b) *no excited-state decay* evaluated for the case of no momentum-changing collisions can be extended to the present case by using the two solutions given by Eqs. (24) and (25), and by replacing $\Delta\rho(t)$ by $\langle\Delta\rho(t)\rangle$ and $\sigma_i(\omega)$ by σ_i of (37).

Low rate of velocity-changing collisions (*case* 3). We now consider the case where $\beta[t-t']$ is always small but β is still large enough to satisfy (31). The former will be true if $2(\Delta\omega_D)^2/\beta^2 \gg 1$, so that

$$\exp[-(t-t')\tfrac{1}{2}\sigma^2(2\pi/\lambda)^2]$$

is negligible for large $(t-t')\beta$. It will also be true if $\beta T_2' \ll 1$, since in (29) the integral over t' only contributes for $(t-t') \lesssim T_2'$, making $(t-t')\beta \ll 1$. Physically this latter condition means that although the velocity-changing collision rate may be high compared to the Doppler width, it is still considerably less than the dephasing rate; in other words, the mean free path for loss of momentum is much longer than that for dephasing of the atom. In the case that $(t-t')\beta$ is always small we can let $e^{-(t-t')\beta}-1+(t-t')\beta \approx \frac{1}{2}(t-t')^2\beta$, and from (32) obtain

$$\left\langle \exp\left(i\frac{2\pi}{\lambda}[z(t')-z(t)]\right)\right\rangle = \exp[-\tfrac{1}{2}(t-t')^2(\Delta\omega_D)^2]\,, \tag{38}$$

and (29) becomes

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle = -\sum_i (2\hbar^2)^{-1}|p_i|^2 E_i(t)\int_0^t dt'\,E_i(t')\langle\Delta\rho(t')\rangle \times\left\{\exp\left[\left(i\Delta\omega_{0i}-\frac{1}{T_2'}\right)(t-t')\right] \times\exp[-\tfrac{1}{2}(t-t')^2(\Delta\omega_D)^2]\right.$$

$$+\text{c.c.}\Big\}-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}. \quad (39)$$

In the above equation, evaluation of the time integral is possible, if we write

$$\exp[-\tfrac{1}{2}(t-t')^2(\Delta\omega_D)^2]=(2\pi)^{-1/2}\int_{-\infty}^{\infty}d\omega g(\omega)\,e^{i(t-t')\omega}, \quad (40)$$

so that (39) becomes

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle$$

$$=-\sum_i\hbar^{-2}|p_i|^2E_i(t)(2\pi)^{-1/2}\int_0^t dt'\int_{-\infty}^{\infty}d\omega g(\omega)E_i(t')$$

$$\times\langle\Delta\rho(t')\rangle\exp\left(-\frac{t-t'}{T_2'}\right)$$

$$\times\cos[(\Delta\omega_{0i}+\omega)(t-t')]-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}. \quad (41)$$

Following steps very similar to those in going from Eqs. (16) to (18), we obtain

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle=-\sum_i\hbar^{-2}|p_i|^2E_i^2(t)(2\pi)^{-1/2}\langle\Delta\rho(t)\rangle$$

$$\times\int_{-\infty}^{\infty}d\omega g(\omega)\frac{T_2'}{1+[(\Delta\omega_{0i}+\omega)T_2']^2}$$

$$-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}. \quad (42)$$

Using (40) we can evaluate $g(\omega)$,

$$g(\omega)=(2\pi)^{-1/2}\int_{-\infty}^{\infty}d\tau\exp[-\tfrac{1}{2}(\Delta\omega_D)^2\tau^2]e^{-i\omega\tau}$$

$$=(\Delta\omega_D)^{-1}\exp\left(-\frac{\omega^2}{2(\Delta\omega_D)^2}\right), \quad (43)$$

so that (42) becomes

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle=-\sum_i\hbar^{-2}|p_i|^2E_i^2(t)(2\pi)^{-1/2}\langle\Delta\rho(t)\rangle\,T_2'$$

$$\times[\Delta\omega_D]^{-1}\int_{-\infty}^{\infty}d\omega\frac{\exp[-\omega^2/2(\Delta\omega_D)^2]}{1+[(\Delta\omega_{0i}+\omega)T_2']^2}$$

$$-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}. \quad (44)$$

We can rewrite (44) in terms of the Voigt integral $\Phi_i(x,\xi)$ for which numerical values are readily available[20]:

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle=-\sum_i\hbar^{-2}|p_i|^2E_i^2(t)\langle\Delta\rho(t)\rangle T_2'\,\Phi_i(x,\xi)$$

$$-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}, \quad (45)$$

where

$$\Phi_i(x,\xi)=(\xi^2\pi)^{-1/2}\int_{-\infty}^{\infty}dy\frac{\exp[-(x-y)^2/\xi^2]}{1+y^2}, \quad (46)$$

with

$$x=\Delta\omega_{0i}T_2',\quad y=(\Delta\omega_{0i}+\omega)T_2',\quad \xi=\sqrt{2}\Delta\omega_D T_2'. \quad (47)$$

Using Eq. (20) we can write (45) as

$$\frac{\partial}{\partial t}\langle\Delta\rho(t)\rangle=-\sum_i 2\eta_i(t)\sigma_i\langle\Delta\rho(t)\rangle-\frac{\langle\Delta\rho(t)\rangle+1}{T_1'}, \quad (48)$$

where $\eta_i(t)$ is the number of photons $\text{cm}^{-2}\text{sec}^{-1}$ as before, but now

$$\sigma_i=2\pi e^2f(mc)^{-1}T_2'\Phi_i(x,\xi). \quad (49)$$

We have written the dipole matrix element in terms of the absorption oscillator strength as in Eq. (21). The solution to (48) is given by (35) and (36) with the above value of σ_i replacing that given in Eq. (37). The limits (a) *constant laser intensity* and (b) *no excited-state decay* can be obtained from (24) and (25) by substituting $\langle\Delta\rho(t)\rangle$ for $\Delta\rho(t)$ and σ_i [Eq. (49)] for $\sigma_i(\omega)$.

Summary of Cases 1–3

We can summarize the equation of motion by noting that in all three of our cases the differential equation reduces to the form

$$\frac{\partial}{\partial t}A(t)=-\sum_i 2\eta_i(t)\sigma_iA(t)-\frac{A(t)+1}{T_1'}. \quad (50)$$

This is the rate equation for two-body interactions between atoms and photons with a flux $\eta_i(t)$ of photons, a cross section σ_i, a relaxation time T_1', and when $\eta_i(t)=0$, an equilibrium value $A=-1$. Equation (50) is a direct consequence of the fact that we have assumed that the phase relaxation time T_2' is short, so that $\Delta\rho(t)$ and $E_i(t)$ can be pulled out of the time integral, and the effects of phase coherence in the exciting light can be neglected—the coherent nature of the light becomes irrelevant.

For case 1 (no momentum-changing collisions) A denotes the excitation of atoms having a given velocity, and σ_i is the cross section between the atoms and laser photons of frequency ω_i. The absorption cross section has a Lorentzian profile which is to be expected for atoms in a particular velocity subset. The excitation is different for each subset and results in hole burning. To get the total number of excited atoms it is necessary to sum over all the velocity subsets after solving for the excitation.

For cases 2 and 3 the redistribution of velocities is sufficiently fast that there is no hole burning and A is the excitation averaged over the entire ensemble. For case 2, where the rate of momentum-changing collisions is higher than the rate of dephasing collisions, the effect of collisions is to constrain the movement of the atom and results in a narrowing of the absorption profile as has been discussed, for example, by Rautian and Sobel'man.[21] In this limit the profile is seen to be a Lorentzian.

The absorption profile in case 3 is the familiar Voigt profile obtained by the convolution of a Lorentzian profile with a Gaussian profile.

For a general solution of the cross section σ, we must know the time history of the velocity. For cases with intermediate collision rates between our limiting cases one would, in general, need to know the explicate behavior of the velocity of the atoms in the gas.

Let us consider our equations with the aim of finding the conditions of maximum efficiency in producing excited states. Comparing (18) and (44) we see that case 3 differs from the no-collision case in that the cross section in case 3 is an average over the various velocity subsets. In considering the total number of excited states for case 1, one has to average (22) over all velocity subsets. If the laser intensity is weak, then the exponential in (23) can be expanded and the average over velocities will yield the same value for σ_i as the value for case 3 given by (49). The average of $\Delta\rho(t)$ will go over to the value of $\langle \Delta\rho(t) \rangle$ obtained from (44). In the low-intensity case the excitation rate is insensitive to the collision rates in the gas. As soon as the laser intensity becomes large enough that $2\eta_i(t)\sigma_i(\omega)T_1' \approx 1$, the exponential can no longer be expanded and the average of $\Delta\rho$ in the no-collision case is less than the average of $\Delta\rho$ in case 3. Physically this means that at high laser intensity hole burning takes place and saturation begins to occur for some velocity subsets. As a result the incident photons are used less efficiently. In case 3 the pumping is spread over all atoms, and saturation does not occur until all the atoms are heavily pumped and, consequently, the pumping process is more efficient. It is also clear that if the width given by $1/T_2'$ is much greater than the mode spacing with equal intensity modes, there will be no hole burning.

Finally, we should make an extremely important point about the atomic state after excitation. If one waits a time $t \gg T_2'$ after the laser is off, the density matrix will be diagonal and the atomic state entirely defined by the populations. There will be no peculiarities of the atomic state due to coherent excitation, and any of the traditional experiments of spectroscopy or atomic physics can be performed with confidence that the nature of excitation will not affect the results.

IV. LABORATORY VALUES OF β AND T_2'

In this section we briefly indicate the typical range of parameters used in our calculations. For any given experiment the values of these parameters must of course be estimated for the particular case; here we attempt to convey only a feeling for their magnitudes.

The important parameters in our calculations are the excited-state lifetime T_1', the dephasing time T_2', the velocity coherence time $1/\beta$, the laser-pulse length τ_0, and the laser-pumping time τ_p. In general, little is gained in having the laser-pulse length much greater than T_1'. This is demonstrated by Eq. (24) in which one can see that the atomic system responds to a laser pulse with a time constant T_1' or shorter. Laser pulses have been reported with widths from $\sim 10^{-12}$ sec to continuous operation with phase coherence times for tunable lasers $\sim 10^{-7}$ sec. The typical range of T_1' in atomic systems is from $\sim 10^{-8}$ to ~ 1 sec.

The most important parameter in our treatment is T_2', since it establishes the conditions for describing the absorption process by phase insensitive photon-atom collisions; T_2' must be smaller than τ_p the laser-pumping time. The value of T_2' can be estimated using the typical values for pressure broadening of absorption spectra by assuming that van der Waals broadening is essentially a measure of T_2'.

A useful approximation has been given for van der Waals broadening of electric dipole transitions by hydrogen.[22,23] It is

$$1/T_2' = \Delta\omega \approx 20 C^{2/5} v^{3/5} N , \tag{51}$$

where

$$C \approx 1.6 \times 10^{-33} n^4 / Z^2 , \tag{52}$$

with v the velocity of the perturbers, N the number density of the perturbers, n the principal quantum number of the upper level of the transition, and $Z-1$ the charge of the ion undergoing the transition. For $Z=1$, $n=5$, $v = 2.5 \times 10^5$ cm sec^{-1}, and $N = 5 \times 10^{18}$ cm^{-3}, we obtain $T_2' \approx 10^{-11}$ sec. Measured values of C for several perturbers and atoms show that this approximation is the typical range for T_2'.[24,25] It is clear that with buffer gas pressures ranging between 100–500 Torr and temperatures in the 500–1000 °C range, for example, T_2' is much smaller than any atomic lifetime for optical transitions. Thus, we can satisfy the conditions of our theoretical treatment by using laser pulses $\gtrsim 10^{-9}$ sec.

At lower buffer-gas pressures resonance broadening may be important; in this case we make the following estimate assuming $1/T_2'$ is dominated by resonance broadening[23]:

$$1/T_2' = \Delta\omega \approx 4\pi^3 C N , \tag{53}$$

$$C \approx e^2 \lambda f (8\pi^2 mc)^{-1} . \tag{54}$$

Recalling that the spontaneous lifetime of an atom is given by

$$1/T_1' = (8\pi^2 e^2/mc)(g_a/g_b)(1/\lambda^2) f , \tag{55}$$

where g_a and g_b are the respective degeneracies of the lower and upper states of the transitions, we

see that

$$T_2'/T_1' = 16\pi(g_a/g_b)\,1/N\lambda^3 \quad , \tag{56}$$

so that if $N\lambda^3 \gg 1$ then $T_2' \ll T_1'$. For $\lambda = 5000$ Å this requires $N \gg 10^{13}$ cm^{-3}. At 300 °C this corresponds to a pressure of approximately 10^{-3} Torr.

If one is dealing with an ionized gas, the main dephasing process may be Stark broadening. The broadening for this process is difficult to estimate as it depends in detail on the transition involved and on the temperature and pressure.[26] For hydrogenic levels the Stark broadening can be very large and could easily dominate other types of broadening.

The second parameter of interest in our treatment is the velocity redistribution time as characterized by the parameter β. This value can be estimated by considering the typical atomic diameters to be $d \approx 3\times10^{-8}$ cm.[27] For a velocity $v = 2.5\times10^{5}$ cm sec^{-1} and $N = 5\times10^{18}$ cm^{-3}, the collision frequency is $\sqrt{2}vN\pi d^2 = 5\times10^{9}$ sec^{-1}. One must further consider the persistance of velocities after a collision.[27,28] Even if individual masses of the colliding atoms are the same, the velocity of an atom in a given direction after a collision will, on the average, have a component in the original direction that is ~ 0.4 times the original velocity; in other words there is a persistence of velocity in the original direction. If a helium buffer gas is used with much heavier calcium atoms, for example, the calcium atoms will average 0.88 of their original velocity after the collision. It is clear that β, the rate at which the velocities randomize, will in general be much slower than the collision rate. By comparing the collision frequency with the value for T_2' due to van der Waals broadening, we see that, in general, $\beta T_2' \ll 1$, so that case 3 rather than case 2 is applicable. To obtain collisional narrowing as in case 2, one must usually use quadrupole transitions or magnetic transitions for which T_2' may be very long.

It is also clear that for $1/\beta$ to be much shorter than the laser-pumping time τ_p, in order to make either case 2 or case 3 applicable, one should use an adequate pressure of a heavy buffer gas to reduce the persistence of velocities in the atoms under study. From Eq. (24) we see that if there is to be significant pumping, then $\tau_p \lesssim T_1'$. For allowed transitions with $T_1' \approx 10^{-8}$ sec we need a buffer-gas pressure on the order of an atmosphere to obtain $1/\beta \ll T_1'$. If $\tau_p < T_1'$ due to high laser power, then the pressure will have to be even higher to ensure that the velocity-changing rate β is sufficient to satisfy (31). If one is pumping weak transitions with long T_1' using a flashlamp-pumped laser, then the typical times of the experiment may be ~ 10^{-6} sec, in which case it is feasible to use buffer-gas pressures of 10–100 Torr.

To go to the opposite limit and operate with no velocity-changing collisions so that case 1 is applicable, it is necessary that $1/\beta$ be much longer than the time scale of the experiment. For a Q-spoiled ruby or Nd^{3+}: glass laser, typical pumping times are on the order of 10^{-8} sec. These times also characterize dye lasers pumped by Q-spoiled s systems. For velocities ~ 10^{5} cm sec^{-1} and densities of 10^{17} cm^{-3}, we find a collision frequency of 10^{7} sec^{-1}, so that if a light buffer gas is used to yield a high persistence of velocities, then case 1 should be applicable for a laser pulse of ~ 10^{-8} sec. For these parameters, van der Waals broadening gives $T_2' \approx 5\times10^{-10}$ sec, and the requirement for short T_2' is still reasonably well satisfied.

V. SUMMARY

In considering the interaction between a multimode laser and an atomic gas, we have found that as long as the dephasing time of the atomic system is sufficiently short, the interaction reduces to a two-body collision between the atoms and photons, where coherency effects do not occur. We have also shown that if after the excitation one waits for a time longer than the dephasing time, all memory of the method of excitation is lost, and experiments can be performed on the excited state without regard to the details of the excitation process.

Pumping is seen to be most efficient when the laser-pulse length is shorter than the lifetime of the excited state but long enough to allow redistribution of the excited atoms within the velocity space, which prevents hole burning. Expressions are derived for the degree of pumping under several conditions.

Finally, various laboratory values for the parameters introduced in the theory are discussed and their magnitudes estimated to demonstrate that the various cases calculated in this paper are valid for a wide range of typical laboratory conditions.

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APPENDIX: GLOSSARY OF PRINCIPAL TERMS

$a(t), b(t)$; amplitudes of wave functions: ground state, excited state.
β; rate of decay of correlation of velocities.
c; speed of light.
$\chi(\tau)$; correlation function of velocities.
e; absolute value of the charge on the electron.
E_a, E_b; energy of state $|\Psi_a\rangle$, $|\Psi_b\rangle$.

$\vec{E}(z,t)$; electric field of laser pulse.
$E_i(t)$; electric field amplitude of ith mode of laser.
$\hat{\epsilon}_i$; polarization of ith mode of laser.
$\eta_i(t)$; flux of photons in the ith mode of laser.
f; absorption oscillator strength.
g_a, g_b; degeneracies of state $|\Psi_a\rangle$, $|\Psi_b\rangle$.
$\mathcal{H}$; Hamiltonian.
k_i; wave number of ith mode of laser.
λ; resonant wavelength of an atom at rest in the laboratory frame.
m; mass of the electron.
N_a, N_b; population of state $|\Psi_a\rangle$, $|\Psi_b\rangle$.
N; number density of atoms or perturbers.
n; principal quantum number.
ω [or $\omega(t)$]; resonant frequency of the atoms in the laboratory frame.
ω_i; frequency of the ith mode of laser.
$\Delta\omega_i(t)$; $\omega(t) - \omega_i$.
ω_{ij}; $\omega_i - \omega_j$.
ω_0; resonant frequency of atom at rest in the laboratory frame.
$\Delta\omega_{0i}$; $\omega_0 - \omega_i$.
$\Delta\omega_0$; $\omega\dot{z}_0/c$.
$\Delta\omega$; linewidth due to collisional broadening.
$\Delta\Omega$; frequency spacing between adjacent modes of laser.
Ω; frequency linewidth of laser pulse.
p_i; electric dipole moment of atom.
$\Phi_i(x,\xi)$; Voigt integral.
x, y, ξ; variables in definition of Voigt integral.
$|\Psi_a\rangle$, $|\Psi_b\rangle$; energy eigenfunction for two-level atom.
$|\Psi\rangle$; total wave function of two-level atom.
$\rho(t)$; 2×2 density matrix.
ρ_{aa}, ρ_{bb} and ρ_{ba}, ρ_{ab}; elements of density matrix.
$\Delta\rho(t)$; $\rho_{bb} - \rho_{aa}$.
$\sigma_i(\omega)$; atomic cross section for absorption of photon of frequency ω_i by atoms at frequency ω.
σ_i; atomic cross section for absorption of photon of frequency ω_i by an atom.
$\sigma^2(\tau)$; variance of the distribution of diffusion distance of atoms.
T_1'; decay time of excited-state population.
T_2'; damping time of off-diagonal elements of density matrix.
τ_p; laser-pumping time.
τ_0; laser-pulse length.
$V(t)$; interaction operator of Hamiltonian.
v; velocity of perturbers.
$\dot{z}_0$; root mean square of velocity distribution of atoms.
$Z-1$; charge on ion.

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[1]B. I. Stepanov and A. N. Rubinov, Usp. Fiz. Nauk 95, 45 (1968) [Sov. Phys. Usp. 11, 304 (1968)].

[2]C. F. Dewey, Jr., in *Modern Optical Methods in Gas Dynamic Research* edited by D. S. Dosanjh (Plenum, New York, 1971).

[3]T. J. McIlrath, Appl. Phys. Letters 15, 41 (1969). This paper describes a preliminary experiment with Ca that verifies the general results of the theory. Details of the experiment and its relation to the theory will be published separately.

[4]E. W. Smith, J. Cooper, W. R. Chappell, and T. Dillon, J. Quant. Spectry. Radiative Transfer 11, 1567 (1971); P. R. Berman, Phys. Rev. A 5, 927 (1972); P. R. Berman and W. E. Lamb, Jr., *ibid.* 2, 2435 (1970); 4, 319 (1971).

[5]E. W. Smith, J. Cooper, W. R. Chappell, and T. Dillon, J. Quant. Spectry. Radiative Transfer 11, 1567 (1971).

[6]W. Feller, *Probability Theory and its Applications* (Wiley, London, 1950).

[7]R. H. Dicke, Phys. Rev. 93, 99 (1954).

[8]F. T. Arecchi and E. Courtens, Phys. Rev. A 2, 1730 (1970).

[9]S. L. McCall and E. L. Hahn, Phys. Rev. 183, 457 (1969).

[10]This is usually a very good approximation for short-pulsed lasers. For experiments with long laser pulses, where the atom may move into and out of the laser beam during the experiment, an appropriate time variation of the electric field would have to be included in $E_i(t)$ and would have to include the history of the velocity of the various atoms.

[11]The term $1/T_2'$ represents the effect of collisions in the impact regime and is introduced phenomenologically. Any imaginary component of $1/T_2'$ has the effect of adding a constant to the resonant frequency $\omega(t)$ and represents a level shift. We will assume that any such shift has been incorporated into the resonance frequency and assume $1/T_2'$ is real. The real part of $1/T_2'$ leads to a Lorentzian line shape as predicted by the impact approximation for line broadening. This approximation is adequate in neutral gases up to several atmospheres pressure at laboratory temperatures, but at very high densities or at more modest densities with charged perturbers the duration of collisions becomes comparable to or longer than the time between collisions and the line shape deviates from a Lorentzian. In the latter case, Eq. (6a) will not accurately represent the equation of motion. For a discussion of the region of applicability of various line broadening approximations see, for example, D. Mihalas, *Steller Atmospheres* (Freeman, San Francisco, 1970).

[12]See, for example, H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957), Chap. IV.

[13]J. L. Doob, in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover, New York, 1954).

[14]See, for example, J. Keilson and J. E. Storer, Quart. J. Math. 10, 243 (1952); and *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover, New York, 1954).

[15]S. G. Rautian, Zh. Eksperim. i Teor. Fiz. 51, 1176 (1966) [Sov. Phys. JETP 24, 788 (1967)].

[16]P. W. Smith and T. Hänsch, Phys. Rev. Letters 26, 740 (1971).

[17]R. H. Dicke, Phys. Rev. 89, 472 (1953); J. I. Gersten and H. M. Foley, J. Opt. Soc. Am. 58, 933 (1968).
[18]J. P. Wittke and R. H. Dicke, Phys. Rev. 103, 620 (1956).
[19]D. H. Rank and T. A. Wiggins, J. Chem. Phys. 39, 1348 (1963).
[20]J. T. Davies and J. M. Vaughan, Astrophys. J. 137, 1302 (1963).
[21]S. G. Rautian and I. I. Sobel'man, Usp. Fiz. Nauk 90, 209 (1966) [Sov. Phys. Usp. 9, 701 (1967)].
[22]A. Unsöld, *Physik der Sternatmosphären*, 2nd ed. (Springer-Verlag, Berlin, 1955).
[23]J. T. Jefferies, *Spectral Line Formation* (Blaisdell, Waltham, Mass., 1968).
[24]A. Unsöld and V. Weidemann, in *Vistas in Astronomy* edited by A. Beer (Pergamon, London, 1955), Vol. I.
[25]N. P. Penkin and L. N. Shabanova, Opt. i Spektroskopiya 25, 795 (1968) [Opt. Spectry. USSR 25, 446 (1968)].
[26]H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill, New York, 1964).
[27]S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge U.P., Cambridge, England, 1970).
[28]J. Jeans, *An Introduction to the Kinetic Theory of Gases* (Cambridge U.P., Cambridge, England, 1940).

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Nuclear-Spin-Lattice Relaxation of Solid Hydrogen at Low Temperatures*

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We report systematic measurements of the nuclear-spin-lattice relaxation times T_1 in the ordered phase of solid hydrogen. The dependence of T_1 on temperature T and on the ortho content X is found to be described by $T_1 = AX^4T^{-1}e^{B/T}$, where $A = 1.0 \pm 0.3$ min, $B \simeq [0.4(1.8X - 1) + 0.24]$ °K for $X > 0.56$ and $B \simeq 0.24$ °K for $X < 0.56$. This functional dependence is in qualitative agreement with that calculated from the rotational correlation times of the quantum crystal lattice. The applied field was 75 kG and the temperature range investigated was 0.075 to 1.5 °K.

I. INTRODUCTION

The quantum properties of solid mixtures of ortho-para hydrogen have received considerable attention in recent years both experimentally and theoretically. For ortho concentrations greater than 60% these properties lead to a singularity in the specific heat[1-4] and a change in the profile of the NMR absorption line.[5-7] It is now generally accepted that these are associated with the cooperative ordering of the rotational degrees of freedom arising from their collective molecular quadrupolar interactions.

NMR affords a direct means of investigating the rotational excitations arising from these interactions. First, as a consequence of the quenching of the rotational molecular motion the intramolecular magnetic dipole-dipole interaction does not average to zero, and this results in a fine structure which is a direct measure of the orientational order parameter.[8] Second, thermal equilibrium between the nuclear spins and the quantum-crystal lattice is established by the modulation of the intramolecular magnetic dipolar couplings. The correlation times of these thermal fluctuations, given by the rapid transitions between the orientational states, determine the nuclear-spin-lattice relaxation times.

Following a brief theoretical survey in Sec. II, the experimental method is outlined in Sec. III and the results are discussed in Sec. IV. Section V summarizes the conclusions that can be drawn from the results.

II. THEORETICAL SURVEY

A. Molecular Orientational Ordering

X-ray diffraction[9,10] has shown that a crystal lattice change occurs at a temperature close to that of the order-disorder transition. Studies of neutron diffraction[11] and ir absorption spectra[12] have shown that the low-temperature face-centered cubic (fcc) phase is represented by the space group Pa^3 in agreement with the classical calculations of Felsteiner.[13] This space group is a fcc lattice with four distinct simple cubic sublattices such that in each sublattice the equilibrium direction of the molecules is aligned along a threefold axis, one of the body diagonals of the fcc lattice. The electric field at a given molecular site, due to the quadrupoles of its neighbors, has axial symmetry, thereby lifting the degeneracy of the $J = 1$ state. The states $J_z = \pm 1$ are separated from the ground state $J_z = 0$ by an energy gap Δ. One of the four body diagonals forms the quantization axis for each of the four sublattices for the intermolecular interactions.

The orientational ordering of solid hydrogen on