

Cooperative Bistability in Dense, Excited Atomic Systems

M. P. Hehlen and H. U. Güdel

Institut für Anorganische Chemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Q. Shu, J. Rai,* S. Rai,† and S. C. Rand

Division of Applied Physics, 1049 Randall Laboratory, University of Michigan, Ann Arbor, Michigan 48109-1120

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We report a new mechanism of intrinsic bistability, operative in excited atomic systems with substantial atom-atom coupling. Predictions and observations of bistable luminescence from Yb^{3+} pairs in crystalline $\text{Cs}_3\text{Y}_2\text{Br}_9:\text{Yb}^{3+}$ are in good agreement and have interesting implications for local field effects in solids and dense, ultracold gases.

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As first reported by Gibbs [1] many years ago, the transmission of nonlinear optical systems can sometimes exhibit two stable values for a single input intensity, a phenomenon known as bistability. Because of potential applications in all-optical switching for communications and optical computing, many different mechanisms of bistability have been studied. Mirrorless or intrinsic bistability in *dense media* was first considered by Bowden and Sung [2] and elaborated by subsequent authors [3–6] who found that ground-state, near dipole-dipole (NDD) interactions responsible for making the local or Lorentz field different from the incident field could cause optical switching. To our knowledge, however, there have been no experimental reports of all-optical switching mediated by NDD interactions nor any theoretical treatments considering resonant contributions from cooperative excited state dynamics. Here we extend the two-level density matrix model to incorporate new contributions expected from strong, dipolar interactions among *excited states* [7] pertinent to a variety of systems, including quiresonant energy exchange collisions in gases [8], avalanche up-conversion [9], and cooperative up-conversion [10] in solids. Intrinsic bistability dependent on a combination of ground- and excited-state couplings is predicted and this phenomenon observed in cooperative pair luminescence of the dimeric compound $\text{Cs}_3\text{Y}_2\text{Br}_9:\text{Yb}^{3+}$ for the first time.

Pairs of atoms in dense systems, whether gases or solids, can relax through energy transfer mediated by exchange or multipolar electromagnetic interactions at close range, as depicted in Figs. 1(a) and 1(b). In dense cesium vapor, for example, an atom prepared in the $6d^2D_{3/2}$ level can relax nonradiatively to the $6p^2P_{3/2}$ or $2P_{1/2}$ level through a collision with a ground-state atom which undergoes a simultaneous, energy-conserving dipole transition upward to $6p$ [8]. Such a process corresponds to Fig. 1(a). As a second example, in crystals doped with Tm^{3+} impurities, ions prepared in the 3H_4 state may decay nonradiatively to 3F_4 if a neighbor makes a simultaneous transition to 3F_4 in a condensed matter process [11] referred to as cross relaxation. In either example, excitation energy is partitioned between the excited atom and

a ground-state “collision” partner at a rate which is bilinear in their respective densities, and therefore *non-linear* with respect to occupation probabilities. Somewhat surprisingly, under selected initial conditions, nonlinear dynamics of this kind can dominate collisional relaxation in gases [12] or lead to cross relaxation avalanches in solids [11]. The reverse process, sketched in Fig. 1(b) and called cooperative up-conversion, can also be efficient and is the process responsible for the observations reported here.

Our up-conversion experiments were performed in single crystals of $\text{Cs}_3\text{Y}_2\text{Br}_9:10\% \text{Yb}^{3+}$, one of a family of compounds $\text{Cs}_3M_2X_9$ ($M = \text{Ho}^{3+}, \dots, \text{Lu}^{3+}, \text{Y}^{3+}$ when $X = \text{Cl}^-$; $M = \text{Sm}^{3+}, \dots, \text{Lu}^{3+}, \text{Y}^{3+}$ when $X = \text{Br}^-$) crystallizing with space group $R\bar{3}c$ such that rare earth dimer units $[M_2X_9]^{3-}$ form with trigonal axes coinciding with the trigonal crystal axis. A key feature of these dimer or pair-forming materials is that the M - M distance between lanthanide ions is much shorter than in most compounds [13], including the phosphate crystal in which Yb^{3+} cooperative luminescence was observed originally [14]. Since the coupling between lanthanides depends strongly on interion separation, materials of this type exhibit intense cooperative up-conversion emission, and give other indications of strong ground- and excited-state interactions. Neutron scattering measurements of the Yb^{3+} ground-state electronic splitting in $\text{Cs}_3\text{Yb}_2\text{Br}_9$, [15], for example, yield the value 3.0 cm^{-1} , which is exceptionally large for rare earth ions. A low power, continuous-wave $\text{Ti}:\text{Al}_2\text{O}_3$ laser tuned to various Stark components of

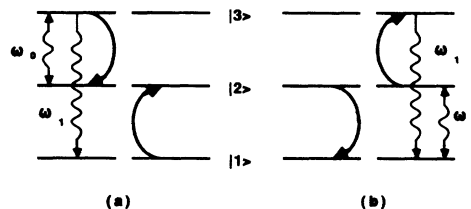


FIG. 1. Cooperative dynamics involving two three-level atoms, giving rise to (a) cross relaxation and (b) pair up-conversion. Wiggly arrows indicate photons. Curved arrows indicate (nonradiative) coupled atom (cooperative) dynamics.

the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} was adequate to excite green pair luminescence at a wavelength of 500 nm in samples cooled to liquid helium temperatures. The intensity of the emission was carefully recorded as temperature and incident intensity were slowly varied.

The dynamics of interest [Fig. 1(b)] can be treated with a two-level pair model of cooperative processes (Fig. 2). This model incorporates ground-state dipolar interactions which produce local field corrections in the optical polarization, following previous work [5,16]. However, excited-state interactions are also included. Of the three states shown in Fig. 1, we note that one participates merely as an intermediate state. Its role as a virtual state can nevertheless be preserved in a two-level model, as illustrated in Figs. 2(a) and 2(b), by the incorporation of relaxation terms in the equations of motion with density-dependent rates. For example, in Fig. 2(b), cooperative up-conversion mediates decay of state $|2\rangle$ population ρ_{22} at a rate of $2\alpha\rho_{22}$, where α is the pair up-conversion rate constant and the factor of 2 refers to the two excited atoms which decay for each cooperative event. This contributes a term $-\alpha(\sigma_3 - \sigma_{30})^2$ to decay of the inversion $\sigma_3 \equiv \rho_{22} - \rho_{11}$ with respect to its equilibrium value σ_{30} in the absence of fields, provided there is negligible thermal occupation of the excited state ($\sigma_{30} = -1$). From the Schrödinger equation of motion for the density matrix, the dynamic equations for the off-diagonal coherence σ_{21} and the inversion σ_3 are therefore

$$\dot{\sigma}_{21} = -i(\Delta + \varepsilon\sigma_3)\sigma_{21} - \frac{1}{2}i\Omega\sigma_3 - \Gamma\sigma_{21}, \quad (1)$$

$$\dot{\sigma}_3 = -i\Omega(\sigma_{21} - \sigma_{21}^*) - \gamma(\sigma_3 - \sigma_{30}) - \alpha(\sigma_3 - \sigma_{30})^2. \quad (2)$$

Here $\varepsilon = n\mu^2/s\hbar\varepsilon_0$ is the local field correction term, which has units of frequency, just like α . n is the number density, μ is the dipole transition moment, s is a factor (equal to 3 in cubic solids) determined by a lattice sum [17], ε_0 is the permittivity of vacuum, γ is the excited-state decay rate, and Γ is the dephasing rate. The detuning of light from the resonance frequency at ω_0 is $\Delta = \omega_0 - \omega$, and $\Omega = \mu E/\hbar$ is the Rabi frequency. $\sigma_{21} = -i\tilde{\rho}_{21}$ is a convenient, slowly varying amplitude of the off-diagonal density matrix element $\rho_{21} = \tilde{\rho}_{21}\exp[-i(\omega t - kr)]$. Overdots indicate time derivatives.

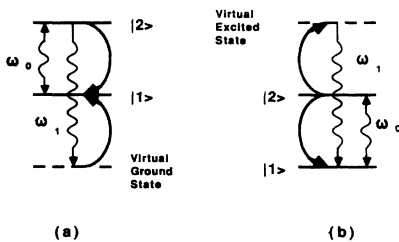


FIG. 2. Two-level theoretical models of the cooperative dynamics depicted in Fig. 1 in which the third (intermediate) states are treated as virtual states. Wiggly arrows indicate photons. Curved arrows indicate (nonradiative) cooperative relaxation processes.

From (1) and (2) the population inversion σ_3 and the slowly varying envelope of the optical polarization $P = 2ni\mu_{12}\sigma_{21}$ may be calculated. Since cooperative up-conversion and cross relaxation are inverse processes, they are both described by very similar dynamical equations and conclusions drawn below also pertain to avalanche up-conversion processes [Figs. 1(a) and 2(a)]. In steady-state conditions the time derivatives in (1) and (2) equal zero. This yields

$$\sigma_{21} = \frac{-\frac{1}{2}i\Omega\sigma_3[\Gamma - i(\Delta + \varepsilon\sigma_3)]}{\Gamma^2 + (\Delta + \varepsilon\sigma_3)^2}. \quad (3)$$

By substituting (3) into (2) and simplifying, we find

$$a\sigma_3^4 + b\sigma_3^3 + c\sigma_3^2 + d\sigma_3 + e = 0, \quad (4)$$

where the coefficients are given by

$$a = \alpha\varepsilon^2, \quad b = -2\alpha\sigma_{30}\varepsilon^2 + \gamma\varepsilon^2 + 2\alpha\Delta\varepsilon,$$

$$c = -\gamma\sigma_{30}\varepsilon^2 + 2\gamma\Delta\varepsilon + \alpha\sigma_{30}^2\varepsilon^2 + \alpha\Gamma^2 - 4\alpha\sigma_{30}\Delta\varepsilon + \alpha\Delta^2,$$

$$d = -2\gamma\sigma_{30}\Delta\varepsilon + \Omega^2\Gamma + \gamma\Gamma^2 + 2\alpha\sigma_{30}^2\Delta\varepsilon - 2\alpha\sigma_{30}\Gamma^2 + \gamma\Delta^2 - 2\alpha\sigma_{30}\Delta^2,$$

and

$$e = \alpha\sigma_{30}^2\Gamma^2 - \gamma\sigma_{30}\Gamma^2 - \gamma\sigma_{30}\Delta^2 + \alpha\sigma_{30}^2\Delta^2.$$

The quartic equation in (4) has solutions which are multivalued and describe the full features of bistability to be expected in the inversion of cooperative dynamic systems. When the up-conversion rate α is zero, the coefficient of the quartic term $\alpha\varepsilon^2$ vanishes and we recover the results of Refs. [2-6,16]. However when both α and ε are not zero, the fourth order coefficient becomes finite and leads to changes in the nonlinear dynamics which are the *joint* result of ground- and excited-state NDD interactions.

In Fig. 3, the solution of (4) for the steady-state inversion σ_3 is used to plot $(\sigma_3 - \sigma_{30})^2$, a quantity proportional to the pair luminescence intensity, as a function of incident intensity Ω^2 . Without up-conversion, the leftmost curve shows that weak bistability is predicted when the local field factor ε exceeds excited-state relaxation frequencies γ and Γ . The solutions in the central portion of this plot between the turning points (dashed) are demonstrably unstable, causing hysteresis in the inversion versus incident intensity. As intensity is increased from zero, the predicted pair luminescence intensity at first follows the lower branch of the curve, but reaches a point at which the only stable solution available at higher powers lies on the upper branch of the curve. Here, switching to the upper branch occurs and switch down only occurs subsequently if the incident intensity falls below the point at which only a lower branch solution exists.

As the up-conversion rate α is increased from zero to a value comparable to ε (curve farthest to the right in Fig. 3), two significant effects occur. First, a higher

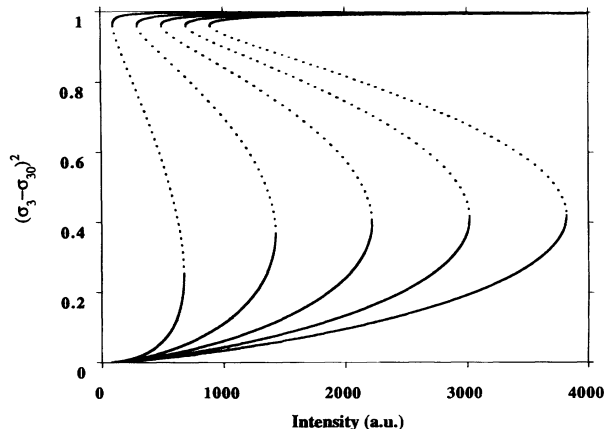
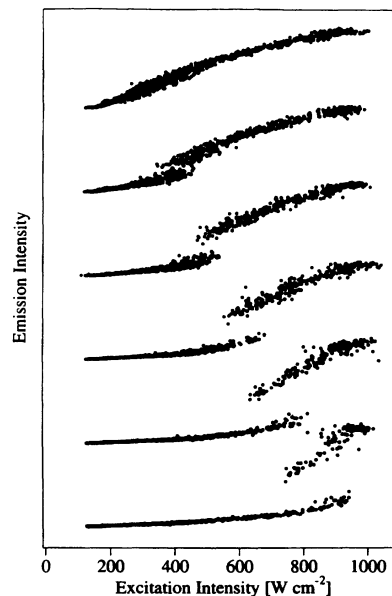


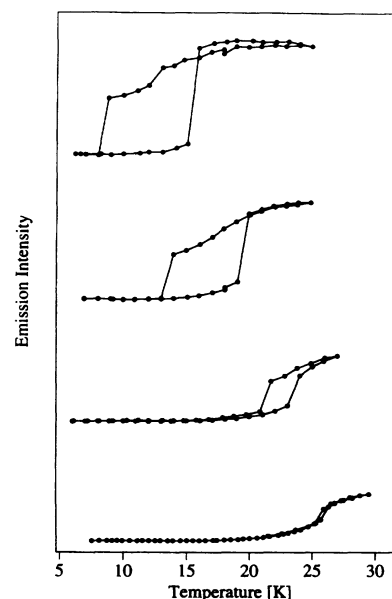
FIG. 3. Calculated pair luminescence intensity [proportional to $(\sigma_3 - \sigma_{30})^2$] in a system undergoing pair emission, plotted as a function of incident intensity (Ω^2) on resonance ($\Delta = 0$). The solid (dashed) curves indicate stable (unstable) solutions. From left to right, the five plotted curves correspond to values of interatomic coupling of $\alpha = 0, 2, 4, 6,$ and $8,$ respectively. All frequencies are referenced to $\gamma = \Gamma = 1$ and the local field parameter has the fixed value $\epsilon = 10\epsilon_{cr}$, where $\epsilon_{cr} = 3\sqrt{3}$ is a critical field needed for bistability when $\alpha = 0$.

input power is required to reach bistability. Second, an immense magnification of the area of the hysteresis loop occurs with only minor changes in the relative shape of the curve. This is evidence that excited-state dipole-dipole interactions influence nonlinear dynamics in much the same way ground-state interactions do, in keeping with the fact that both enter the coefficient of the quartic term on a similar footing as the product αe^2 . However, for reasons not yet completely understood but possibly related to the resonant nature of excited-state interactions considered here, the effect of α is much greater than that of ϵ .

In Fig. 4, experimental results are shown which confirm basic predictions of the model. In Fig. 4(a) up-conversion emission abruptly increases at a well-defined intensity as the incident power increases. Sample emission maintains an almost constant value as the incident intensity is increased further and switches down only when the power is decreased well below the original switching point. As the atom-atom coupling increases toward lower temperatures, the hysteresis loops enlarge and move to higher excitation energies as expected. However, the step height enlarges in a trend which is not understood at present. This trend may result from resonant energy migration in the excited state, capable of enhancing cooperative interactions, but impossible to include in a two-level model based on single atom states. In Fig. 4(b), similar hysteresis is apparent when the incident intensity is held fixed and temperature is varied. In this case the effective interatom coupling changes, because the overlap integral and competing decay processes are temperature dependent. Hence this is roughly equivalent to varying α at a fixed intensity in our model, in which case the



(a)



(b)

FIG. 4. (a) Up-conversion emission intensity at $\lambda = 500$ nm versus incident laser power from Yb^{3+} - Yb^{3+} pairs in $\text{Cs}_3\text{Y}_2\text{Br}_9:10\% \text{Yb}^{3+}$ at various fixed temperatures (top to bottom): 31, 27, 23, 19, 15, and 11 K. (b) Up-conversion emission intensity at $\lambda = 500$ nm versus temperature in $\text{Cs}_3\text{Y}_2\text{Br}_9:10\% \text{Yb}^{3+}$ at various fixed incident intensities (top to bottom): 814, 640, 539, and 415 W/cm^2 .

theory predicts very similar bistability results. Both sets of observations clearly show that cooperative emission exhibits hysteresis without feedback (mirrors).

Broad inferences may be drawn from the present work by adopting the following perspective. In both gases and solids, cooperative interactions like cross relaxation or

up-conversion may be pictured as “collisional” processes which occur on time scales comparable to or shorter than the average collision time. In gases, collision times are typically very short, and collisional interactions brief. On the other hand, near-neighbor rare earth impurities in solids, separated by short distances as if in a “frozen” collision, interact in excited states on time scales limited by lifetimes of the energy levels, which can be as long as 10 ms. This analogy with gaseous collisions is in fact more apt than generally recognized, since collisional depolarization ratios of rare gases, for example, can be calculated from elasto-optic coefficients of rare gas solids [18]. Hence when long interaction times are encountered, such as in rare earth solids or for nearly stationary atoms in optical traps, the concept of *slow collisions* can be invoked to unify the seemingly distinct domains of coupled dopants in solids and colliding ultracold atoms in vacuum. The model presented here, in which atoms are assumed to be effectively at rest, is expected to encompass both physical situations.

Although not explicitly reported here, optical absorption in this and other coupled systems is also expected to undergo switching, since it is proportional to σ_3 . That is, absorption by coupled atoms in dense excited systems with transition energy coincidences should exhibit hysteresis. This implies that many related effects may be observable in dense vapors and gases. For example, the absorption behavior of ultracold colliding atoms which happen to have nearly identical ground and excited state transition energies should exhibit hysteresis on selected transitions. At microkelvin temperatures and below, atoms are essentially at rest on the time scale of excited-state relaxation processes. Consequently, we expect behavior related to that calculated and observed here for stationary atoms in a concentrated rare earth solid to apply to ultracold dense gases too.

In summary, we have shown that pair emission of Yb^{3+} ions in $\text{Cs}_3\text{Y}_2\text{Br}_9$: Yb^{3+} exhibits intrinsic bistability as a function of incident intensity and temperature. A model in which contributions to the nonlinear polarization from ground- and excited-state interactions between Yb^{3+} ions are treated on an equal footing gives good agreement with experiments. Furthermore, the mere fact that the first example of bistability due to atom-atom interactions has emerged from a cooperative up-conversion system supports the general conclusion that resonant excited-state interactions amplify nonlinear response associated with the Lorentz field, rendering bistability much easier to observe. It confirms experimentally that cooperative nonlinearities can induce hysteretic behavior in crystals without a cavity. Bistability from this mechanism can be expected to occur also in avalanche systems which decay by runaway cross relaxation. Furthermore, while our results are most pertinent to stationary atoms in solids, we have argued that they have broader implications for selected transitions in vapors which induce quiresonant collisional interactions. Similar effects may occur in high

density optical traps below the Doppler cooling limit when internuclear separation does not change appreciably during an excited-state lifetime. Finally, these results suggest new extensions of theories of the local field [17] in dense atomic systems.

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*On leave from Department of Physics, Indian Institute of Technology, Kanpur 208016 India.

†On leave from Department of Physics, Indian Institute of Technology, New Delhi, India.

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