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Coupled ion pairs in solids under the influence of a coherent radiation field

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The coupled ion pairs were modeled by two coupled two-level systems. The resulting Bloch equations were derived by the density-matrix formalism. They were solved numerically for identical ions and for slightly detuned ions with identical wave functions as a first approximation to the problem of inhomogeneous line broadening in solids. The following results were found: (1) intrinsic optical bistability as a function of the applied laser field; (2) regions of stability, instability, and multistability for different detunings and couplings of the ions at different laser fields; (3) asymmetric shapes of the absorption lines with unstable regions; and (4) suppression of the photon echo due to the nonlinear chaotic dynamics of the coupled ions. Experimental evidence is given which supports the computer calculations. [S1050-2947(96)09810-1]

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I. INTRODUCTION

Coupled atoms or ions can behave quite differently in a radiation field as compared to the isolated species. Concerning the absorption and emission probabilities this fact was demonstrated by Dicke [1] introducing the concept of superradiance. The influence of ion-ion coupling on the photon echo was studied by Skinner, Andersen, and Fayer [2] using a model of a pair of weakly coupled two-level systems and including relaxation and energy transfer processes. The influence of purely electronic interactions on optical dephasing and photon echo for both diagonal and substitutional disorder in solids was treated by Root and Skinner [3]. In both latter papers the influence of the ion-ion interaction was treated in a perturbative way not taking into account the renormalization of the resonance frequency of the ions due to the excitation status of their neighbors they interact with. Because of the narrow homogeneous linewidth of the ions, especially at low temperatures, the renormalization of the resonance frequency can easily be of the order of the homogeneous linewidth or even much greater already for moderate ion-ion interactions (see Appendix). From this point of view drastic changes in the resonance response of coupled ions compared to single ones can be expected including strong nonlinearities. Hopf, Bowden, and Louisell [4] have been the first ones to demonstrate this fact. They could show that already the near-field coupling of the ionic transition dipoles can lead to an intrinsic optical bistability (IOB), i.e., a bistability without any external feedback. In a number of following papers [5–9] this concept has been developed further. In this sense one of the authors of this paper [10] could show that the interaction leading to IOB is not restricted to the electromagnetic near-field coupling only but can be of more general character. Furthermore, he could show that the diagonal and nondiagonal matrix elements of the ion-ion interaction can compensate one another completely or partly in their influence on the inversion-dependent renormalization of the resonance frequency. So all effects based on this renormalization including IOB can disappear for certain interactions and wave functions of the ions.

Unfortunately, there is not much experimental work done in this field. IOB which can be explained on the basis of the discussed renormalization was found only recently for $Cs_3Y_2Br_9$:Yb^{3+} [11].

The effect of the inversion-dependent renormalization of the resonance frequency and the IOB based on it has been discussed so far only in systems of identical two-level systems [4–10]. But in real doped solids the ions sit on sites with slightly different crystal fields. This fact gives rise to a slight detuning of the energy levels of the ions resulting in the well known inhomogeneous spectral line broadening. The question now arises how an ion pair behaves in a coherent radiation field as a function of mutual detuning and coupling. To answer this question we studied the dynamics of a pair of two-level systems in a classical electromagnetic radiation field by means of the density matrix formalism. To take into account the inhomogeneous line broadening, we assumed slightly different energy levels of the ions but assumed the wave functions and all other matrix elements to be identical.

In Sec. II we formulate the problem and set up the differential equations for the matrix elements of the density operator in a general form for two coupled different two-level systems. By a proper transformation we introduce the Bloch equations of the coupled pair and show how the resonance frequency and the Rabi frequency of the ions are changed by the ion-ion coupling: they become dependent on the current status of the other ion. The resulting system of Bloch equations cannot be solved anymore in an analytical form. In Sec. III we formulate the conditions for our numerical computer treatment of the problem for some characteristic couplings and detunings of the two ions. The calculations are made in relative units using the dephasing time and the homogeneous halfwidth (HWHM) of the unperturbed ions as the units of time and energy, respectively. Furthermore, the approximation for the inhomogeneous line broadening has been introduced as discussed above. In Sec. IV we discuss the results of the computer calculations concerning IOB, regions of stability and instability, spectral line shape, and quenching of the photon echo. Some experimental evidences supporting the theoretical results are presented in Sec. V. Section VI finally gives a discussion and summary of the results.

The parameters of the computer calculations are adapted to experiments with rare-earth and transition metal ions in

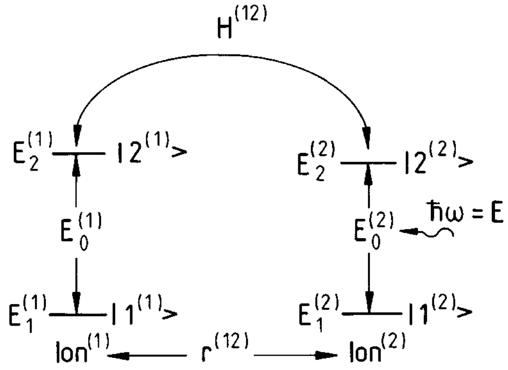

FIG. 1. Scheme of the two interacting ions in the coherent radiation field.

solids at low temperatures. In the Appendix we give a numerical example to our calculations for characteristic parameters of these ions.

II. FORMULATION OF THE PROBLEM

The physical situation is shown in Fig. 1. The Hamiltonian for the two ions (1) and (2) has the form

$$H = H_0^{(1)} + H_0^{(2)} + H^{(12)} + H_r^{(1)} + H_r^{(2)}. \tag{1}$$

The first two terms are the Hamiltonians for the unperturbed ions with the two energy values $E_1^{(i)}$ and $E_2^{(i)}$ belonging to the wave functions $|1^{(i)}\rangle$ and $|2^{(i)}\rangle$, $i=1,2$. $H^{(12)}$ represents the interaction between the two ions. For reasons of mathematical simplicity we assume that it factorizes into two single-ion factors:

$$H^{(12)} = h^{(1)} h^{(2)}. \tag{2}$$

Physically, this is not a real restriction, because the interaction can usually be represented by products of spin or multipole operators.

The last two terms of Eq. (1) represent the interaction of the two ions with the radiation field. We take them in the usual dipole approximation:

$$H_r^{(i)} = \vec{E}(\vec{r}^{(i)},t)\vec{p}^{(i)}. \tag{3}$$

The first factor represents the electric field vector of the incident classical radiation field at the positions $\vec{r}^{(i)}$ of the ions (1) or (2). The second one is the electric transition dipole moment between the two states $|1^{(i)}\rangle$ and $|2^{(i)}\rangle$. Because the distance $\vec{r}^{(1,2)}$ between the interacting ions is usually small as compared to the wavelength of the radiation λ, the phase of the electrical field can be chosen identical for both ions:

$$\vec{E}(\vec{r}^{(i)},t) = \vec{E}(t) = \tfrac{1}{2}\vec{\xi}(t)(\exp(-i\omega t) + \text{c.c.}). \tag{4}$$

$\vec{\xi}(t)$ means the slowly varying amplitude of the radiation field ($\dot{\xi}/\xi \ll \omega$) and ω its frequency. The calculations are analogous to [10] using the reduced density matrix formalism and the slow-varying-amplitude approximation. As in [10] we use for the off-diagonal elements of the reduced density matrix ρ the form

$$\rho_{12}^{(i)} = iR_{12}^{(i)}(t)\exp(-i\omega t), \tag{5}$$

where $R_{12}^{(i)}(t)$ means the slowly varying amplitude of the matrix element. For ion (2) the results of the calculations are the following differential equations:

$$\frac{d\rho_{22}^{(2)}}{dt} = \frac{1}{\hbar}\{-\tfrac{1}{2}\vec{\xi}\vec{p}^{(2)}(R_{12}^{(2)} + R_{21}^{(2)}) - ih_{12}^{(1)}h_{21}^{(2)}R_{21}^{(1)}R_{12}^{(2)} + ih_{21}^{(1)}h_{12}^{(2)}R_{12}^{(1)}R_{21}^{(2)}\} - \gamma_{22}^{(2)}\rho_{22}^{(2)}, \tag{6}$$

$$\frac{dR_{21}^{(2)}}{dt} = \frac{1}{\hbar}\{-i(E_0^{(2)} - E)R_{21}^{(2)} - i(h_{22}^{(2)} - h_{11}^{(2)})(h_{11}^{(1)}\rho_{11}^{(1)} + h_{22}^{(1)}\rho_{22}^{(1)})R_{21}^{(2)} + \tfrac{1}{2}(\rho_{22}^{(2)} - \rho_{11}^{(2)})(\vec{\xi}\vec{p}^{(2)} + 2ih_{12}^{(1)}h_{21}^{(2)}R_{21}^{(1)})\} - \gamma_{12}^{(2)}R_{21}^{(2)}, \tag{7}$$

$$\frac{d\rho_{11}^{(2)}}{dt} = -\frac{d\rho_{22}^{(2)}}{dt}, \tag{8}$$

$$\frac{dR_{12}^{(2)}}{dt} = \frac{dR_{21}^{(2)*}}{dt}. \tag{9}$$

$E_0^{(i)}$ is the resonance energy of the ions and E the quantum energy of the radiation field (Fig. 1). For ion (1) we get the same set of differential equations by interchanging the ion indices (1) and (2).

$\gamma_{22}^{(i)}$ and $\gamma_{12}^{(i)}$ represent the phenomenologically introduced relaxation rate of the population of the excited state and the dephasing rate, respectively, both for the single ions. As relaxations to a bath both are assumed to be exponential. For metastable states in solids both relaxations are generally dominated by different processes. Therefore they are not directly related with each other, and the loss of coherence is usually much faster than the decay of the population of the excited state. Thus $\gamma_{12}^{(i)}$ describes dominantly the phase relaxation of the ions.

Following Feynman, Vernon, and Hellwarth [12] the dynamics of a two-level system can be described by a "Bloch vector" with the three components

$$w^{(i)} = \rho_{22}^{(i)} - \rho_{11}^{(i)},$$

$$u^{(i)} = R_{21}^{(i)} + R_{12}^{(i)},$$

$$v^{(i)} = i(R_{21}^{(i)} - R_{12}^{(i)}). \tag{10}$$

For the computer calculations this transformation has the advantage that we have to deal for every ion with three real variables only. Furthermore, the resulting coupled Bloch equations can easily be compared with the well known Bloch equations for the uncoupled ions [13] and the alterations due to the ion-ion coupling show up directly. For ion (2) under the influence of the electromagnetic field and of ion (1) we get the following Bloch equations:

$$\frac{dw^{(2)}}{dt} = \frac{1}{\hbar}[-\tilde{\chi}^{(2)}(u^{(1)},v^{(1)})u^{(2)} + (au^{(1)} + bv^{(1)})v^{(2)}] - \gamma_{22}^{(2)}(w^{(2)} + 1),$$

$$\frac{du^{(2)}}{dt}=\frac{1}{\hbar}\,[\tilde{\chi}^{(2)}(u^{(1)},v^{(1)})w^{(2)}-\tilde{\delta}^{(2)}(w^{(1)})v^{(2)}]-\gamma_{12}^{(2)}u^{(2)},$$

$$\frac{dv^{(2)}}{dt}=\frac{1}{\hbar}\,[\tilde{\delta}^{(2)}(w^{(1)})u^{(2)}-(au^{(1)}+bv^{(1)})w^{(2)}]-\gamma_{12}^{(2)}v^{(2)}, \tag{11}$$

with the following abbreviations.

(1) The detuning $\tilde{\delta}$ between the photon energy of the electromagnetic field $E=\hbar\omega$ and the renormalized resonance energy of the coupled ions

$$\tilde{\delta}^{(2)}(w^{(1)})=\delta^{(2)}+\tfrac{1}{2}(h_{22}^{(2)}-h_{11}^{(2)})(h_{22}^{(1)}-h_{11}^{(1)})w^{(1)}. \tag{12}$$

The first term δ contains the basic detuning and a constant additional shift due to the ion-ion coupling

$$\delta^{(2)}=(E_0^{(2)}-E)+\tfrac{1}{2}(h_{22}^{(1)}+h_{11}^{(1)})(h_{22}^{(2)}-h_{11}^{(2)}). \tag{13}$$

The second term represents a detuning which depends on the inversion w of the other ion. In both cases the renormalization depends only on the diagonal matrix elements of the interaction Hamiltonians $h^{(1)}$ and $h^{(2)}$.

(2) The renormalized Rabi frequency

$$\tilde{\chi}^{(2)}(u^{(1)},v^{(1)})=\vec{\xi}\vec{p}^{(2)}+av^{(1)}-bu^{(1)}, \tag{14}$$

with the abbreviations

$$b=\mathrm{Im}\{h_{12}^{(1)}\}\mathrm{Re}\{h_{12}^{(2)}\}-\mathrm{Re}\{h_{12}^{(1)}\}\mathrm{Im}\{h_{12}^{(2)}\},$$

$$a=\mathrm{Re}\{h_{12}^{(1)}\}\mathrm{Re}\{h_{12}^{(2)}\}+\mathrm{Im}\{h_{12}^{(1)}\}\mathrm{Im}\{h_{12}^{(2)}\}. \tag{15}$$

Thus the renormalization of the Rabi frequency depends only on the phase status of the other ion and on the off-diagonal matrix elements of the interaction Hamiltonians.

In addition to the renormalizations of the detuning and of the Rabi frequency, the coupling between the ions introduces into Eq. (11) another factor depending on the status of the partner ion. It is

$$(au^{(1)}+bv^{(1)}), \tag{16}$$

which connects the phase component $v^{(2)}$ with the time derivative of the inversion $w^{(2)}$ and vice versa.

The Bloch equations are, of course, symmetric in the ions (1) and (2). So the Bloch equations for ion (1) are given by Eq. (11) by interchanging the ion indices (1) and (2). In this sense the asymmetric parameter b [Eq. (15)] changes its sign. The full set of coupled Bloch equations for both ions is a complex nonlinear system of differential equations. It cannot be solved analytically. To get an idea about the physical behavior of such a system of two coupled two-level ions in a coherent radiation field, the differential equations were integrated numerically for a set of reasonable parameters.

III. NUMERICAL CALCULATIONS

To make a reasonable choice of the parameters for the numerical calculations, it is useful to discuss first the problem of inhomogeneous line broadening. For rare-earth ions at low temperatures the typical inhomogeneous linewidth due to variations in the crystal field is of the order of 10^{-1} cm^{-1} at transition energies of the order of 10^{4} cm^{-1}. So, the relative detunings between the rare-earth ions in the same electronic state are of the order of 10^{-5}. Let us assume that the relative variations of the other matrix elements and parameters are of the same order of magnitude, too. As long as these quantities enter the Bloch equations directly their variations can be neglected and their values can be assumed to be identical. This argument holds for the electric dipole moment, for the ion-ion interaction, and for the relaxation rates. So we can take

$$\vec{p}^{(1)}=\vec{p}^{(2)}=\vec{p},$$

$$h^{(1)}=h^{(2)}=h,$$

$$\gamma_{12}^{(1)}=\gamma_{12}^{(2)}=\gamma_{12},$$

$$\gamma_{22}^{(1)}=\gamma_{22}^{(2)}=\gamma_{22}. \tag{17}$$

The situation is different for the energies of the ions. They do not enter the Bloch equations explicitly but only via the detuning between the ions and the radiation field, $E_0^{(i)}-E$. As resonant systems the ions respond very sensitively to variations of the detuning of the order of the homogeneous linewidth. In solids this linewidth is primarily determined by the dephasing rate. At low temperatures the homogeneous linewidth is only of the order of 10^{-3} of the inhomogeneous one or even less. So, different ions in the same state may be detuned one from another by 10^{3} homogeneous linewidths or more. By these arguments it is clear that the differences in the energies of the ions due to the inhomogeneous crystal field have to be taken into account and the ion energies $E_0^{(i)}$ cannot be taken identical.

Next it is useful to rewrite the Bloch equations in relative units. This way the results of the computer calculations have a more general meaning and can be compared easier with real experiments. Looking at the physical processes and at the Bloch equations it is suggested to take the reciprocal dephasing rate as the unit of time and half of the homogeneous linewidth as the unit of energy. Denoting the relative units by a prime, we have for the time and the energies

$$t'=t\gamma_{12}, \quad \varepsilon'=\frac{\varepsilon}{\hbar\gamma_{12}}, \tag{18}$$

respectively.

There is some arbitrariness in the choice of the parameters of the ion-ion interaction. From experiment we know that for rare-earth ions the ion-ion interaction is of the order of the inhomogeneous linewidth, for the close pairs somewhat stronger [14]. So, we chose for our calculations the following interaction matrix:

$$\|h'\|=\begin{vmatrix} h'_{11} & h'_{12} \\ h'^{*}_{12} & h'_{22} \end{vmatrix}=\begin{vmatrix} -h'_{22} & h'_{12} \\ h'^{*}_{12} & h'_{22} \end{vmatrix}=\begin{vmatrix} 20 & 20+10i \\ 20-10i & -20 \end{vmatrix}. \tag{19}$$

The diagonal matrix elements were chosen to be equal by their absolute values but different in signs. This way we allow for different ion-ion interactions in the excited and in the ground states but avoid, for mathematical simplicity, a constant renormalization of the detuning. So, Eq. (13) reduces to

$$\delta' = E_0' - E'. \tag{20}$$

To get an idea about the relation of the chosen parameters to the experiment we give some characteristic numerical values in the Appendix.

Since in crystals doped with rare-earth and transition metal ions the transverse relaxation rate γ_{12} is usually much faster than the longitudinal one, γ_{22}, we took in all our following numerical calculations:

$$\gamma_{22}' = 10^{-2}\gamma_{12}'. \tag{21}$$

With the discussed simplifications and parameters the Bloch equations [Eqs. (11)–(15)] used for our computer calculations take the form

$$\frac{dw^{(2)}}{dt'} = -\tilde{\chi}^{(2)\prime}(v^{(1)})u^{(2)} + |h_{12}'|^2 u^{(1)} v^{(2)} - \gamma_{22}'(w^{(2)}+1),$$

$$\frac{du^{(2)}}{dt'} = \tilde{\chi}^{(2)\prime}(v^{(1)})w^{(2)} - \tilde{\delta}^{(2)\prime}(w^{(1)})v^{(2)} - u^{(2)},$$

$$\frac{dv^{(2)}}{dt'} = \tilde{\delta}^{(2)\prime}(w^{(1)})u^{(2)} - |h_{12}'|^2 u^{(1)} w^{(2)} - v^{(2)}. \tag{22}$$

The renormalized detuning and the renormalized Rabi frequency are given by

$$\tilde{\delta}^{(2)\prime}(w^{(1)}) = (E_0^{(2)\prime} - E') + 2|h_{22}'|^2 w^{(1)} \tag{23}$$

and

$$\tilde{\chi}^{(2)\prime}(v^{(1)}) = (\vec{\xi}\vec{p})' + |h_{12}'|^2 v^{(1)}, \tag{24}$$

respectively.

The Bloch equations for the ion (1) can be found by interchanging the ion indices (1) and (2) as before. The resulting system of Bloch equations for both ions was solved numerically for the inversions $w^{(1)}$ and $w^{(2)}$ as functions of the Rabi frequency of the uncoupled ions

$$\chi' = (\vec{\xi}\cdot\vec{p})'. \tag{25}$$

The numerical calculations were carried out by the damped Newton method. Because of the limited local convergence of this procedure a number of different starting values had to be taken to find the various possible solutions. The results were proved for stability by a linear stability analysis [15].

IV. NUMERICAL RESULTS

A. Stationary solutions

First, we want to discuss the stationary solutions for the inversion as a function of the Rabi frequency, i.e., of the applied electromagnetic field. Figure 2 shows the calculated diagrams for two identical coupled ions in a resonant electromagnetic field. The diagrams are given for three different couplings, off-diagonal, diagonal, and both together. As can be seen the diagrams are qualitatively identical and confirm the results of [10]. They show the characteristic behavior of a bistability: a stable increase of the inversion w from -1 up to about -0.5 and an unstable region with negative slope between $w \approx -0.5$ to 0 where the system becomes stable again. Increasing the Rabi frequency the inversion rises up to the first critical point at $w \approx -0.5$ where it jumps into saturation and stays there. Coming back the system stays saturated until it reaches the second or upper critical point from where the inversion drops down to almost -1. The Rabi frequencies for both critical points are quite different, so that safe optical switching is feasible. The switching time for this IOB can be expected to be of the order of the phase relaxation time γ_{12}^{-1}. This means that it can be quite fast and can be chosen suitable for applications by a proper choice of the temperature of the host lattice. The question which now arises is of course the question of the effect of inhomogeneous line broadening on the IOB, i.e., the question of how the system behaves if the ions are slightly detuned one from another. To answer this question we calculated the stationary solutions for the case that the ions are detuned symmetrically to both sides from the frequency of the electromagnetic field. The results are shown in Fig. 3. Already at small detunings of $\delta^{(i)\prime} = \pm 10$ we find for real off-diagonal coupling a strong

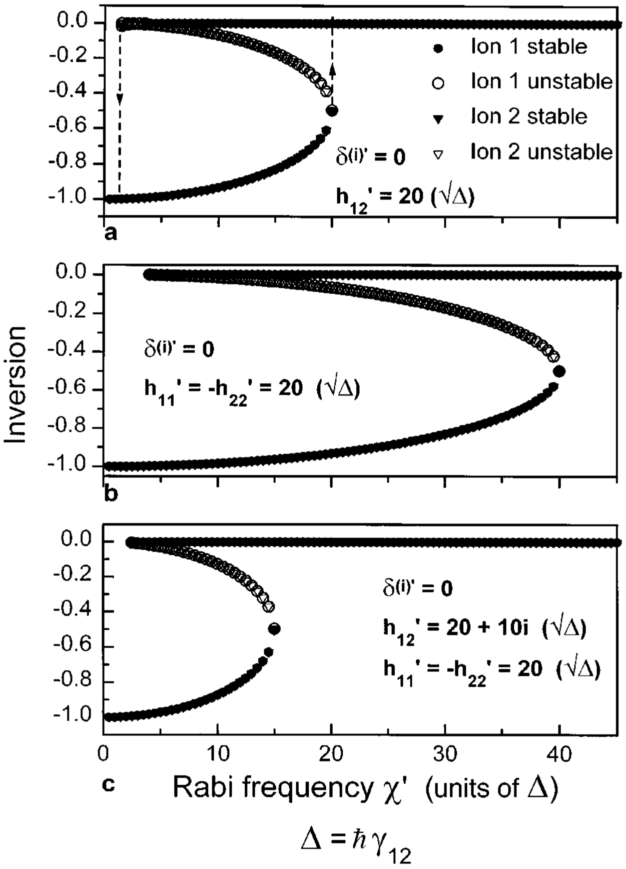

FIG. 2. Stationary solutions for the inversion as a function of the Rabi frequency χ' for identical ions ($E_0^{(1)\prime} = E_0^{(2)\prime}$) and no detuning ($\delta^{(i)\prime} = E_0^{(i)\prime} - E' = 0$). $\gamma_{12}' = 1$; $\gamma_{22}' = 10^{-2}$. (a) Real off-diagonal interaction. (b) Real diagonal interaction. (c) Complex off-diagonal and real diagonal interaction. Energies in relative units of $\hbar\gamma_{12} = \Delta$ (HWHM of the homogeneous linewidth).

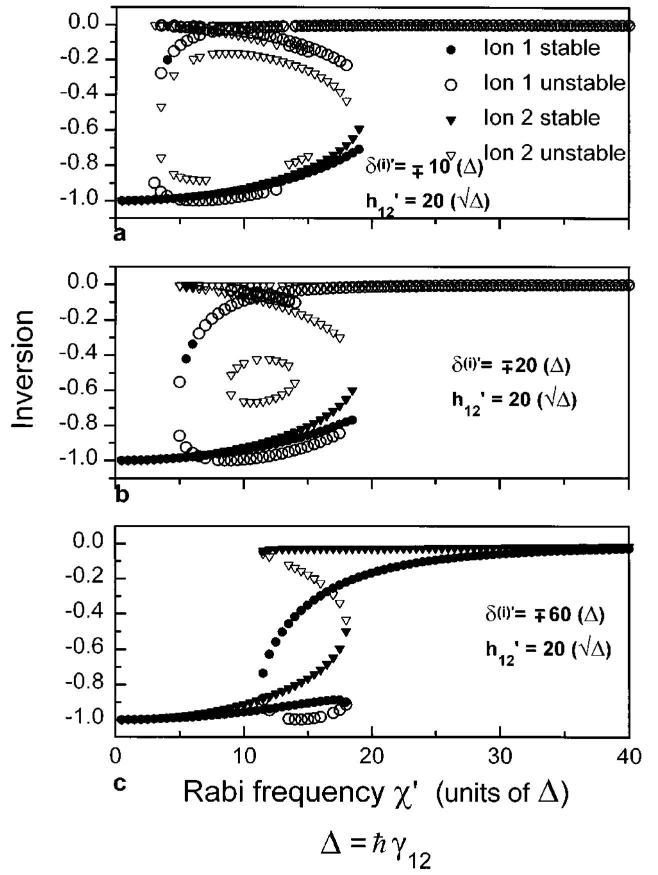

FIG. 3. Stationary solutions for the inversion of two ions with different resonance frequencies. The detuning $\delta^{(i)\prime}$ of the ions is symmetrical to the frequency of the electromagnetic field. Real off-diagonal interaction $h_{12}^{\prime}=20$, different detunings. Relative units $\Delta=\hbar\gamma_{12}$.

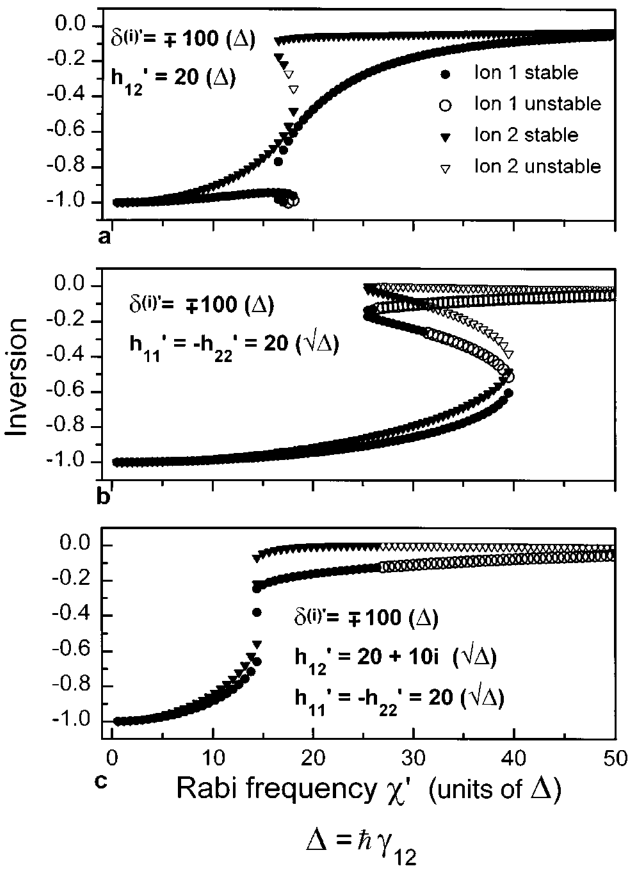

FIG. 4. Stationary solutions for the inversion of two ions with a detuning $\delta^{(i)\prime}=\pm 100$ symmetrical to the frequency of the electromagnetic field.

deviation from the case of identical ions. Stable solutions are found only for low Rabi frequencies up to the first critical point which is located almost at the same Rabi frequency as before. The rest of the solutions is unstable. In addition to the two open branches we find two loops of unstable solutions. If we go to higher detunings of $\delta^{(i)\prime}=\pm 20$ [Fig. 3(b)] the open branches do not change very much. Their critical points stay almost at the same Rabi frequencies. But the loops of unstable solutions reduce in size considerably and are easier to recognize. Again, the open branches are stable only up to the first critical point except for some small isolated regions. If we go further to $\delta^{(i)\prime}=\pm 60$ [Fig. 3(c)] the unstable loops disappear and the open branches become stable regions for higher Rabi frequencies again. So useful IOB cannot be found anymore at these detunings.

Figure 4 compares the three different couplings at a quite high detuning of $\delta^{(i)\prime}=\pm 100$. The coupling between the ions is obviously still strong enough to show coupled dynamics. In all three cases the Rabi frequencies of the first critical points can still be recognized as characteristic points of the inversion, whereas the second critical points are strongly shifted or have disappeared at all. For the off-diagonal interaction [Fig. 4(a)] the inversion is stable over almost the whole range of Rabi frequencies except for a small range around the first critical point. So an IOB does not exist anymore. Figure 4(b) shows the situation for diagonal coupling. Although the absolute value of the coupling is of the same magnitude as for the former off-diagonal case, the dependence of the inversion on the Rabi frequency looks quite different. It resembles more the behavior of the pair of identical ions demonstrating that the diagonal interaction destroys the IOB to a smaller degree than the off-diagonal one does. Nevertheless, the system is not useful for applications anymore because of its instability for Rabi frequencies just above the upper critical point. Figure 4(c) finally shows the case of mixed diagonal and off-diagonal coupling. The system does not show any tendency to IOB anymore. It has stable solutions for the inversion up to Rabi frequencies slightly higher than the first critical point. Then it becomes unstable. Calculations for still higher detunings show that the solutions for both ions get more and more stable and independent one from another as expected.

B. Spectral line shape

An interesting question is the question of the spectral line shape of a coupled ion pair in a coherent radiation field. Since the macroscopic scanning of the laser frequency is expected to be much slower than the relaxation rate of the microscopic system of the ions into equilibrium with the radiation field, we can calculate the spectral lineshape as a succession of steady-state solutions of the inversion as a function of the detuning δ' between the ions and the radia-

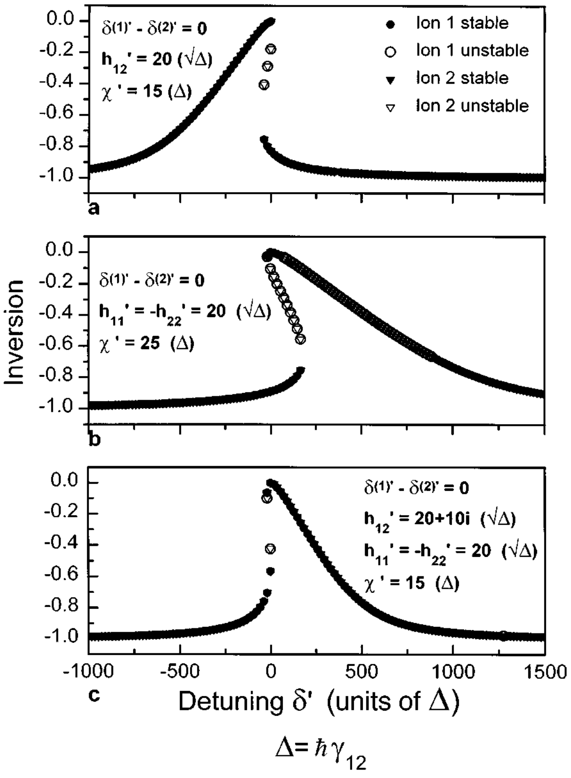

FIG. 5. Spectral line shape of a pair of coupled identical ions. $\delta' = E_0' - E'$.

tion field. Of course the spectral line shape of such a strongly nonlinear system will depend on the intensity of the incident radiation field. So we have the problem of a suitable choice of the Rabi frequency for which we want to do our calculations. Looking at the previous results given in Fig. 2 a Rabi frequency of $\chi' = 15$ seems to be reasonable for the off-diagonal and mixed couplings between the ions and $\chi' = 25$ for the diagonal one. This way the Rabi frequencies are located in the interesting region of strong nonlinearity. First, we want to discuss the line shape for a pair of identical ions. Figure 5(a) shows the inversion of the ions as a function of the detuning for real off-diagonal interaction. Starting from negative detunings $\delta' = E_0' - E'$ the inversion shows a quite flat increase over hundreds of homogeneous linewidths and reaches its maximum at zero detuning. Behind the maximum the inversion drops very steeply through an unstable region with even some backlash to negative detunings. After this the inversion becomes stable again and approaches its minimum value.

Figure 5(b) shows the spectral line shape for real diagonal coupling between the ions. As before the line shape is strongly asymmetric but inverted with the flat wing on the side of positive detunings. The backlash of the steep wing is even stronger. In contrast to the previous case both wings of the line have unstable solutions. Only for zero inversion, where the inversion-dependent detuning disappears [Eq. (23)], we have a small region of stability. The region of instability on the flat wing side covers a detuning range of about 800. This is just the maximum range of the inversion-dependent detuning as given by Eq. (23). Outside of this region the inversion is stable again.

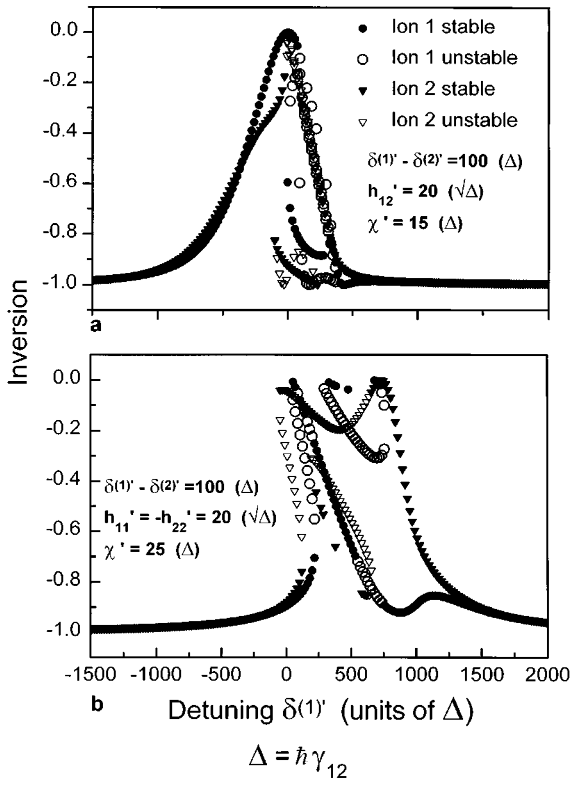

FIG. 6. Spectral line shapes of a pair of coupled detuned ions. The relative detuning is $\delta^{(1)'} - \delta^{(2)'} = 100$.

Figure 5(c) finally gives the line shape for mixed diagonal and off-diagonal coupling. Obviously the diagonal part dominates the line shape resulting in the flat wing on the side of positive detuning. But in contrast to pure diagonal coupling this wing shows no instability. The steep wing on the other side has again a region of instability, but it is smaller than in both cases before and has a smaller backlash, too. Obviously, the mixed coupling stabilizes the inversion to some degree and makes the line shape more symmetric.

All three cases show that in a coherent radiation field, even for identical ions, the ion-ion coupling can cause strong deviations from the line shape of the uncoupled ions. The lines become asymmetric with partly unstable regions. Furthermore, the halfwidth of the lines can be increased drastically and reach the order of the ion-ion coupling energies, in our case several hundred halfwidths of the single ions. The nonlinearity of the system allows the external field to drag the ''resonance response'' of the pair on the flat wing of the resonance line over quite a wide frequency region whereas at the other side of the line the nonlinearity causes a sharp cutoff at the inversion-independent resonance frequency.

As expected the line shape becomes more complicated if both ions have different resonance frequencies. The simplest case we get is for off-diagonal coupling of the ions. It is shown in Fig. 6(a) for a relative detuning of the ions of 100. For reasons of better understanding the inversions of both ions are given separately. The experimental line shape would be the sum of both. As can be seen, the general linewidth is broader than the ion-ion detuning. This means that the linewidth is again influenced by the ion-ion coupling. As for the identical pair [Fig. 5(a)] the line shape is asymmetric with the flat wing on the side of negative detunings. Whereas ion (1) has, as expected, a stable maximum inversion at $\delta^{(1)\prime}=0$ ion (2) has neither a stable nor an unstable maximum at $\delta^{(2)\prime}=0$, $\delta^{(1)\prime}=100$. It is obviously suppressed by the ion-ion coupling. The inversion for positive detunings consists of stable and unstable solutions. As a consequence the line shape becomes different scanning the laser frequency from negative to positive detunings or in the reverse way. The situation becomes more complicated for diagonal coupling as demonstrated in Fig. 6(b). Around its resonance frequency $\delta^{(1)\prime}=0$ ion (1) behaves similar to the case of identical ions [Fig. 5(b)], but its halfwidth is smaller and the resonance frequency is slightly shifted to positive detunings. Ion (2) behaves quite differently: it shows two inversion maxima. This fact nicely demonstrates the meaning of the inversion-dependent resonance frequency as given by Eq. (23). The resonance condition $\widetilde{\delta}^{(2)\prime}=0$ can have two extreme solutions for $\delta^{(2)\prime}$ differing by $2|h'_{22}|^2$ for the two limiting cases of the inversion $w^{(1)}=0$ and $w^{(1)}=-1$. With our choice of parameters this difference is 800 and reproduces nicely the difference between the two maxima found by computer calculations. So the two maxima can be explained by the inversion-dependent detuning of ion (2) by ion (1). Since the inversion of ion (2) is almost constant in the ''resonance region'' such a double maximum cannot be expected for ion (1) by the same arguments. This is in accordance with the computer calculations.

With our set of parameters the line shape for a mixed diagonal and off-diagonal interaction looks quite similar to the case of a pure diagonal one. As before ion (1) shows only one maximum of inversion and ion (2) two of them. But in the region between the two maxima the number of unstable solutions increases considerably.

C. Dynamics and photon echo

Exciting a two-level system with a coherent radiation field results in a transient behavior of the inversion which is called optical nutation. It is given by a damped oscillation of the inversion around its future steady state. The frequency of the nutation is given by [13]

$$\Omega' = \sqrt{\delta'^2+\chi'^2}. \tag{26}$$

In the case of two identical coupled ions the detuning δ' between the ions and the radiation field has to be replaced by its inversion dependent quantity $\widetilde{\delta}'$ [Eq. (12)] and the Rabi frequency χ' by its corresponding quantity $\widetilde{\chi}'$ [Eq. (14)]. So, both of these quantities are not constants of the dynamics anymore but depend on the current status of excitation. If in addition the ions are detuned one from another, the harmonic character of the oscillations gets lost more and more. Figure 7 shows an example for off-diagonal ion-ion coupling and symmetric detuning of the ions relative to the radiation field. The small asymmetry due to the relative detuning of the ions is already sufficient for a well pronounced asymmetry in the inversion dynamics of both ions. For higher couplings and relative detunings of the ions the modulation of the inversions of the ions gets smaller and faster and under certain conditions instabilities can occur.

Switching off the laser field leads to a free relaxation process of the coupled ions. For a symmetric ion pair with identical conditions at the end of the applied laser field the coupled Bloch equations (22) take the following form for both ions:

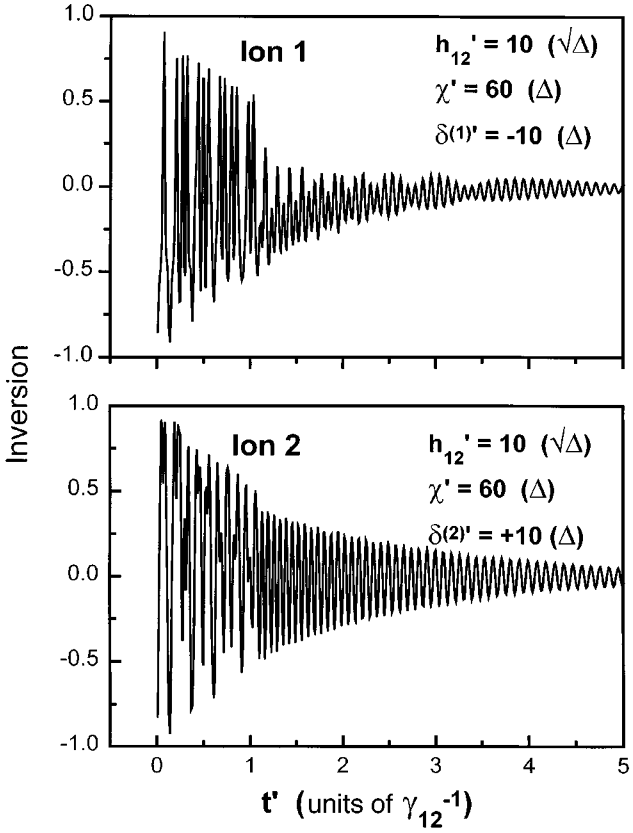

FIG. 7. Coherent transients of a weakly coupled and slightly detuned pair of two-level ions in a coherent radiation field. Time in relative units of γ_{12}^{-1}.

$$\frac{dw}{dt'} = -\gamma'_{22}(w+1),$$

$$\frac{du}{dt'} = -[\delta' + (2|h'_{22}|^2 - |h'_{12}|^2)w]v - u,$$

$$\frac{dv}{dt'} = [\delta' + (2|h'_{22}|^2 - |h'_{12}|^2)w]u - v. \tag{27}$$

They can be solved analytically. The inversion decays exponentially with the time constant of the single ions

$$w(t') = K\exp(-\gamma'_{22}t') - 1. \tag{28}$$

The constant K is given by the initial conditions at $t'=0$.

The phase components u and v show an oscillatory time dependence with a time-dependent frequency due to the ion-ion coupling. The solutions are

$$u(t') = e^{-t'}[u_0\cos\alpha(t') - v_0\sin\alpha(t')],$$

$$v(t') = e^{-t'}[u_0\sin\alpha(t') + v_0\cos\alpha(t')]. \tag{29}$$

The phase angle $\alpha(t')$ after switching off the laser field is given by

$$\alpha(t') = \delta' t' - (2|h'_{22}|^2 - |h'_{12}|^2)[t' + \gamma'^{-1}_{22}(w(t') - w(0))]. \tag{30}$$

The first term represents the standard single-ion dynamics with a fixed detuning δ'. The second term contains the corrections of the phase angle due to the ion-ion coupling and the inversion-dependent resonance frequency. Its first linear part in the square bracket can be interpreted as a constant correction of the detuning δ'. The second part is not linear in time anymore and describes the dependence of the phase angle on the inversion:

$$\Delta\alpha(t') = -(2|h'_{22}|^2 - |h'_{12}|^2)\gamma'^{-1}_{22}(w(t') - w(0)). \tag{31}$$

With our set of parameters it amounts to $\Delta\alpha(t') = -3\times10^4(w(t') - w(0))$. This gives an idea about the phase corrections due to the inversion dependence of the resonance frequency.

A combination of the transient behavior in an applied electromagnetic field and the following free relaxation after switching it off is the photon echo [13]. The photon echo is often used to probe the loss of coherence in an inhomogeneous ensemble of single two-level ions. It is generated by a sequence of two pulses of coherent radiation with a delay time τ between them. The first pulse called $\pi/2$ pulse is used to bring the ions into a state with inversion $w \cong 0$. In the following time of free relaxation the ions dephase one from another because of the inhomogeneous detuning between them. The second pulse called π pulse is of double pulse area and turns the phase components u to $-u$. As a consequence the dephased ions rephase in the following time of free relaxation with the same speed as they dephased before and after a second time interval τ all ions are in phase again. This means that the electric dipoles of the ions

$$\langle\vec{p}\rangle = \mathrm{Tr}(\rho\vec{p}) = \vec{p}u \tag{32}$$

are in phase, too, and emit a coherent radiation burst called the photon echo. Of course, the photon echo is produced only by those ions which did not undergo a phase destroying process. So, the intensity of the photon echo is a measure of conservation of coherence of the ions. These arguments hold for ions with identical resonance frequencies in the dephasing and rephasing process. But for coupled pairs of two-level ions we have to deal with a nonlinear system with renormalized resonance and Rabi frequencies which depend on the time-dependent status of the partner ion. So the question arises if we still can expect to find a photon echo and if it is still a measure of conservation of coherence of the ion pairs.

To answer this question we modeled the photon echo experiment by computer calculations. The calculations were made with pairs of identical ions. This is the optimum case for expecting a photon echo. The inhomogeneous line broadening was simulated by distributing 500 ion pairs over an energy range of 400 in a statistical way without any weighting to generate a specific inhomogeneous line shape. The applied laser field was simulated with a Rabi frequency $\chi' = 4000$ for both pulses. The laser frequency was located in the center of the ion frequencies. The length of the first pulse was taken to generate an inversion $w \cong 0$ at the center frequency. The second pulse of the laser field after the delay time τ was taken twice as long according to the theory of photon echo generation. The dynamics of the photon echo experiment was calculated for every ion pair separately. The results for the phase components u responsible for the light emission and for the inversion w were averaged over all 500 ion pairs. The computer calculations were done for a number of coupling parameters and delay times between the pulses using the classical Runge-Kutta method. To check the program, first the echo signal was calculated setting all interaction matrix elements equal to zero. The result is given in Fig. 8. It shows the increase of the mean inversion $\overline{w}$ from -1 to a small positive value due to the $\pi/2$ pulse. The π pulse is applied at $t' = \tau' = 0.5$ and can be recognized by the change of the small inversion to a negative value. The mean phase component $\overline{u}$ increases by the $\pi/2$ pulse to its maximum value. After the pulse the ions dephase and $\overline{u}$ shows small irregular fluctuations around the ideal value of zero due to the finite number of interfering ions taken for the calculations. At the time $t' = 2\tau' = 1$ we see the constructive interference of the rephased ions with the expected negative value for $\overline{u}$ which represents the photon echo. For longer times the fluctuations of $\overline{u}$ disappear due to the relaxation of the phase components of all ions to zero.

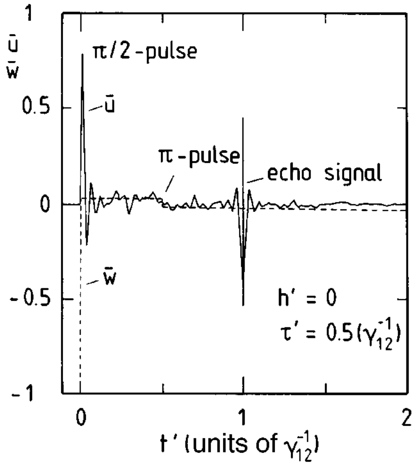

FIG. 8. Simulated echo signal for uncoupled ions. $\overline{w}$ and $\overline{u}$ are the mean values of the inversions and phase components of the chosen ensemble of ions, respectively. Time in relative units of γ_{12}^{-1}.

Figure 9(a) and 9(b) show the simulation of the same experiment, but now with off-diagonal and diagonal ion-ion coupling of the pairs, respectively. The positions of the expected echo signals are given. No echo signal exceeding the statistical fluctuations of $\overline{u}$ can be seen. A reduction of the pulse separation down to $\tau' = 0.2$ did not give any other results. Only for $\tau' = 0.1$ (Fig. 10) we found a small signal for $\overline{u}$ which exceeded the statistical fluctuations to some extend but had the wrong sign in the sense of the classical photon echo. The reason for this partial rephasing is not clear to us yet. Maybe, it is by accident. But in experiment it would show up as a weak echo signal.

Looking at Figs. 8–10, we see that the statistical fluctuations of the mean phase component $\overline{u}$ of the uncoupled ions and of the coupled ion pairs last over the same time period. They result from interferences of the individual phase com-

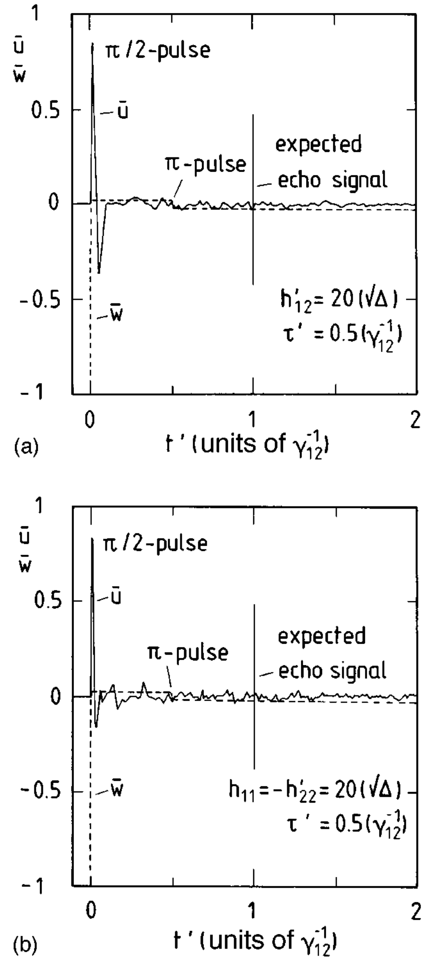

FIG. 9. Simulated photon echo experiment for pairs of identical ions. (a) Off-diagonal ion-ion interaction. (b) Diagonal ion-ion interaction.

ponents u. This means that the phase memory of the ions is not reduced or quenched by coupling them to pairs. The missing photon echo of the pairs on the time scale of coherence of the single ions simply means that the coupling between the ions in the pair leads to phase dynamics which cannot be rephased anymore by the usual photon echo procedure. This can be understood on the basis of the renormalization of the resonance and Rabi frequencies by the partner ion: The parts of the phase angle α [Eq. (30)] linear in time compensate during the dephasing and rephasing period of the photon echo experiment as in the case of uncoupled ions. But the inversion-dependent parts of the phase angles cannot compensate because the inversion w is different during both periods. The resulting uncompensated phase angle can be calculated by means of Eq. (31). It is given by the difference of the phase angles during both periods:

$$\Delta\alpha_1-\Delta\alpha_2=-(2|h'_{22}|^2-|h'_{12}|^2)\gamma_{22}^{-1}(w_1(\tau')-w_1(0)-w_2(2\tau')+w_2(\tau')). \qquad (33)$$

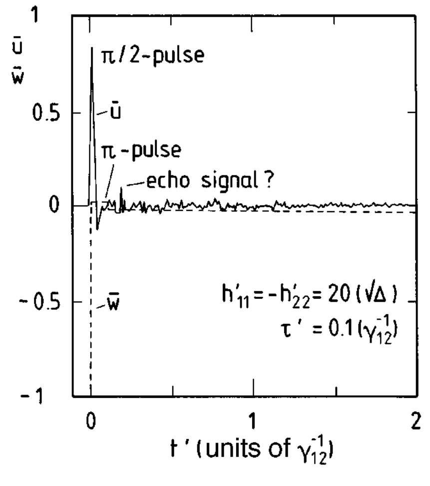

FIG. 10. Simulated photon echo experiment for pairs of identical ions at a short pulse delay. Diagonal ion-ion interaction.

Because of the inhomogeneous line broadening different pairs are excited to different degrees of inversion by the photon echo generating pulses. This results in different values of $\Delta\alpha_1-\Delta\alpha_2$. Even if the differences in the inversions are small from pair to pair, the great value of the prefactor, with our parameters 3×10^4, leads to strong relative statistical dephasings of the ion pairs and consequently to quenching of the photon echo as found by our computer simulations.

So, the photon echo experiment, even if it succeeds for short delay times, may not give a meaningful measure of the phase memory or dephasing time of the individual ion pairs.

V. EXPERIMENTAL EVIDENCES

The presented computer calculations were undertaken after we tried to do coherent-transient experiments on Pr^{3+} pairs in Pr^{3+}:LaF_3 without success. Although we could reproduce the known results for Pr^{3+} single ions in LaF_3 and $LaAlO_3$ [16,17], we could not find the corresponding signals for ion pairs. But negative results do not mean very much. Usually, they can have more than one explanation.

A better and more convincing experiment is demonstrated in Fig. 11. It shows the fluctuations of the fluorescence intensity of the ${}^1_aD_2\rightarrow{}^3_aH_4$ transition of a Pr^{3+} pair in LaF_3 at low temperature over a time interval of 600 sec. The fluorescence was excited by a tunable dye ring laser (Spectra Physics 380A) into the resonance level ${}^1_aD_2$ and into the higher crystal field component ${}^1_bD_2$. Single-mode operation and frequency stability of the laser were monitored by a high-resolution Fabry-Pérot interferometer. The experiment was done with ‘‘weakly’’ coupled Pr^{3+} pairs with their absorption lines in the central region of the inhomogeneously broadened transition ${}^3_aH_4\rightarrow{}^1_aD_2$ and ${}^3_aH_4\rightarrow{}^1_bD_2$. Tuning on a pair transition was accomplished by monitoring and optimizing the upconverted Pr^{3+} fluorescence from the higher ${}^3P_0$ level [14]. Upconversion by energy transfer means a process in which one ion in a doubly excited pair is transferred into a higher excited level on expense of the other one. The intensity of the upconverted fluorescence was quite weak. So it can be used as an indicator for a pair transition but with negligible influence on the basic pair dynamics.

Because of this tuning procedure one can expect that a considerable part of the measured ${}^1_aD_2$ fluorescence originates from the selected pair. Unfortunately, the crystallographic character of the pair cannot be given by its transition frequency having in mind the variety of pair transitions [14]

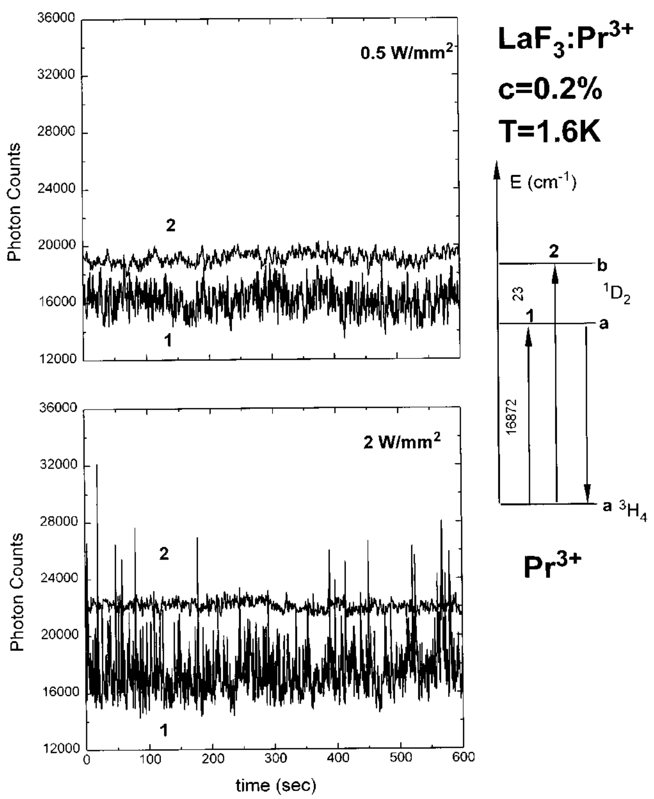

FIG. 11. Fluorescence of the transition ${}^1_aD_2 \rightarrow {}^3_aH_4$ of Pr^{3+} pairs in LaF$_3$ under single mode cw excitation into the levels ${}^1_aD_2$ (1) and ${}^1_bD_2$ (2) at two different power densities.

found in this relatively complicated crystal.

Already at excitation densities of 0.5 W/mm^2 the fluctuations of the ${}^1_aD_2$ fluorescence are remarkably stronger for direct excitation into the fluorescence level [(1) Fig. 11] than for indirect excitation into the higher crystal-field component (2). The mean statistical deviations from the average intensities are $\sigma_1=918$ and $\sigma_2=388$ photon counts, respectively, at almost the same intensity. The energy difference between the two crystal field components is 23 cm^{-1}. Due to one-phonon emission the lifetime and dephasing time of the upper crystal-field component are of the order of 1 ns or even less [18,19]. Therefore, even by coherent pumping into the upper crystal-field component ${}^1_bD_2$ the following spontaneous radiationless transition leads to an incoherent population of the fluorescent level ${}^1_aD_2$ and the fluctuations of the emitted fluorescence represent photon statistics and instrumental noise. The situation is different for direct coherent pumping of the level ${}^1_aD_2$. At lower temperatures the dephasing time of this level is dominated by one-phonon scattering processes between the two crystal-field components [18,19]. At 2 K it has a value of the order of several microseconds [16,17] and decreases with rising temperature according to the thermal population of resonant phonons of 23 cm^{-1}. So, at low temperatures coherence effects can be expected for ion pairs pumped directly by coherent radiation into the resonance level ${}^1_aD_2$. As was shown in Figs. 3 and 4 ion pairs can have unstable solutions for the inversion at higher Rabi frequencies, i.e., with increasing laser power density. So fluctuations of the inversion can be expected at higher power densities resulting in additional noise of the fluorescence. Indeed, the fluorescence of ${}^1_aD_2$ shows stronger fluctuations ($\sigma_a=918$) for direct coherent pumping than for indirect pumping ($\sigma_2=388$) already at 0.5 W/mm^2. The interpretation of the fluctuations as coherent pair effects is supported by the following additional facts.

(a) Increasing the laser power density to 2 W/mm^2 increases the mean statistical deviations for direct pumping to $\sigma_1=2092$ whereas the deviations for indirect pumping stay with $\sigma_2=419$ almost at the previous value. At this power level the fluctuations by direct pumping are so strong that they can easily be seen by the naked eye. This is in accordance with the expected increasing number of unstable pairs with increasing intensity.

(b) Increasing the temperature from 1.6 to 4.2 K decreases the mean statistical deviations for direct pumping to the value for indirect pumping in accordance with the strong decrease of the dephasing time of the metastable level ${}^1_aD_2$ [18,19].

(c) Detuning the laser within the inhomogeneous linewidth from a position with pair absorption to a position with single-ion absorption only, i.e., with no upconversion, reduces the fluctuations of the ${}^1_aD_2$ fluorescence for direct excitation to the same level as for indirect excitation.

Instabilities of a similar kind were already reported by Wannemacher and Heber in 1987 for ruby [20]. In this paper the cooperative emission of photons from doubly excited weakly coupled Cr^{3+} pairs has been reported. Taking the excitation spectra of the cooperative emission in the region of the *R* lines with a ring laser, strong fluctuations of the emission intensity have been detected. For Cr^{3+} concentrations $c \leqslant 0.3\%$ only fast fluctuations were detected which could be explained by the model calculations presented in Fig. 6. For higher concentrations asymmetric line shapes were found depending on the direction of scan. In addition a deep decrease of the absorption in the center of the inhomogeneous line was found with persistent character. This decrease, of course, cannot be explained by coherent pair instabilities and probably is due to other effects like two-step or cooperative ionization of Cr^{3+} ions [21].

VI. DISCUSSION AND SUMMARY

The ions of a coupled pair in a coherent radiation field are exposed to two phase-sensitive and nonlinear interactions, the interaction with the pair partner and with the electromagnetic field. The calculations have shown that if these interactions are of the same order of magnitude, instabilities and multistabilities can occur. If in addition the detuning of the two ions is of the same order of magnitude the tendency to these effects is generally increased. If the detunings are increased further the pairs of course tend to behave more and more like isolated ions. The general explanation of these effects is that the two phase-sensitive interactions are competing one with another and the ions can lock in either to the one or to the other interaction. If one of the interactions is dominating we get more or less stable or metastable regimes. Changing between the regimes or if none of both interactions can dominate leads to unstable situations with deterministic-chaotic changes of the status of the ions. Experimentally this can show up, e.g., by strong fluctuations of the fluorescence intensity under direct coherent excitation.

TABLE I. Comparison of our model parameters with the parameters of a characteristic ion with the following data: Resonance energy $E_0=20\,000$ cm^{-1} ($\lambda_0=0.5$ μm), radiative lifetime $\gamma_{22}^{-1}=1$ ms, and transverse relaxation time $\gamma_{12}^{-1}=10$ μs. Radiation field $s=0.1$ W/mm^2 ($\xi=7\times10^3$ V/mm). (t') and (ε') are the chosen relative units of time and energy.

	γ_{22}	$\gamma_{12}=10^2\ \gamma_{22}$	(t')	(ε')	$(\mathrm{Re}\ h_{12})^2=\lvert h_{ii}\rvert^2$	$\lvert h_{12}\rvert^2$	χ	p
Abs. units	10^3 s^{-1}	10^5 s^{-1}	10 μs	10^5 Hz 5.3×10^{-7} cm^{-1}	4×10^7 Hz 2.1×10^{-4} cm^{-1}	5×10^7 Hz 2.7×10^{-4} cm^{-1}	3.65 MHz	3.4×10^{-3} e Å
Rel. units	10^{-2}	1	1	1	400	500	36.5	

The free decay of the excited pairs is strongly influenced by the ion-ion interaction, too. The dynamics of the ions depends on the current status of the partner ion. The simplest documentation of this fact is the renormalized resonance frequency of the ions depending on the inversion of the other one. As a result of this dependence the photon echo becomes quenched. This quenching has nothing to do with a loss of phase memory. The pairs keep their phase memory on the time scale of the dephasing time of the uncoupled ions but the standard method of rephasing as used for photon echos of single ions does not work anymore due to renormalization.

An important question to be answered is if the IOB found for pairs of identical ions can be used for applications in photonics. The calculations give the answer in the way that the detuning of the two ions making up the pair should not exceed their homogeneous linewidth. In real crystals this means that the inhomogeneous linewidth should be smaller than the homogeneous one. This means very perfect crystals to reduce the inhomogeneous linewidth or a reduction of the dephasing time to increase the homogeneous linewidth. The last solution is not a very prospective one because short dephasing times mean high power densities for driving the IOB [10]. But, maybe, a combination of both ways can give an acceptable solution.

The last question to be discussed is the one why the fluorescence instabilities could be observed by us only for ‘‘weakly’’ coupled Pr^{3+} pairs with their absorptions near the center of the inhomogeneous line. The answer is simply that the interaction between the ions, the mutual detuning, and the Rabi frequency have to be of the same order of magnitude. Because of the small dipole moments of the involved transitions, which are parity forbidden in first approximation, the resulting Rabi frequencies are only small. Therefore coherence instabilities can be expected only from weakly coupled pairs in the center of the inhomogeneous line as found by us experimentally. For higher Rabi frequencies these instabilities should be observable for stronger coupled pairs, too.

APPENDIX

To relate the model calculations with reality it is useful to compare the model parameters with characteristic data of optical centers in solids, e.g., of rare-earth ions. This is done in Table I. The resonance energy of the characteristic ion was taken $E_0=20\,000$ cm^{-1} and the radiative lifetime of the excited state $\gamma_{22}^{-1}=1$ ms. From both data the transition dipole moment p can be evaluated. With this result the Rabi frequency χ was calculated for a power density of the radiation field of 0.1 W/mm^2. The dephasing rate γ_{12} and the interaction matrix elements were taken like in the model calculations.

An interesting role in the ion-ion interaction plays the near-field interaction of the coherently driven transition dipoles which also is called the local-field correction to the externally applied electromagnetic field. This interaction is always present independently of other interactions. For parallel dipoles it is given by

$$W^{(12)}=\frac{p^2}{4\pi\varepsilon_0\kappa(r^{(12)})^3}\,(1-3\cos^2\Theta^{(12)}). \tag{A1}$$

Here κ denotes the dielectric constant at the transition frequency and $\Theta^{(12)}$ the angle between the direction of the parallel dipoles and the distance vector $r^{(12)}$ between them. In stoichiometric crystals of higher symmetry the local-field energies to all neighbors cancel completely or almost completely for geometrical reasons. This is not the case in moderately doped crystals. Because of the strong dependence of the dipole-dipole interaction on distance, the interaction with the nearest neighbor ion is the dominating one and no significant cancellation by other ions can be expected. Thus the order of magnitude of the near-field interaction can be estimated knowing the transition dipole moment from the radiative lifetime and neglecting the directional dependence. Identifying the near-field interaction with the interaction of our model calculations we have

$$W^{(12)}=(\mathrm{Re}h_{12})^2\approx\frac{p^2}{4\pi\varepsilon_0\kappa(r^{(12)})^3}. \tag{A2}$$

Setting $(\mathrm{Re}\ h_{12})^2=400$ as in our calculations and solving for the ion-ion distance $r^{(12)}$ we get for our characteristic ions a quite great value of

$$r_0{}^{(12)}\sim14\ \text{Å}. \tag{A3}$$

This value is reasonable for weakly coupled pairs as used in our experiment on Pr^{3+}:LaF$_3$.

From [10] we know that the diagonal matrix elements of the ion-ion interaction contribute to the inversion-dependent renormalization of the resonance frequency, too (Eqs. (22) and (23) in [10]). In our notation the full renormalization[1] is given by

---

[1] For identical ions the renormalization of the resonance frequency can be done in another way not renormalizing the Rabi frequency.

$$(\varepsilon-\varepsilon_{12})w=\frac{w}{2\hbar}\,[(h_{11}-h_{22})^2-2|h_{12}|^2]. \tag{A4}$$

Here h_{11} and h_{22} mean the static dipole-dipole interaction of the ions in the ground and in the excited states, respectively. Following Judd, Ofelt, and Peacock [22–24] the transition dipole moments of the rare-earth ions are induced by the noninversion symmetric parts of the crystal field admixing wave functions of opposite parity to the $4f^n$ wave functions. The same mechanism induces static dipole moments as well. So both dipole moments, the off-diagonal and diagonal ones, are of the same origin. Therefore they can be expected to be of the same order of magnitude as well and some mutual reduction of their influence on the inversion-dependent renormalization of the resonance frequency [Eq. (A4)] can be expected. So the estimate for $r_0^{(12)}$ [Eq. (A3)] is rather an upper limit.

Another way to relate our calculations to experiment is to compare the near-field interaction energy of our characteristic ions over a characteristic distance of about $r^{(12)}=10$ Å with typical homogenous linewidths which we used as relative units. The orientation independent part of Eq. (A1) gives

$$\frac{W_0^{(12)}}{\hbar}=112\ \text{MHz}. \tag{A5}$$

Typical homogeneous linewidths of rare-earth ions at low temperatures are of the order of MHz and KHz and extend down to 122 Hz [25]. This proves our choice of the order of magnitude of the interaction parameters for the model calculations which introduce an interesting field of nonlinear molecular dynamics.

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