Dynamics of the infrared-to-visible upconversion in an Er^{3+} -doped KPb_2Br_5 crystal

A. J. Garcia-Adeva,¹ R. Balda,^{1,2} J. Fernández,^{1,2} Ei Ei Nyein,³ and U. Hömmerich³

¹*Departamento Física Aplicada I, Escuela Superior de Ingenieros, Alda. Urquijo s/n, 48013 Bilbao, Spain*

²*Unidad Física de Materiales CSIC-UPV/EHU and Donostia International Physics Center, Apartado 1072, 20080 San Sebastian, Spain*

³*Department of Physics, Hampton University, Hampton, Virginia 23668, USA*

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In this work we report infrared-to-visible upconversion luminescence in the low-phonon-energy host material KPb_2Br_5 doped with Er^{3+} ions under $^4I_{9/2}$ excitation. Different upconversion emissions are observed depending on the excitation wavelength. Resonant excitation in the $^4I_{9/2}$ level (≈ 805 nm) originates emissions from levels $^2H_{9/2}$ and $^2H_{11/2}/^4S_{3/2}$. These upconverted emissions occur via energy transfer upconversion processes. However, under nonresonant excitation at lower energies than $^4I_{9/2}$, the main emission results from the $^2H_{9/2}$ level. This latter upconverted emission can be attributed to excited-state absorption of the pump radiation. The excitation mechanisms have been investigated in detail using steady-state and time-resolved spectroscopy and the dynamics has been studied by using a rate equation model.

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I. INTRODUCTION

Rare-earth- (RE-)doped materials capable of converting infrared radiation into visible light in an efficient way are potential candidates for photonic applications in several areas such as color displays, sensors, detection of infrared radiation, and upconversion laser.¹ Upconversion luminescence is considered as a promising solution to obtain efficient visible lasers pumped by commercial infrared laser diodes. Efficient upconversion laser action has been demonstrated in crystals and fibers doped with, e.g., Pr^{3+} ,² Tm^{3+} ,^{3,4} Ho^{3+} ,⁵ and Er^{3+} .⁶ In particular, upconversion laser at the green emission $^4S_{3/2} \rightarrow ^4I_{15/2}$ of Er^{3+} ions pumped with a laser diode at 800 nm has been obtained with a higher efficiency than the one achieved by harmonic generation technique.⁶ Most of these results correspond to fluoride systems. In fluorides, the green emission $^4S_{3/2} \rightarrow ^4I_{15/2}$ can be pumped under excitation into the $^4I_{9/2}$ level (at ≈ 800 nm) or into the $^4I_{11/2}$ level (at ≈ 980 nm), where diode pumping is possible. In the first case, excitation into the $^4I_{9/2}$ level is followed by fast nonradiative decay to the $^4I_{11/2}$ level due to the relatively high phonon energies, the $^4I_{11/2}$ level acting as a long-lived intermediate state for upconversion. This is different in materials with lower phonon energies such as chlorides, bromides, and iodides, where multiphonon relaxation of the $^4I_{9/2}$ level is negligible. In these low-phonon-energy materials, due to the reduction of multiphonon relaxation rates and the increased lifetime of the $^4I_{9/2}$ level, this one acts as an intermediate state for upconversion, leading to different upconversion mechanism.⁷⁻¹² For instance, blue, green, and red emissions from the $^2H_{9/2}$ level by sequential upconversion excitation from the $^4I_{9/2}$ level has been demonstrated.⁹⁻¹² However, the $^2H_{9/2}$ level is not significantly populated after excitation in the $^4I_{11/2}$ one because more than two photons are needed in this case and upconversion processes involving more than two photons are generally less efficient. As a consequence, excitation into the $^4I_{9/2}$ level in low-phonon-energy lattices results in different upconversion luminescence spectra and

different excited-state dynamics than in fluoride hosts. Unfortunately, one drawback of chloride and bromide systems is that these materials usually present poor mechanical properties, moisture sensitivity, and are difficult to synthesize. An important advance in the search for new low-phonon-energy materials has been the identification of potassium lead halide crystals KPb_2X_5 ($\text{X}=\text{Cl}, \text{Br}$) as new low-energy phonon hosts for rare-earth ions. These crystals are nonhygroscopic and readily incorporate rare-earth.¹³⁻¹⁹ Efficient ir-to-visible upconversion in Pr^{3+} -doped and Yb^{3+} - Pr^{3+} -codoped KPb_2Cl_5 ,¹⁶ in Er^{3+} -doped¹² KPb_2Cl_5 , and Nd^{3+} -doped¹⁷ KPb_2Cl_5 has been recently reported by some of the present authors and the mechanisms responsible for these upconversion processes have been investigated. The maximum phonon energy in this crystal is 203 cm^{-1} .¹⁵ Very recently, Rademaker *et al.*¹⁸ have studied the optical properties of Nd^{3+} and Tb^{3+} in a KPb_2Br_5 crystal in order to assess the potentialities of these materials for long-wavelength infrared applications. Also, Hömmerich *et al.*¹⁹ have reported on the material preparation and optical properties of Er^{3+} in this crystal. The crystal is monoclinic²⁰ (space group $P2_1/c$) with lattice parameters $a=0.9264\text{ nm}$, $b=0.8380\text{ nm}$, $c=1.3063\text{ nm}$, and $\beta=90.06^\circ$. Similarly to RE-doped KPb_2Cl_5 , RE ions are supposed to substitute for the lead (Pb^{2+}) ions and potassium (K^+) vacancies are assumed to provide charge compensation.¹⁴ Pb^{2+} ions occupy two nonequivalent lattice sites, one site Pb(1) is a distorted octahedron and the second site Pb(2) a distorted trigonal prism. Very recently, some of the authors have demonstrated the existence of three different local environments around the RE ions in KPb_2Cl_5 by using the fluorescence line-narrowing technique. The study reveals that the RE ions may occupy both the Pb and K sites but the luminescence results suggest that RE ions occupying the Pb(2) site is most likely to occur.²¹

The potassium lead bromide crystal KPb_2Br_5 presents similar properties to KPb_2Cl_5 but with the advantage of even lower phonon energies, due to the higher mass of the bromine constituent. According to Raman-scattering measure-

ments the maximum phonon energy, measured at the highest-energy peak of the spectrum, is 138 cm^{-1} .¹⁸ This lower phonon energy significantly reduces nonradiative decay due to multiphonon relaxation, allowing an increased lifetime of some excited levels that can relax radiatively or can store energy for further upconversion, cross-relaxation, or energy transfer processes. Since the competition between radiative, multiphonon relaxation, and nonradiative processes based on energy transfer such as upconversion and cross relaxation determines the excited-state dynamics under pulsed excitation, one can find different upconversion behaviors depending on the relative influence of these processes. For instance, under 975 nm excitation, a $\text{KPb}_2\text{Br}_5:\text{Er}$ crystal shows an intense blue emission corresponding to the $^4F_{7/2}$ level, whereas in the case of KPb_2Cl_5 , this level is quenched by multiphonon relaxation, and the main upconverted emission corresponds to the green emission from the $^4S_{3/2}$ level, which is populated nonradiatively from $^4F_{7/2}$.¹⁹

In this work we present a detailed analysis of the upconversion dynamics in an Er^{3+} -doped KPb_2Br_5 crystal following excitation into the $^4I_{9/2}$ level by using both steady-state and time-resolved luminescence spectroscopy. Resonant excitation of the $^4I_{9/2}$ level leads to fluorescence from the $^2H_{9/2}$ and $^4S_{3/2}$ levels, whereas excitation at energies below the barycenter of the $^4I_{9/2}$ level results in emission mainly from $^4H_{9/2}$. This latter upconversion emission can be attributed to a sequential two-photon absorption. However, under resonant pumping of the $^4I_{9/2}$ level, the mechanisms that populate the $^2H_{9/2}$ and $^4S_{3/2}$ levels are energy transfer upconversion processes. The mechanisms involved in the upconversion dynamics have been theoretically investigated by using a rate equation formalism.

II. EXPERIMENTAL TECHNIQUES

Single crystals of nonhygroscopic ternary potassium lead bromide KPb_2Br_5 doped with Er^{3+} ions were grown by the Bridgman technique. The material preparation has been reported in Ref. 19. The Er^{3+} content in the melt was 1 wt %. The Er^{3+} concentration was measured to be ≈ 0.14 wt % using inductively coupled plasma optical emission spectroscopy. It is well known that binary and ternary lead halides are prone to contamination caused by oxyhalides and other impurities, which can lead to infrared absorption features. The transmission spectra of $\text{KBP}:\text{Er}^{3+}$ present impurity absorption bands at around 3, 3.4, and $6.3\text{ }\mu\text{m}$, in addition to the Er^{3+} absorption bands from 400 to 1600 nm. Similar absorption bands around $3\text{ }\mu\text{m}$ have been also reported for zone-refined Er-doped KPC crystals and attributed to Ohio impurities.¹⁹

The sample temperature was varied between 4.2 and 300 K with a continuous-flow cryostat. Conventional absorption spectra between 175 and 3000 nm were performed with a Cary 5 spectrophotometer. The steady-state emission measurements were made with a Ti-sapphire ring laser (0.4 cm^{-1} linewidth) as exciting light source. The excitation beam was focused on the crystal by using a 50 mm focal lens. The fluorescence was analyzed with a 0.25 m monochromator, and the signal was detected by a Hamamatsu R928 photo-

FIG. 1. Upconversion emission spectra obtained under near-infrared excitation at $12\,422\text{ cm}^{-1}$ at 295 K (a) and 77 K (b) and under excitation at $12\,092\text{ cm}^{-1}$ at 295 K (c) and 77 K (d).

multiplier and finally amplified by a standard lock-in technique. Lifetime measurements were obtained by exciting the sample with a dye laser pumped by a pulsed nitrogen laser and a Ti-sapphire laser pumped by a pulsed frequency-doubled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (9 ns pulse width), and detecting the emission with Hamamatsu R928 and R5509-72 photomultipliers. The data were processed by a Tektronix oscilloscope.

III. RESULTS

We have observed visible upconversion at room temperature under continuous wave (cw) and pulsed laser excitation in the $^4I_{9/2}$ level. The upconverted emission spectra obtained under cw excitation were measured by using a Ti-sapphire ring laser. Cutoff filters were used to remove the pump radiation. Upconversion luminescence spectra were measured at 77 and 295 K and the main features were found to be nearly temperature independent. However, the upconversion emission spectra are strongly dependent on the excitation energy. Figure 1 shows the upconverted emission spectra of Er^{3+} -doped KPb_2Br_5 obtained under cw near infrared excitation for two different energies at 295 and 77 K. The spectra in Figs. 1(a) and 1(b) were excited at $12\,422\text{ cm}^{-1}$ in resonance with the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition. As can be observed the most intense emission corresponds to the green emission $^4S_{3/2} \rightarrow ^4I_{15/2}$ ($18\,298\text{ cm}^{-1}$). In addition to this transition, the spectrum also shows blue, green, and red emissions corresponding to the transitions $^2H_{9/2} \rightarrow ^4I_{15/2}$ ($24\,450\text{ cm}^{-1}$),

FIG. 2. Logarithmic plot of the integrated intensities of the upconverted emission from $^2H_{9/2}$ ($24\,450\text{ cm}^{-1}$) and $^4S_{3/2}$ ($18\,298\text{ cm}^{-1}$) levels obtained under excitation at $12\,422\text{ cm}^{-1}$.

$^2H_{11/2} \rightarrow ^4I_{15/2}$ ($19\,098\text{ cm}^{-1}$), $^2H_{9/2} \rightarrow ^4I_{13/2}$ ($17\,921\text{ cm}^{-1}$), and $^2H_{9/2} \rightarrow ^4I_{11/2}$ ($14\,389\text{ cm}^{-1}$), respectively. Very weak red emission at around $15\,015\text{ cm}^{-1}$ corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition is also observed. The ratio between the luminescence corresponding to the $^2H_{11/2} \rightarrow ^4I_{15/2}$ emission and the green emission from the level $^4S_{3/2}$ increases with decreasing temperature from 0.261 at 295 K to 0.357 at 77 K, which indicates a decreasing multiphonon relaxation rate. The energy gap between the $^2H_{11/2}$ and the $^4S_{3/2}$ is 800 cm^{-1} which corresponds to 5.7 phonons of the highest energy. Multiphonon relaxation becomes dominant when the ratio between the energy gap and the energy of the highest energy phonons gets smaller than 5–6. As a consequence, radiative relaxation is competitive with multiphonon relaxation processes in this bromide crystal.

The upconverted emission spectra obtained under excitation at $12\,092\text{ cm}^{-1}$, below the $^4I_{9/2}$ level, are mainly characterized by emissions from the level $^2H_{9/2}$. The spectra show three main bands corresponding to transitions $^2H_{9/2} \rightarrow ^4I_{15/2,13/2,11/2}$ [Figs. 1(c) and 1(d)] with no significant differences on temperature.

To investigate the excitation mechanisms that populate the $^4H_{9/2}$ and $^4S_{3/2}$ levels after ir excitation, we have obtained the ir emission intensities for different pumping powers. The upconversion emission intensity (I_{em}) depends on the incident pump power (P_{pump}) according to the relation $I_{em} \propto (P_{pump})^n$, where n is the number of photons involved in the pumping process. The upconversion intensities were recorded at $24\,450\text{ cm}^{-1}$ ($^2H_{9/2}$) and $18\,298\text{ cm}^{-1}$ ($^4S_{3/2}$) for different pump powers. Figure 2 shows a logarithmic plot of the integrated emission intensity of the upconverted fluorescence as a function of the pump laser intensity. The dependence of the intensity on the pump power is close to quadratic, which indicates that a two-photon upconversion process populates the $^2H_{9/2}$ and $^4S_{3/2}$ levels.

Excitation spectra of the blue emission at $24\,450\text{ cm}^{-1}$ ($^2H_{9/2}$), the green emission at $18\,298\text{ cm}^{-1}$ ($^4S_{3/2}$), and the red emission at $15\,015\text{ cm}^{-1}$ ($^4F_{9/2}$) were performed between 4.2 and 295 K in the spectral region corresponding to the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition. Figure 3 shows for comparison the room-temperature excitation spectra for the upconverted emissions by monitoring the $^2H_{9/2} \rightarrow ^4I_{15/2}$ transition at $24\,450\text{ cm}^{-1}$, the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at $18\,298\text{ cm}^{-1}$, and

FIG. 3. Excitation spectra of the upconverted emission from levels $^2H_{9/2}$ ($24\,450\text{ cm}^{-1}$), $^4S_{3/2}$ ($18\,298\text{ cm}^{-1}$), and $^4F_{9/2}$ ($15\,051\text{ cm}^{-1}$) corrected for the spectral variation of the laser intensity. The one-photon absorption spectrum corresponding to $^4I_{15/2} \rightarrow ^4I_{9/2}$ is also included for comparison.

the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition at $15\,015\text{ cm}^{-1}$ together with the one-photon (OP) absorption spectrum. The excitation spectrum corresponding to the green emission from the $^4S_{3/2}$ level is very similar to the absorption spectrum, whereas the excitation spectrum of the blue emission from the $^2H_{9/2}$ level resembles the absorption spectrum in the high-energy region but presents some additional peaks not observed in the OP absorption spectrum. These peaks are also present in the excitation spectrum of the red emission from $^4F_{9/2}$ level, though less prominently. Figure 4 shows the excitation spectrum of the blue upconverted emission from level $^2H_{9/2}$ obtained at different temperatures. The two groups of peaks observed in the excitation spectrum show a different temperature dependence. At low temperature, the intensity of peaks located at lower energies than the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition decrease in intensity and disappear completely below 25 K, which is a clear signature of a thermally activated process.

We also investigated the temporal evolution of the upconverted emissions and the infrared emission of the $^4I_{9/2} \rightarrow ^4I_{15/2}$ transition by exciting the sample in resonance with the $^4I_{9/2}$ level and nonresonantly at $12\,092\text{ cm}^{-1}$ with a Ti-sapphire laser pumped by a frequency-doubled pulsed Nd-YAG laser. The decays and lifetimes of the $^2H_{9/2}$ and $^4S_{3/2}$ levels were also obtained under direct excitation with a dye laser. Figure 5 shows the time evolution of the upconverted $^2H_{9/2}$ emission at room temperature for two different excitation energies obtained after an infrared excitation pulse of

FIG. 4. Excitation spectra of the upconverted emission from the $^2H_{9/2}$ level ($24\,450\text{ cm}^{-1}$) obtained at different temperatures, corrected for the spectral variation of the laser intensity.

9 ns. The insets show the same decays but in a semilogarithmic plot. The decay obtained under excitation at $12\,422\text{ cm}^{-1}$ in resonance with the $^4I_{15/2} \rightarrow ^4I_{9/2}$ absorption [Fig. 5(a)] shows a rise and a decay with a lifetime much longer than that of the $^2H_{9/2}$ level under OP excitation, whereas the decay obtained by exciting at $12\,092\text{ cm}^{-1}$ in the low-energy peaks of the excitation spectrum [Fig. 5(b)] is single exponential with a lifetime similar to the one obtained under OP direct excitation of the $^2H_{9/2}$ level ($34\text{ }\mu\text{s}$). Figure 6 shows the experimental decays of the green emission from the level $^4S_{3/2}$ at room temperature by exciting at $19\,121\text{ cm}^{-1}$ (523 nm , one-photon excitation) [Fig. 6(a)] and $12\,422\text{ cm}^{-1}$ (805 nm) [Fig. 6(b)]. As can be seen, the decay curve of the upconverted emission shows a lifetime much longer than that of the level $^4S_{3/2}$ under direct excitation ($180\text{ }\mu\text{s}$).

IV. DISCUSSION

As mentioned above, under resonant excitation into the $^4I_{9/2}$ level the main emission correspond to the $^2H_{9/2}$ and $^2H_{11/2}$, $^4S_{3/2}$ levels, whereas excitation at lower energies than $^4I_{9/2}$ originates upconverted emission from the $^2H_{9/2}$ level. The pumping power dependence of the upconverted emissions indicates that a two-photon upconversion process is responsible for the emissions from the $^2H_{9/2}$ and $^4S_{3/2}$ levels. This process may be associated with excited-state absorption (ESA) and/or energy transfer upconversion (ETU).^{22,23} There are two possibilities to distinguish between these two pro-

FIG. 5. (Color online) Temporal behavior of the blue upconversion luminescence from the $^2H_{9/2}$ level obtained at two different excitation energies (a) $12\,422\text{ cm}^{-1}$ (open circles) and the fit to Eq. (3c) (solid line) and (b) $12\,092\text{ cm}^{-1}$. The inset shows the same curves in a semilogarithmic representation.

cesses: upconversion luminescence excitation spectra and the temporal evolution of the upconversion luminescence after pulsed excitation.²⁴ In the first mechanism (ESA) a single ion is involved, whereas two ions are involved in the second one (ETU). The ESA upconversion process requires an exact resonance between the ground-state absorption (GSA) and an excited-state absorption. Therefore, the ESA upconversion excitation spectrum is the product of the GSA and ESA spectra and it may differ from the GSA of the intermediate state. An ETU process can be phonon assisted and it requires no exact energy resonance between the intermediate and upper states involved in the upconversion process. Therefore, the excitation spectrum is very similar to the GSA of the intermediate state.

The excitation spectrum of the $^2H_{9/2}$ level for this particular system shows the presence of peaks corresponding to the $^4I_{15/2} \rightarrow ^4I_{9/2}$ absorption of the Er^{3+} ions (Figs. 3 and 4). This indicates that an ETU process from the $^4I_{9/2}$ multiplet takes place. Furthermore, the spectrum also presents additional intense peaks at energies that are resonant with the $^4I_{9/2} \rightarrow ^2H_{9/2}$ transition. This means that ESA is the dominant mechanism for the $^2H_{9/2}$ emission obtained under nonresonant excitation at lower energies than the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition and it can be explained by the pumping mechanism described in Fig. 7. In a first step, the absorption of one ir pump photon excites the ions to the $^4I_{9/2}$ level and a subsequent ESA of a second pump photon promotes the ions to the $^2H_{9/2}$ level. In this process the first step $^4I_{15/2} \rightarrow ^4I_{9/2}$ needs to

FIG. 6. (Color online) Temporal behavior of the green upconversion luminescence from the $^4S_{3/2}$ level obtained at two different excitation energies (a) 19 120 and (b) 12 422 cm^{-1} (open circles) and the fit to Eq. (3b) (solid line). The inset shows the same curves in a semilogarithmic representation.

be thermally activated because the excitation energy is 330 cm^{-1} lower than for the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition. The thermal activation can be achieved at room temperature by absorption from higher crystal-field levels of the ground state,

FIG. 7. Energy level diagram of Er^{3+} in KPb_2Br_5 and the proposed upconversion mechanisms to populate the $^2H_{9/2}$ and $^4S_{3/2}$ levels. The dashed lines refer to ETU processes after resonant excitation in the $^4I_{9/2}$ level.

as can be seen in the absorption spectrum of Fig. 3. As a consequence this ESA process is less efficient at low temperature disappearing below 25 K as shown in Fig. 4. In conclusion, as shown in the energy level diagram of Fig. 7, both ESA and ETU processes contribute to the upconversion luminescence from the $^2H_{9/2}$ level depending on the excitation energy. These results are further confirmed by the time evolution of the upconverted luminescence.

The excitation spectrum of the upconverted green emission from the level $^4S_{3/2}$ follows the same wavelength dependence as the OP absorption spectrum. This fact clearly indicates that we are dealing with an energy transfer upconversion (ETU) to populate the $^4S_{3/2}$ state. The population of the $^4S_{3/2}$ level through the $^2H_{9/2}$ level as intermediate state by multiphonon relaxation can be disregarded because of the energy gap between these two levels and the phonon energies involved. From the energy levels of Er^{3+} in this crystal, there are two possible energy transfer upconversion processes to populate the $^4S_{3/2}$ level. One is $(^4I_{9/2}, ^4I_{9/2}) \rightarrow (^4I_{13/2}, ^4S_{3/2})$, namely, ETU II in Fig. 7. In this process, when two Er^{3+} ions are excited by an ir photon directly to the $^4I_{9/2}$ state, a transfer occurs by which one ion loses energy and goes to the $^4I_{13/2}$ state whereas the other one gains energy and goes to the $^4S_{3/2}$ state. This process is nearly resonant with an energy mismatch of -22 cm^{-1} . Another possibility is an energy transfer process involving an erbium ion in the $^4I_{9/2}$ state that decays to the ground state transferring its energy to a nearby ion in the $^4I_{13/2}$ level, which is promoted to the $^4S_{3/2}$ level. The energy mismatch for such a process is $+214.6 \text{ cm}^{-1}$, which could be easily bridged by the emission of two phonons at room temperature (ETU III in Fig. 7).

Concerning the weak red emission from level $^4F_{9/2}$, the excitation spectrum is similar to the absorption spectrum, but there are also peaks at lower energies similar to the excitation spectrum for $^2H_{9/2}$, but less intense. According to the energy level diagram there are two possible energy transfer mechanisms that could populate this level. One involves the $^2H_{9/2}$ and $^4I_{13/2}$ levels: one ion in the $^2H_{9/2}$ level interacts with another one in the $^4I_{13/2}$ level ending both of them in the $^4F_{9/2}$ level. This process is energetically favorable because the energy mismatch for $^2H_{9/2} \rightarrow ^4F_{9/2}$ is larger by 303 cm^{-1} than the corresponding one for $^4I_{13/2} \rightarrow ^4F_{9/2}$. There exists another possible process to populate the $^4F_{9/2}$ level in which two Er^{3+} ions interact, one of them in the $^4I_{9/2}$ level and the other one in the $^4S_{3/2}$ level, both going to level $^4F_{9/2}$. This process is also energetically favorable with an energy mismatch of $+267 \text{ cm}^{-1}$. Both mechanisms can exist at low temperature in agreement with the observation of the $^4F_{9/2}$ level emission at low temperature. Based on the excitation spectrum the, $^4F_{9/2}$ level is at least in part populated from the $^2H_{9/2}$ level, because the $^4I_{9/2} \rightarrow ^2H_{9/2}$ ESA peaks are present. This is clearly seen in the excitation spectra at 77 K shown in Fig. 8. As can be observed, the excitation spectrum of the $^4F_{9/2}$ level shows the same peaks that the one of $^2H_{9/2}$ level in the region of the $^4I_{9/2} \rightarrow ^2H_{9/2}$ ESA. These peaks are less intense than in the excitation spectrum of the $^2H_{9/2}$ level because only one of the ions in the ETU process carries the ESA signature. However, we cannot rule out the participation of the second mechanism.

FIG. 8. Excitation spectra of the upconverted emission from levels $^2H_{9/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ obtained at 77 K, corrected for the spectral variation of the laser intensity.

The time evolution of the upconversion luminescence after an excitation pulse provides a useful tool in discerning what the operative mechanism is. The radiative ESA process occurs during the excitation pulse and leads to an immediate decay of the upconversion luminescence after excitation. Upconversion by energy transfer leads to a time-dependent emission that shows a rise of the upconverted population after the laser pulse followed by a decay of the population with a lifetime longer than the one after direct excitation. This distinction is possible when the pulse width is much shorter than the time constant of the relevant energy transfer step.²⁴ The time evolution of the blue emission from the level $^2H_{9/2}$ obtained after an infrared excitation pulse of 9 ns shows a different behavior depending on the excitation energy. As shown in Fig. 5(b), after nonresonant pulsed infrared excitation the resulting $^2H_{9/2} \rightarrow ^4I_{15/2}$ upconversion luminescence intensity decays instantaneously after the laser pulse with a lifetime similar to that of the $^2H_{9/2}$ level under direct excitation (34 μ s). Therefore, we conclude that the infrared to visible upconversion mechanism is the ESA process displayed in Fig. 7. For resonant excitation into the $^4I_{9/2}$ state (12 422 cm^{-1}), however, the decay curve of the upconverted fluorescence shows a rise time of ~ 36 μ s, which is very close to the lifetime of this level under direct excitation, and a double exponential decay [Fig. 5(a)]. The two components of this decay are especially noticeable in the semilogarithmic plot. The fast component has a lifetime of 166 μ s and the lifetime of the long component is about 0.97 ms. The decay time of the long component is very close to half the

lifetime of the $^4I_{9/2}$ level measured under one-photon excitation, 1.93 ms, whereas the decay time of the short component is very close to $(1/\tau_3 + 1/\tau_5)^{-1}$ with $\tau_3 = 1.93$ ms and $\tau_5 = 180$ μ s the lifetimes of the $^4I_{9/2}$ and $^4S_{3/2}$ levels, respectively. This indicates that the upconversion emission from the $^2H_{9/2}$ level is not only caused by the interaction between two Er^{3+} ions in the $^4I_{9/2}$ level (ETU I in Fig. 7), but another ETU involving the population of the $^4S_{3/2}$ level and that of the $^4I_{9/2}$ one is necessary in order to describe the short-time component of the decay (ETU IV in Fig. 7).

The time evolution of the emission from the $^4S_{3/2}$ level obtained after an infrared excitation pulse of 9 ns in resonance with the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition shows a rise time of 48 μ s and a double exponential decay. The fast component of the decay has a lifetime ~ 635 μ s. The long component has a lifetime of ~ 1.4 ms that is larger than half the lifetime of the $^4I_{9/2}$ level. Interestingly, the only level that has an experimental lifetime somewhat related to the rise time is the $^4F_{9/2}$ one ($\tau_4 \approx 100$ μ s). A plausible explanation for this rise time is, thus, an ETU process in which two ions in the $^4F_{9/2}$ level interact (ETU V in Fig. 7). The long tail of the decay curve, on the other hand, decays with a characteristic time that is suspiciously close to $(1/\tau_3 + 1/\tau_2)^{-1} \approx 1.36$ ms, where $\tau_2 \approx 4.6$ ms is the experimental lifetime of the $^4I_{13/2}$ level. Therefore, a possible explanation for the long-time decay of the upconversion from the $^4S_{3/2}$ level could be a cross-relaxation process in which one ion in $^4I_{9/2}$ decays to the $^4I_{15/2}$ level and another ion in the $^4I_{13/2}$ level is promoted to the $^4S_{3/2}$ level (ETU III in Fig. 7). The most puzzling part of the decay curve is the one with a characteristic decay time of 635 μ s. This time cannot be expressed as a combination of the form $(1/\tau_i + 1/\tau_j)^{-1}$ for the lifetimes of the levels that emit radiatively in this system. However, it is very close to one-third of the experimental lifetime of the $^4I_{9/2}$ level. This could mean one of two things: there is an upconversion process in which three ions in the $^4I_{9/2}$ level interact or an ETU (ETU II in Fig. 7) process involving two ions in the $^4I_{9/2}$ level gives a non-negligible higher-order contribution in a perturbative expansion of the dynamical equations. The former possibility seems less likely, as it involves a three-photon process whereas the power dependence of the upconverted intensity is nearly quadratic, which clearly indicates that only two-photon processes operate in this system.

One key point about the fast rise of the population of the $^4S_{3/2}$ level is that in order for this to happen, the $^4F_{9/2}$ must be populated at very short times. In order to identify the mechanism responsible for populating this level at very short times, we measured the time evolution of the upconverted $^4F_{9/2}$ emission after an infrared excitation pulse of 9 ns in resonance with the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition. The curve obtained in this way is shown in Fig. 9. This curve shows an initial rise with a characteristic time of ~ 35 μ s and a decay at intermediate times with a decay constant of ~ 595 μ s. The rise time is very close to the lifetime of the $^2H_{9/2}$ level, whereas the decay time is close (with less than 7% deviation) to one third of the lifetime of the $^4I_{9/2}$ level. Therefore, it seems clear that the rise of the population of the $^4F_{9/2}$ level occurs by means of an ETU process in which one ion in the $^2H_{9/2}$ level decays into the $^4F_{9/2}$ level and another one in the

FIG. 9. (Color online) Temporal behavior of the red upconversion luminescence from the $^4F_{9/2}$ level obtained under excitation at $12\,422\text{ cm}^{-1}$ (open circles) and the fit to Eq. (3a) (solid line). The inset shows the same curves in a semilogarithmic representation.

$^4I_{13/2}$ level is promoted to the $^4F_{9/2}$ level (ETU VI in Fig. 7). The intermediate time decay can be interpreted, on the other hand, as a process in which one ion in the $^4S_{3/2}$ level decays into the $^4F_{9/2}$ level and another ion in the $^4I_{9/2}$ is promoted into the $^4F_{9/2}$ level (ETU VII in Fig. 7), as will be explained below in more detail.

Bearing these facts in mind, the simplest approach to theoretically investigate the upconversion mechanisms operating in Er-doped KPb_2Br_5 crystal is a rate equation analysis. In the following, we will use the notation n_1, n_2, n_3, n_4, n_5 , and n_6 to represent the populations of the $^4I_{15/2}, ^4I_{13/2}, ^4I_{9/2}, ^4F_{9/2}, ^4S_{3/2}$, and $^2H_{9/2}$ levels, respectively. The rate equations that include all the ETU mechanisms for infrared upconversion described above are given by

$$\dot{n}_1(t) = \frac{n_2}{\tau_2} + \frac{n_3}{\tau_3} + \frac{n_4}{\tau_4} + \frac{n_5}{\tau_5} + \frac{n_6}{\tau_6} + \gamma_I n_3^2 + \gamma_{III} n_2 n_3, \quad (1a)$$

$$\dot{n}_2(t) = -\frac{n_2}{\tau_2} + \gamma_{II} n_3^2 - \gamma_{III} n_2 n_3 + \gamma_{IV} n_3 n_5 - \gamma_{VI} n_2 n_6, \quad (1b)$$

$$\begin{aligned} \dot{n}_3(t) = & -\frac{n_3}{\tau_3} - 2\gamma_I n_3^2 - 2\gamma_{II} n_3^2 - \gamma_{III} n_2 n_3 - \gamma_{IV} n_3 n_5 \\ & + \gamma_V n_4^2 - \gamma_{VII} n_3 n_5, \end{aligned} \quad (1c)$$

$$\dot{n}_4(t) = -\frac{n_4}{\tau_4} - 2\gamma_V n_4^2 + 2\gamma_{VI} n_2 n_6 + 2\gamma_{VII} n_3 n_5, \quad (1d)$$

$$\dot{n}_5(t) = -\frac{n_5}{\tau_5} + \gamma_{II} n_3^2 + \gamma_{III} n_2 n_3 - \gamma_{IV} n_3 n_5 + \gamma_V n_4^2 - \gamma_{VII} n_3 n_5, \quad (1e)$$

$$\dot{n}_6(t) = -\frac{n_6}{\tau_6} + \gamma_I n_3^2 + \gamma_{IV} n_3 n_5 - \gamma_{VI} n_2 n_6. \quad (1f)$$

In these expressions, $\gamma_I, \gamma_{II}, \gamma_{III}, \gamma_{IV}, \gamma_V, \gamma_{VI}$ and γ_{VII} are the coefficients of the ETU mechanisms depicted in Fig. 7 and described above and τ_i are the experimental lifetimes ob-

tained under OP excitation. Equations (1a)–(1f) are the simplest set of equations that take into account the one- and two-photon processes described in the above sections. In writing down the set of equations (1), some approximations are involved. Indeed, the terms describing the ESA processes are not included. The reason is that these processes occur on a time scale much shorter (pulse duration) than the time scale of the $^2H_{9/2}$ and $^4S_{3/2}$ decays. This implies that by the time the first data points are acquired, the ESA processes have already taken place. Therefore, the effect of these processes on the time scale of interest (milliseconds) can be substituted to an excellent approximation by initial populations of the levels involved. Another approximation that has been used in (1) consists in neglecting radiative decays from various levels other than into the ground state. The validity of this approximation is discussed in detail in Appendix B.

It is easy to realize that the coupled system (1) does not admit a closed solution in terms of elementary functions. However, it is easy to find analytical approximations to this solution by using perturbation theory and this is explained in detail in Appendix A. In particular, assuming that

$$\frac{n_3}{\tau_3} \gg 2\gamma_I n_3^2 + 2\gamma_{II} n_3^2 + \gamma_{III} n_2 n_3 + \gamma_{IV} n_3 n_5 - \gamma_V n_4^2 + \gamma_{VII} n_3 n_5, \quad (2)$$

i.e., the radiative component is much larger than any other term that depopulates $^4I_{9/2}$, the rate equations (1) can be solved to leading order in the ETU coefficients. This approximation is usually well justified and, in our particular case, it is experimentally observed that n_3 follows an exponential decay with a rate constant similar to τ_3 , which implies that (2) constitutes a very good approximation. Under this condition, Eqs. (1e) and (1f) can be easily solved perturbatively to first order in the ETU coefficients, as was done in Ref. 12 for a similar case. However, this solution does not provide the correct time dependence for the upconverted emission from the $^4S_{3/2}$ level in the present case. In particular, a term describing the short-time behavior of the decay (the one with a characteristic time of $635\text{ }\mu\text{s}$) does not appear in the solution. This means that condition (2) is likely not enough to describe the upconversion dynamic in the present system. In fact, if we take a look at Eq. (1c) one can easily realize that there are three types of terms on the right-hand side of that equation, the orders of magnitude of which are quite different. First, there is the term that describes the radiative decay. If only this term were present, the solution would be proportional to the initial population of the $^4I_{9/2}$ level at the time when the first data point is acquired (the so-called n_{30} in the paragraphs below). Second, if we use units in which n_{30} is one, there is also the term $-2\gamma_I n_3^2 - 2\gamma_{II} n_3^2$ that will give a contribution to the decay weighted by a factor $\sim \gamma_\alpha \tau_3$ to first order in γ_α , where α takes the value I or II. Finally, there are the terms $\gamma_{III} n_2 n_3, \gamma_{IV} n_3 n_5, \gamma_V n_4^2$, and $\gamma_{VII} n_3 n_5$. To first order, these terms contribute to the time dynamics of the $^4I_{9/2}$ level with terms that are weighted by factors of the form $n_{20} \gamma_{III} \tau_2, n_{50} \gamma_{IV} \tau_5, n_{40}^2 \gamma_V \tau_4$, and $n_{50} \gamma_{VII} \tau_5$, respectively. As these latter populations are experimentally found to be two or three orders of magnitude

smaller than n_{30} , the corresponding terms will be smaller than the ones associated to the γ_I and γ_{II} ETUs with regards to the dynamics of the $^4I_{9/2}$ level, even if we assume all the γ_α to be about the same. Moreover, one reaches the conclusion that second order terms in γ_I or γ_{II} could not only give a non-negligible contribution to the dynamics of the $^4S_{3/2}$ and $^2H_{9/2}$ levels, but they could even dominate the dynamics of the upconverted emission in a certain time range. Therefore, we solved the set of equations (1) perturbatively to first order in the terms that contain γ_{III} , γ_{IV} , γ_V , γ_{VI} , or γ_{VII} and to second order in the terms that contain γ_I or γ_{II} (see Appendix A). The resulting time evolution of the decays from the $^4F_{9/2}$, $^4S_{3/2}$, and $^2H_{9/2}$ levels is given by

$$n_4(t) = n'_{40}e^{-t/\tau_4} + n_{40}\gamma_V^{(4)}e^{-2t/\tau_4} - n_{60}\gamma_{VI}^{(4)}e^{-t/\tau_6} + n_{50}\gamma_{VII}^{(4)}e^{-t/\tau_5} + n_{30}\gamma_{VII}^{(4)}\gamma_{II}^{(5)}e^{-3t/\tau_3}, \quad (3a)$$

$$n_5(t) = -n_{40}\gamma_V^{(5)}e^{-2t/\tau_4} + n'_{50}e^{-t/\tau_5} + n_{30}(\gamma_I^{(3)} + \gamma_{II}^{(3)})\gamma_{II}^{(5)}e^{-3t/\tau_3} + n_{20}\gamma_{III}^{(5)}e^{-t/(1/\tau_2+1/\tau_3)} + n_{30}\gamma_{II}^{(5)}e^{-2t/\tau_3}, \quad (3b)$$

$$n_6(t) = n'_{60}e^{-t/\tau_6} + n_{30}\gamma_I^{(6)}e^{-2t/\tau_3} + n_{50}\gamma_{IV}^{(6)}e^{-t/(1/\tau_5+1/\tau_3)}. \quad (3c)$$

In these equations, we have used the following abbreviations:

$$n'_{40} = n_{40} - n_{40}\gamma_V^{(4)} + n_{60}\gamma_{VI}^{(4)} - n_{50}\gamma_{VII}^{(4)} - n_{30}\gamma_{VII}^{(4)}\gamma_{II}^{(5)}, \quad (4a)$$

$$n'_{50} = n_{50} - n_{30}\gamma_{II}^{(5)} + 2(\gamma_I^{(3)} + \gamma_{II}^{(3)})\gamma_{II}^{(5)} - (\gamma_I^{(3)} + \gamma_{II}^{(3)})\gamma_{II}^{(5)} - n_{20}\gamma_{III}^{(5)}, \quad (4b)$$

$$n'_{60} = n_{60} - n_{30}\gamma_I^{(6)} - n_{30}\gamma_{IV}^{(6)}, \quad (4c)$$

$$\gamma_I^{(3)} = 2n_{30}^2\gamma_I\tau_3, \quad (4d)$$

$$\gamma_{II}^{(3)} = 2n_{30}^2\gamma_{II}\tau_3, \quad (4e)$$

$$\gamma_V^{(4)} = 2n_{40}\gamma_V\tau_4, \quad (4f)$$

$$\gamma_{VI}^{(4)} = 2n_{20}\gamma_{VI}\left(\frac{1}{\tau_6} - \frac{1}{\tau_4}\right)^{-1}, \quad (4g)$$

$$\gamma_{VII}^{(4)} = 2n_{30}\gamma_{VII}\left(\frac{1}{\tau_4} - \frac{1}{\tau_5}\right)^{-1}, \quad (4h)$$

$$\gamma_{VII}^{(4)} = 2n_{30}\gamma_{VII}\left(\frac{1}{\tau_4} - \frac{3}{\tau_3}\right)^{-1}, \quad (4i)$$

$$\gamma_{II}^{(5)} = n_{30}\gamma_{II}\left(\frac{1}{\tau_5} - \frac{2}{\tau_3}\right)^{-1}, \quad (4j)$$

$$\gamma_{II}^{(5)} = n_{30}\gamma_{II}\left(\frac{1}{\tau_5} - \frac{4}{\tau_3}\right)^{-1}, \quad (4k)$$

$$\gamma_{III}^{(5)} = n_{30}\gamma_{III}\left(\frac{1}{\tau_5} - \frac{1}{\tau_2} - \frac{1}{\tau_3}\right)^{-1}, \quad (4l)$$

$$\gamma_V^{(5)} = n_{40}\gamma_V\left(\frac{2}{\tau_4} - \frac{1}{\tau_5}\right)^{-1}, \quad (4m)$$

$$\gamma_I^{(6)} = n_{30}\gamma_I\left(\frac{1}{\tau_6} - \frac{2}{\tau_3}\right)^{-1}, \quad (4n)$$

$$\gamma_{IV}^{(6)} = n_{30}\gamma_{IV}\left(\frac{1}{\tau_6} - \frac{1}{\tau_5} - \frac{1}{\tau_3}\right)^{-1}. \quad (4o)$$

The various $\gamma_\alpha^{(i)}$ have been chosen in such a way that they are positive. As mentioned above, the approximations that lead to Eqs. (3a)–(3c) are described in detail in Appendix A below. Let us now review some of the main characteristics of these solutions. Equation (3a) describes the predicted time evolution of the population of the $^4F_{9/2}$ level. The first term on the right-hand side describes a rise or decay in the population of this level (depending on its sign) with a time constant given by the lifetime of the level. The second term describes a decay with a time constant equal to half the lifetime of the $^4F_{9/2}$ level. Due to the fact that these two terms are proportional to the initial populations of this level and these are small quantities, they are masked by other larger terms, and do not appear in the experimental decay curves. The third term describes a rise of the population of this level with a characteristic time equal to the lifetime of the $^2H_{9/2}$ level. The fourth term represents a decay with a decay constant equal to the lifetime of the $^4S_{3/2}$ level. However, this term is proportional to n_{50} and very small and, again, it does not show up in the experimental decay curve. The last term on the right-hand side describes the decay of the population with a decay constant given by $\tau_3/3$, which is the decay observed experimentally at intermediate times.

Equation (3b) corresponds to the predicted time evolution of the population of the $^4S_{3/2}$ level. The first term on the right-hand side of that equation describes a rise in the population of the $^4S_{3/2}$ level with a characteristic time given by half the lifetime of the $^4F_{9/2}$ level. The second term could be a rise or a decay of the population of this level depending on whether the n'_{50} parameter is negative or positive and it “competes” with the third one in the time range $\tau_6 < t < \tau_3/2$. In fact, the best fit to the experimental decay data gives $n'_{50}=0.015$ and $n_{30}(\gamma_I^{(3)} + \gamma_{II}^{(3)})\gamma_{II}^{(5)}=0.059$. Therefore, the later dominates the dynamics in this time range and, experimentally, a decay with a characteristic time equal to $\tau_3/3 \cong 640 \mu s$ is observed. The last two terms in Eq. (3b) correspond to decays with characteristic times 1.36 and 0.97 ms, respectively, and any of them could dominate the long-time dynamics ($t > \tau_3/2$) depending on their relative weights. The best fit to the experimental data gives $n_{20}\gamma_{III}^{(5)}=0.046$ and $n_{30}\gamma_{II}^{(5)}=0.005$ and, thus, the ETU process involving the $^4I_{9/2}$ and $^4I_{13/2}$ levels dominates the long-time dynamics (ETU III).

Let us now turn our attention to the time evolution of the population in the $^2H_{9/2}$ level, described by Eq. (3c). The first term on the right-hand side of that equation could describe a rise or a decay of the population in this level with a characteristic time equal to its lifetime. The best fit to that equation yields a value $n'_{60} = -0.12$ and, thus, the model predicts a rise of the population in the $^2H_{9/2}$ level with a characteristic time equal to its lifetime, in agreement with the experimental observation. The second and third terms on the right-hand side of that expression describe a two-step decay of the population. The short component ($t < \tau_3/2$) has a characteristic time equal to $(1/\tau_3 + 1/\tau_5)^{-1} = 0.165$ ms and the long component has a characteristic time equal to $\tau_3/2 = 0.97$ ms, respectively, in excellent agreement with the experimental data.

Once we have justified that these ETU processes can qualitatively describe the population dynamics of the $^2H_{9/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels under pulsed excitation, we can use the fits to the analytical approximations provided by Eqs. (3) to extract the values of the ETU coefficients by using the set of definitions (4) and the measured lifetimes. The theoretical fits are reported in Figs. 5(a), 6(b), and 9 for the blue, green, and red emissions, respectively. The values for the ETU coefficients obtained from those fits are 246, 2307, 194, 2299, 2241, 2043, and 182 S^{-1} for γ_I , γ_{II} , γ_{III} , γ_{IV} , γ_V , γ_{VI} , and γ_{VII} , respectively. It is worth noticing that the theoretical curves are in excellent agreement with the experimental ones in the whole temporal range and for both emissions, which is a strong support for the validity of the model described above.

V. CONCLUSIONS

We have analyzed the dynamics of the upconversion processes in Er^{3+} -doped low-phonon-energy crystal KPb_2Br_5 under excitation in the $^4I_{9/2}$ level. Resonant excitation of the $^4I_{9/2}$ level leads to emission from the $^2H_{9/2}$ and $^4S_{3/2}$ levels, whereas nonresonant excitation at lower energies than $^4I_{9/2}$ results in emission mainly from the $^2H_{9/2}$ level. The excitation spectra of the upconverted luminescence show that the $^4S_{3/2}$ level is populated by energy transfer upconversion, whereas the $^2H_{9/2}$ level is populated by ESA and ETU depending on the excitation energy. A careful analysis of the temporal dynamics of the upconverted luminescence was necessary in order to identify the nature of the ETU mechanisms. As a conclusion, it is shown that the upconverted emission from the $^2H_{9/2}$ level is due to two ETU processes which involve the $^4I_{9/2}$ and $^4S_{3/2}$ levels, whereas the emission from the $^4S_{3/2}$ level involves three ETU processes which include the populations of the $^4F_{9/2}$, $^4I_{9/2}$, and $^4I_{13/2}$ levels. The temporal dynamics of the upconverted emission from $^2H_{9/2}$ and $^4S_{3/2}$ levels has been modeled by a simple rate equation analysis. This model is found to describe very well the temporal dynamics of both the blue and green emissions in the whole temporal range.

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APPENDIX A

Let us consider the set of equations (1). We will assume that the time dependence of the populations of the electronic levels involved in the upconversion process can be written as

$$n_i(t) = n_i^{(0)}(t) + n_i^{(1)}(t) + n_i^{(2)}(t) + \dots \quad (i = 2, 3, \dots, 6), \quad (A1)$$

where $n_i^{(\alpha)}(t)$ contains α th powers of the ETU coefficients. Therefore, $n_i^{(0)}(t)$ does not depend on the ETU coefficients, $n_i^{(1)}(t)$ is linear in these parameters, $n_i^{(2)}(t)$ is quadratic, and so on. Furthermore, without loss of generality, we will assume that

$$n_i^{(0)}(0) = n_{i0} \quad (A2)$$

and, thus, $n_i^{(\beta)}(0) = 0$ for $\beta \geq 1$. Substituting Eq. (A1) back into the set of equations (1), one gets

$$n_i^{(0)} + \frac{n_i^{(0)}}{\tau_i} = 0 \quad (A3)$$

to zeroth order in γ_α , which has the trivial solution

$$n_i^{(0)}(t) = n_{i0} e^{-t/\tau_i}. \quad (A4)$$

To first order in the ETU coefficients, one gets the following set of equations:

$$n_2^{(1)} + \frac{n_2^{(1)}}{\tau_2} = \gamma_{II} n_3^{(0)} n_3^{(0)} - \gamma_{III} n_2^{(0)} n_3^{(0)} + \gamma_{IV} n_3^{(0)} n_5^{(0)} - \gamma_{VI} n_2^{(0)} n_6^{(0)}, \quad (A5a)$$

$$n_3^{(1)} + \frac{n_3^{(1)}}{\tau_3} = -2(\gamma_I + \gamma_{II}) n_3^{(0)} n_3^{(0)} - \gamma_{III} n_2^{(0)} n_3^{(0)} - \gamma_{IV} n_3^{(0)} n_5^{(0)} + \gamma_V n_4^{(0)} n_4^{(0)} - \gamma_{VII} n_3^{(0)} n_5^{(0)}, \quad (A5b)$$

$$n_4^{(1)} + \frac{n_4^{(1)}}{\tau_4} = -2\gamma_V n_4^{(0)} n_4^{(0)} + 2\gamma_{VII} n_2^{(0)} n_6^{(0)} + 2\gamma_{VII} n_3^{(0)} n_5^{(0)}, \quad (A5c)$$

$$n_5^{(1)} + \frac{n_5^{(1)}}{\tau_5} = \gamma_{II} n_3^{(0)} n_3^{(0)} + \gamma_{III} n_2^{(0)} n_3^{(0)} - \gamma_{IV} n_3^{(0)} n_5^{(0)} + \gamma_V n_4^{(0)} n_4^{(0)} - \gamma_{VII} n_3^{(0)} n_5^{(0)}, \quad (A5d)$$

$$n_6^{(1)} + \frac{n_6^{(1)}}{\tau_6} = \gamma_I n_3^{(0)} n_3^{(0)} + \gamma_{IV} n_3^{(0)} n_5^{(0)} - \gamma_{VI} n_2^{(0)} n_6^{(0)}, \quad (A5e)$$

which can be easily solved to yield

$$n_3^{(1)}(t) \approx n_{30}(\gamma_I^{(3)} + \gamma_{II}^{(3)})(e^{-2t/\tau_3} - e^{-t/\tau_3}), \quad (A6a)$$

$$n_4^{(1)} = [-n_{40}\gamma_V^{(4)} + n_{60}\gamma_{VI}^{(4)} - n_{50}\gamma_{VII}^{(4)}]e^{-t/\tau_4} + n_{40}\gamma_V^{(4)}e^{-2t/\tau_4} - n_{60}\gamma_{VI}^{(4)}e^{-t/\tau_6} + n_{50}\gamma_{VII}^{(4)}e^{-t/\tau_5}, \quad (\text{A6b})$$

$$n_5^{(1)} = [-n_{30}\gamma_{II}^{(5)} - n_{20}\gamma_{III}^{(5)} + n_{40}\gamma_V^{(5)}]e^{-t/\tau_5} + n_{30}\gamma_{II}^{(5)}e^{-2t/\tau_3} - n_{40}\gamma_V^{(5)}e^{-2t/\tau_4} + n_{20}\gamma_{III}^{(5)}e^{-t(1/\tau_2+1/\tau_3)} + n_{50}(\gamma_{IV}^{(5)} + \gamma_{VII}^{(5)}) \times (e^{-t(1/\tau_5+1/\tau_3)} - e^{-t/\tau_5}), \quad (\text{A6c})$$

$$n_6^{(1)}(t) = [-n_{30}\gamma_I^{(6)} - n_{50}\gamma_{IV}^{(6)}]e^{-t/\tau_6} + n_{30}\gamma_I^{(6)}e^{-2t/\tau_3} + n_{50}\gamma_{IV}^{(6)}e^{-t(1/\tau_3+1/\tau_5)} + n_{60}\gamma_{VI}^{(6)}(e^{-t(1/\tau_6+1/\tau_2)} - e^{-t/\tau_6}), \quad (\text{A6d})$$

where we have used the notations (4a)–(4o), $\gamma_{VII}^{(5)} = n_{30}\gamma_{VII}\tau_3$, and $\gamma_{VI}^{(6)} = n_{20}\gamma_{VI}\tau_2$. In order to obtain Eq. (A6a), we have used the fact that terms proportional to the initial populations n_{20} and n_{50} are negligible compared to terms proportional to n_{30} . Also, in writing down Eqs. (3b) and (3c), the last terms in Eqs. (A6c) and (A6d) can be dropped because $\tau_3 \gg \tau_5$ and $\tau_2 \gg \tau_6$, respectively.

As one can easily notice from the results obtained so far, $n_6(t) \equiv n_6^{(0)}(t) + n_6^{(1)}(t)$ qualitatively describes the time dynamics of the blue fluorescence from level $^2H_{9/2}$. However, with regard to the time dependence of the green fluorescence from level $^4S_{3/2}$ and the red fluorescence from level $^4F_{9/2}$, none of the terms obtained so far would correctly describe the decay of the luminescence occurring immediately after the rise. Therefore, let us consider the next term in the perturbation expansion. The second-order equations for the levels of interest are given by

$$n_4^{(2)} + \frac{n_4^{(2)}}{\tau_4} \approx 2\gamma_{VII}n_3^{(0)}n_5^{(1)} \approx 2\gamma_{VII}n_{30}^2\gamma_{II}^{(5)}e^{-3t/\tau_3}, \quad (\text{A7a})$$

$$n_5^{(2)} + \frac{n_5^{(2)}}{\tau_5} \approx 2\gamma_{II}n_{30}^{(0)}n_3^{(1)}, \quad (\text{A7b})$$

$$n_6^{(2)} + \frac{n_6^{(2)}}{\tau_6} \approx 2\gamma_I n_{30}^{(0)}n_3^{(1)}, \quad (\text{A7c})$$

where, again, we have neglected terms proportional to the initial populations n_{20} , n_{40} , n_{50} , and n_{60} (this has been explicitly indicated for n_4). The solution to these equations is given by

$$n_4^{(2)}(t) \approx n_{30}\gamma_{VII}^{(4)}\gamma_{II}^{(5)}(e^{-3t/\tau_3} - e^{-t/\tau_4}), \quad (\text{A8a})$$

$$n_5^{(2)}(t) \approx 2n_{30}\gamma_{II}^{(5)}(\gamma_I^{(3)} + \gamma_{II}^{(3)})(e^{-3t/\tau_3} - e^{-t/\tau_5}) - 2n_{30}\gamma_{II}^{(5)}(\gamma_I^{(3)} + \gamma_{II}^{(3)})(e^{-2t/\tau_3} - e^{-t/\tau_5}), \quad (\text{A8b})$$

$$n_6^{(2)}(t) \approx 2n_{30}\gamma_I^{(6)}(\gamma_I^{(3)} + \gamma_{II}^{(3)})(e^{-3t/\tau_3} - e^{-t/\tau_6}) - 2n_{30}\gamma_I^{(6)}(\gamma_I^{(3)} + \gamma_{II}^{(3)})(e^{-2t/\tau_3} - e^{-t/\tau_6}), \quad (\text{A8c})$$

where $\gamma_I^{(6)} = n_{30}\gamma_I(1/\tau_6 - 3/\tau_3)^{-1}$ and the other notations are defined in Eqs. (4a)–(4o). Using Eqs. (A4), (A6), and (A8) in Eq. (A1), one immediately gets a second-order solution for the set of equations (1) above. Notice, however, that some further approximations have been used in writing down (3). First, the second terms on the right-hand side of both (A8b) and (A8c) can be neglected because they are much smaller than the corresponding ones at first order [see Eqs. (A6)]. Moreover, it is important to notice that $\gamma_I^{(6)}$ is approximately proportional to τ_6 , whereas $\gamma_{II}^{(5)}$ is approximately proportional to τ_5 (because both τ_5 and τ_6 are much smaller than τ_3). Therefore, the second order term $n_5^{(2)}$ is five times larger than $n_6^{(2)}$ and this latter correction can be neglected to a very good approximation. In this way, Eqs. (3a)–(3c) are obtained.

APPENDIX B

As mentioned above, in writing down Eqs. (1) we have neglected radiative decays from various levels other than into the ground state. To see that this approximation is well justified, let us consider a simple case where radiative emission from $^4I_{9/2}$ into $^4I_{13/2}$ is taken into account. This corresponds to adding a term of the form $\beta n_3/\tau_3$ to Eq. (1b), with β the branching ratio for this radiative transition. This term leads to a correction to the zeroth-order expression for n_2

$$n_2^{(0)}(t) = n_{20}e^{-t/\tau_2} + \beta \frac{\tau_2}{\tau_2 - \tau_3}(e^{-t/\tau_2} - e^{-t/\tau_3}). \quad (\text{B1})$$

This term would lead to a contribution to the dynamics of the $^4S_{3/2}$ level given by

$$- \gamma_{III}n_{30}\beta \frac{\tau_2}{\tau_2 - \tau_3} \frac{\tau_5\tau_3}{\tau_3 - 2\tau_5}(e^{-2t/\tau_3} - e^{-t/\tau_5}).$$

The only nontrivial term in this expression is the rise with a characteristic rise time of $\tau_3/2$, which is much longer than $\tau_5/2$ and, thus, is not effective in populating the $^4S_{3/2}$ level.

With regards to the dynamics of the $^2H_{9/2}$ level, the last term of Eq. (B1) leads to a contribution given by

$$\gamma_{VI}n_{60}\beta \frac{\tau_2^2}{\tau_2 - \tau_3}(e^{-t(1/\tau_2+1/\tau_6)} - e^{-t/\tau_6}) - \gamma_{VI}n_{60}\beta \frac{\tau_2\tau_3}{\tau_2 - \tau_3}(e^{-t(1/\tau_3+1/\tau_6)} - e^{-t/\tau_6}),$$

which leads to a negligible contribution to the dynamics of this level because $\tau_2 \gg \tau_6$ and $\tau_3 \gg \tau_6$. A similar line of reasoning applies to the other radiative transitions neglected in (1).

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