Intra-Stark Relaxation of Nd^{3+} in Silicate Glass: Subpicosecond Accumulated Photon Echo Experiments

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UCRL--101088
DE90 002786

We have directly measured in the time domain the rates of phonon-induced population relaxation within the $^4G_{5/2}$, $^2G_{7/2}$ Stark manifold of Nd^{3+} in a silicate glass. At 13 K, these processes occur in the picosecond to subpicosecond time regime. The population relaxation time increases with excitation frequency within each inhomogeneously broadened Stark component. Finally, the location of the Stark components within the entire inhomogeneous profile can be inferred from the data.

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1. Introduction

Information on the dynamics of the relaxation processes within a Stark manifold of rare earth ions is difficult to obtain due to the fast time scale on which these processes occur. This type of information is useful, for example, in the design of solid state lasers and amplifiers based on rare earth ions. Previous work on Nd^{3+} in ED-2 silicate glass [1] elucidated the temperature dependence of the dephasing rate for the transition from the $^4I_{9/2}$ level to the lowest Stark component of the $^4G_{5/2}$, $^2G_{7/2}$ manifold. A partial frequency dependence of the dephasing rate was also measured [1]. We have studied the relaxation processes within the inhomogeneously broadened $^4G_{5/2}$, $^2G_{7/2}$ Stark manifold of Nd^{3+} ions in a silicate glass with subpicosecond accumulated photon echo experiments [2]. We have measured the dephasing rate as a function of spectral position within the entire inhomogeneously broadened Stark manifold, thus providing information on the intra-Stark manifold relaxation mechanisms. The results include the direct measurement in the time domain of the rates of the phonon scattering processes within the Stark manifold. The positions of the Stark components can be inferred from the data.

2. Experimental

The accumulated photon echo technique has been described previously [2]. The subpicosecond laser pulses, of approximately 0.4-0.5 ps width, were generated by a tunable hybridly mode-locked dye laser synchronously pumped by the frequency doubled output of a mode-locked Nd:YAG laser operating at a 76 MHz repetition rate. The total average power incident on the sample did not exceed $1 kW/cm^2$ and was often less, depending on

the optical density of the sample. The sample consisted of a 3 mm thick piece of 0.3 mole % Nd^{3+}-doped silicate glass (Hoya #5010). The sample was held in a closed-cycle helium refrigeration unit cooled to 13 K. The "pump" beam was modulated at 2 kHz and the echo signal, which is coincident with the "probe" beam, was lock-in detected at the modulation frequency. The laser pulses excited the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition of Nd^{3+}, while the $^4F_{3/2}$ state served as the metastable level permitting the accumulation of the phase information in the ground state [2].

3. Results and discussion

The variation of the dephasing rate of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition of Nd^{3+} in a silicate glass as a function of excitation wavelength at 13 K is shown in Figure 1. Deconvolution was performed when the echo decay times were comparable to the laser pulse width. Both single and biexponential photon echo decays were observed, as was also seen in ED-2 glass [1]. Biexponential decays are indicated in Figure 1 by plotting both decay rates of the biexponential at the pertinent wavelength. The slow decay rate of the biexponential is designated in Figure 1 by a cross and the fast decay rate by a circle. Single exponential decays are also designated by a circle. Figure 1 shows that the data can be grouped into regions where the dephasing rate is a smoothly varying function of the excitation wavelength. These regions are encircled in Figure 1. It will be later shown that these regions correspond to the location of individual Stark components.

The absorption spectrum is superimposed in Figure 1 as a solid line. It is apparent that the dephasing rate is not a function of the absorption. Furthermore, rapid dephasing induced by the delocalization of excited electronic states has been shown to involve a wavelength dependent dephasing rate that qualitatively follows the absorption profile [3]. Clearly, this is not the case, as expected, since a low concentration of Nd^{3+} was used (0.3 mole %). Rapid spectral diffusion has also been invoked to explain a previous observation of a nonexponential echo decay [4]. However, such diffusion processes should be present at all wavelengths excited and not just selected ones.

We argue that the smoothly varying regions arise from the excitation of a single inhomogeneously broadened Stark component and reflect the variation of the dephasing rate within that component. Previous work on the $^7F_0 \leftrightarrow {}^5D_0$ transition of Eu^{3+} in a silicate glass, where a single Stark component is involved, demonstrated a similar smooth variation in the homogeneous fluorescence linewidth with wavelength [5]. In the Eu^{3+} system, the linewidth decreased with excitation wavelength [5], while an increase with excitation wavelength is observed here.

The biexponential decays can be understood by realizing that excitation by a subpicosecond laser pulse with a 45 cm^{-1} spectral width, such as was used here, will encounter spectral regions where two or more inhomogeneously broadened Stark components overlap. These Stark components may have different dephasing rates, thus resulting in nonexponential echo decays or biexponential echo decays when two components are excited. Nonexponential fluorescence decays have previously been attributed to the excitation of overlapping Stark components [6].

Further supporting evidence is given by the following observations. Each of the two dephasing rates of a biexponential echo decay fits into a pattern where the dephasing rate varies smoothly with the excitation wavelength. In addition, the $^4G_{5/2}$, $^2G_{7/2}$ Stark manifold should exhibit at most seven Kramers degenerate levels. Our results show seven spectral regions where the dephasing rate varies smoothly with the excitation wavelength. Finally, the coefficients of the two exponentials in a biexponential fit change with wavelength in a manner reflecting the spectral overlap of two lines. Thus, one may infer that the individual Stark components are located in those encircled spectral regions

The question arises as to the origin of the smoothly varying dephasing rate within each Stark component. The dephasing rate decreases with excitation energy. The fluorescence line narrowing (FLN) work in Ref. [5] on Eu^{3+} attributed the homogeneous linewidth to a Raman pure dephasing process, and the variation of the linewidth was concluded to result from the variation of the electron-phonon coupling constant with excitation energy. However, since the $^7F_0 \leftrightarrow {}^5D_0$ transition was studied, the excited and ground states are both single levels, precluding single phonon scattering.

In the Nd^{3+} system, the dephasing rate ($1/T_2$) has four contributions, the rates of which vary widely depending in part on the phonon density of states, the temperature, and the energy splittings. Radiative decay of the excited state accounts for the first contribution, which for f-f transitions of rare earth ions is negligible relative to the other contributions.

The second contribution comes from the interaction of the ion with the "two-level-systems" (TLS) or tunneling states of the glass [7], while the third contribution involves Raman pure dephasing processes. The contribution from the Raman pure dephasing and TLS dephasing mechanisms can be estimated from previous accumulated photon echo data on the same transition in Nd^{3+} in ED-2 silicate glass [1]. The data was taken at the longest possible wavelength (591 nm) to avoid direct phonon processes. At 13 K the data yielded a dephasing rate of 3.8 GHz. We can also consider previous FLN data on the $^7F_0 \leftrightarrow {}^5D_0$ transition of Eu^{3+} in a silicate glass [8]. In this example, direct phonon relaxation processes are strictly absent. The results indicated a dephasing rate of 5.27 GHz at 13 K. These consistently small rates in comparison to our observed dephasing rates demonstrate that the TLS and Raman pure dephasing mechanisms are negligible at 13 K.

Nonadiabatic phonon scattering processes between the Stark components of the excited state and ground state manifolds account for the fourth contribution. This includes one phonon, multiphonon, and Orbach processes. At low temperatures, multiphonon processes, which arise from higher orders in the electron-phonon interaction, are generally much slower than direct one phonon processes, provided that the one phonon density of states spans the relevant energy splittings. Stark splittings for rare earth ions are generally on the order of 10 to 100 cm^{-1} [9]. The width of the entire absorption profile of this manifold is 725 cm^{-1}. A reasonable phonon density of states can be determined from the measured differential Raman cross section [10]. This was done for the differential Raman cross section data on ED-4 silicate glass of Hellwarth et al. [11]. This calculation showed sufficient phonon density of states

to span the entire inhomogeneous line. Accordingly, we eliminate multiphonon processes. Phonon scattering in the $^4I_{9/2}$ ground state manifold is negligible. The nearest Stark level is approximately 100-150 cm^{-1} removed [12], making phonon absorption at 13 K insignificant.

We thus conclude that the predominant dephasing mechanism involves nonradiative population relaxation. This proceeds via one phonon processes and possibly Orbach processes. The rate of population leaving a specific Stark level is then given by twice the dephasing rate shown in Figure 1, and the wavelength dependence of the dephasing rate reflects the wavelength dependence of the population relaxation. It would be useful to continue this study at even lower temperatures where the relaxation simplifies to only phonon emission, thus giving direct information on the electron-phonon coupling constants. One phonon processes have also been observed in the time domain on the $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ transitions of Pr^{3+} in LaF_3 [13].

The dephasing rate for one-phonon absorption and emission processes is given in equation (1a).

$$\frac{1}{T_2} \propto \sum_{s,s'} \{|F(\omega_s)|^2 \rho(\omega_s) n(\omega_s) + |F(\omega_{s'})|^2 \rho(\omega_{s'})[n(\omega_{s'}) + 1]\} \qquad (1a)$$

$$\frac{1}{T_2} \propto \sum_{s,s'} \{F_s^2 \left(\frac{\omega_s}{\omega_D^2}\right)^3 n(\omega_s) + F_{s'}^2 \left(\frac{\omega_{s'}}{\omega_D^2}\right)^3 [n(\omega_{s'}) + 1]\} \qquad (1b)$$

The dephasing rate for an Orbach process is identical to the dephasing rate from phonon absorption. F is the one phonon electron-phonon coupling constant, the ω_s's are the energy splittings to levels to which the relaxation occurs, $\rho(\omega_s)$ is the phonon density of states,

and $n(\omega_s)$ is the Bose-Einstein distribution function. If a Debye density of states and long wavelength phonons are considered, then equation (1b) results, where ω_D is the Debye frequency.

Equation (1) gives two reasons for the variation of the dephasing rate. The first involves the variation of the Stark splittings (ω_s) within the total inhomogeneous line, which appears explicitly in equation (1). In this case, the Stark splittings must decrease with excitation frequency, which implies a strong correlation with the inhomogeneous broadening of the Stark components. The precise splitting pattern can be deduced from the variation of the dephasing rate. If equation (1b) is relevant, then the Stark splittings must decrease with excitation frequency faster than the decrease of the cube root of the dephasing rate with excitation frequency. The second reason involves a variation of the electron-phonon coupling constant, F, within a Stark component. In this case, the coupling constants must decrease with frequency. Of course, both cases may be relevant.

In summary, we have directly measured in the time domain the rates of phonon-induced population relaxation within the $^4G_{5/2}$, $^2G_{7/2}$ Stark manifold of Nd^{3+} in a silicate glass. At 13 K these processes occur in the picosecond to subpicosecond time regime, which is consistent with previous calculations and observations in similar systems [9, 13]. Furthermore, the population relaxation rate decreases with excitation frequency within each inhomogeneously broadened Stark component. However, the correlation of the inhomogeneous broadening among the Stark components is not known. This correlation would provide the energy splittings (ω_s) in equation (1) and help determine whether the observed variation of the dephasing rates with excitation frequency

results from a variation in the Stark splittings or from a variation in the electron-phonon coupling constants, or from both. Finally, the location of the Stark components within the entire inhomogeneous line can be inferred from our data.

4. Acknowledgments

The author wishes to thank R. S. Hughes, Jr. for technical assistance, R. W. Adair for help in the computer programming, and Dr. L. L. Chase for stimulating discussions. The author further thanks Coherent, Inc. for the generous loan of the dye laser until one could be acquired. This work was performed under the auspices of the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, by the Lawrence Livermore National Laboratory under contract no. W-7405-ENG-48.

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Figure Caption

Figure 1. Variation of the dephasing rate of the $^4I_{9/2} \leftrightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition of Nd^{3+} in a silicate glass as a function of excitation wavelength at 13 K. See text for explanation.

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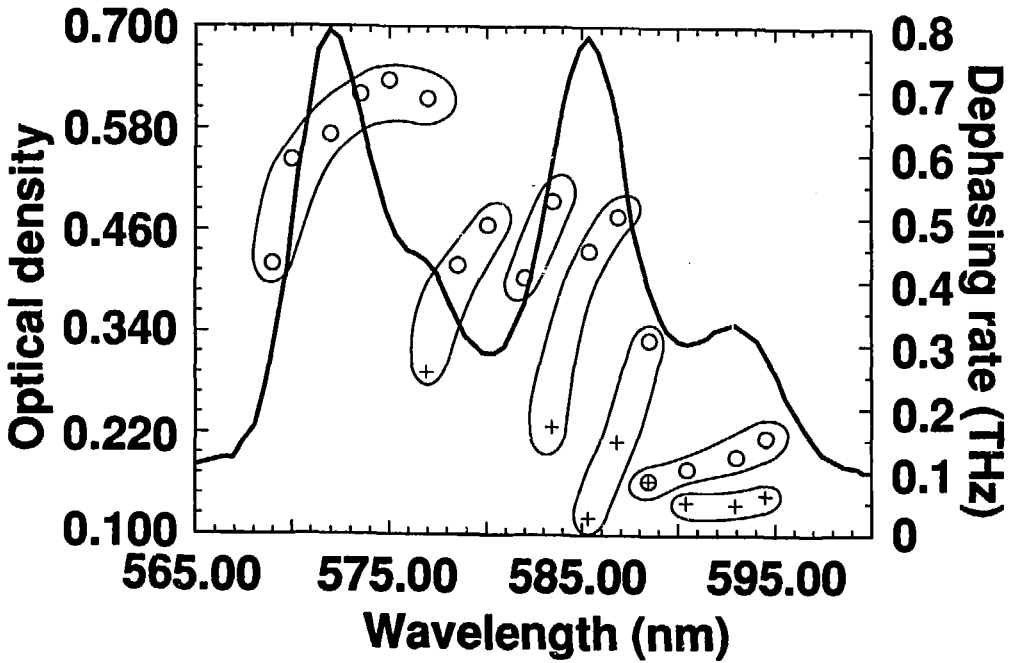
0.700
0.580
0.460
0.340
0.220
0.100
Optical density
565.00
575.00
585.00
595.00
Wavelength (nm)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Dephasing rate (THz)

Figure 1