

Non-equilibrium effects in copper vapor laser pumped Nd^{3+} doped PVA film: Photo-electron paramagnetic resonance and photoacoustic spectral investigations

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Abstract. Photo-EPR measurements carried out on Nd^{3+} -doped polyvinyl alcohol (PVA) films have shown that nearly 100% reduction occurs in the intensity of EPR of Nd^{3+} under *in situ* copper vapor laser (CVL) illumination (510.5 nm and 578.2 nm). The kinetics of decay and recovery were investigated. Photoacoustic (PA) spectra, observed under CVL pump condition had shown that the CVL induced changes were not due to photoinduced valence change, and that the CVL pumping creates highly favorable conditions for non-equilibrium population distribution in the excited electronic states. The complete disappearance of EPR under CVL pumping is attributed either to the possible equalization of population of $|+\rangle$ and $|-\rangle$ Zeeman components, through the decay of many excited states in the presence of magnetic field or configurational changes around Nd^{3+} shifting the resonance frequency. The former appears less probable in view of the relatively slower recovery of EPR signal.

Keywords. Electron paramagnetic resonance; photoacoustic spectroscopy; polyvinyl alcohol.

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1. Introduction

Development of materials for holography and non-linear optics, that respond in real time and involve no chemical or thermal treatment, is of immense current interest. The real time diffraction efficiency of the recorded volume holograms depends basically on the efficiency of the photoinduced electron transfer and the kinetics of recovery under dark conditions. Early attempts in this direction were directed at inorganic crystals like LiNbO_3 , BaTiO_3 , $\text{Bi}_{12}\text{SiO}_{20}$, $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ etc [1]. In most of these compounds, the role of impurities, particularly that of Fe^{3+} , was found to be substantial in the photoinduced electron transfer and, thereby, in the formation of holograms. For the multitude of applications in holography and optics, mechanically flexible systems have obvious advantages and in this connection organic materials exhibiting photoconductivity and non-linear optical properties

are attracting considerable attention [2–4]. There are some reports on Cr(VI)- and Fe(III)-doped polyvinyl alcohol films as real time holographic recording materials [5,6]. The basic step envisaged in the formation of hologram is the photoinduced charge transfer. Such a process would result in valence change and/or creation of unpaired electron centers in the polymers [7]. At low concentration levels, ideal methods of investigating these processes are electron paramagnetic resonance (EPR) and electronic absorption. For thin films, the electronic absorption data can be conveniently obtained by photoacoustic absorption spectroscopy under pump-probe conditions. In this paper we present the EPR results on PVA film doped with Nd^{3+} , in the 13–40 K temperature range and the effects of *in situ* illumination using a copper vapor laser. The most interesting finding is the substantial reduction in the EPR intensity of Nd^{3+} ion on exposure to CVL and the kinetics involved in this process. To the best of our knowledge, this is the only example of near hundred per cent change of an impurity EPR on laser illumination. To examine whether this is due to valence change of Nd^{3+} ion, we have conducted photoacoustic spectral (PAS) investigation under copper vapor laser pump condition. The probing beam is the light from a conventional source. Clear evidence is presented to suggest that there is no valence change, and that the system is highly favorable for creating a population and/or thermal grating. The disappearance of EPR signal appears to be due to possible configurational changes, with many energetically equivalent positions around Nd^{3+} in PVA glass matrix, on laser illumination.

2. Experimental

Polyvinyl alcohol film doped with neodymium (10% by weight) was grown by slow evaporation of aqueous solution at room temperature [8]. A known amount of PVA was dissolved in quartz double distilled water and then slightly heated under infrared lamp. The required amount of neodymium oxide dissolved in HCl was mixed with the PVA solution. The solution mixture was stirred thoroughly and was spread on a plain glass surface. The film formed on evaporation of the solution was peeled off from the glass surface after 48 h. The film was washed with alcohol and completely dried for further experimental use.

The EPR spectra were obtained between 13–40 K on a Bruker ESP-300, X-band spectrometer. A closed cycle helium refrigerator obtained from APD cryogenics, USA was used for temperature variation studies. The film was loaded in a rectangular optical transmission cavity (Bruker model TE_{103}). Optical illumination was done using a 10 W copper vapor laser lasing at 510.5 nm (green) and 578.2 nm (yellow). The laser was situated far from the EPR spectrometer. The power measured at the entrance of the cavity was 100 mW. It is known that 70% of the power is concentrated at 510.5 nm. The sample was loaded on *c*-axis oriented sapphire cold finger or high conductivity oxygen free copper cold finger obtained from M/s APD cryogenics. As we have some impurity EPR lines in sapphire to monitor the possible temperature changes on laser illumination, some experiments were conducted using sapphire cold finger (without sample) filling the whole volume of the cavity. This was done to ascertain that the observed temperature dependent changes in the EPR of impurity in sapphire are not artifacts due to temperature dependent expansion of sapphire. It may be noted that during the experiment the cavity remains at room temperature. Photoacoustic spectral studies were done using a home-built spectrometer described elsewhere [8,9].

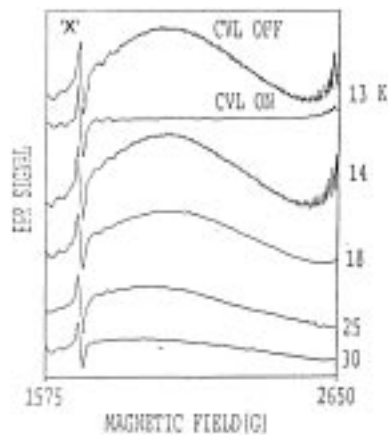


Figure 1. EPR spectra of Nd^{3+} -doped PVA film recorded at 13, 14, 18, 25 and 30 K. The spectrum obtained at 13 K under CVL illumination is also shown. The line marked 'X' is EPR line due to impurity in sapphire (not the one used for estimating temperature rise). It may be noted that it is unaffected by CVL illumination.

3. Results and discussion

3.1 Experimental results

Figure 1 shows the EPR spectra of PVA film doped with Nd^{3+} , recorded at different temperatures in the range 13–30 K with and without CVL illumination. The EPR spectrum of Nd^{3+} :PVA film disappeared almost completely on illumination with CVL. The decay and recovery of EPR signal of Nd^{3+} with CVL illumination ON and OFF respectively were monitored. This was done by recording the time dependence of the intensity of EPR signal with the field locked at the peak position of the EPR signal. These experiments were conducted at different temperatures. The decay and recovery curves at 15 K are shown in figure 2. The experimental decay curves were theoretically fitted using single and double exponential functions. Single exponential gave a reasonably good fit. However, inclusion of a slow decay double exponential has improved the fitting. In view of the very large value of τ_2 (1480 s) compared to τ_1 (0.40 s), it may be inferred that the kinetics are primarily controlled by τ_1 . The decay constants were found to be temperature independent.

3.2 Discussion

3.2.1 EPR identification: The lanthanide ion Nd^{3+} has large orbital contribution in its electronic ground state and its EPR is observable only at rather low temperatures. It has an electronic configuration of $4f^3$ with a free ion ground state of $^4I_{9/2}$. Abragam and Bleaney [10] described the form of the ground state Kramers' doublets and calculated the expected g -values. By considering the admixture of the excited $J = 11/2$ state, the

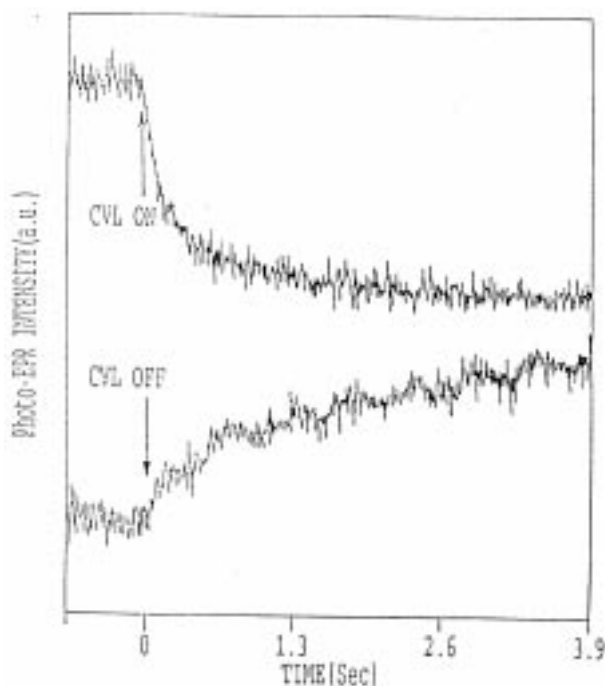


Figure 2. The decay and recovery of Nd^{3+} signal with CVL illumination ON and OFF at 15 K. The magnetic field was kept constant at the peak position of EPR signal.

calculated g -values are $g_{\parallel} = -0.32$ and $g_{\perp} = 2.72$. The total abundance of odd isotopes, ^{143}Nd and ^{145}Nd ($I = 7/2$), amounts to 20% while the 80% abundant even isotope, ^{142}Nd has $I = 0$. Therefore, no prominent hyperfine structure is expected. The field at which the parallel component is expected goes well beyond the range of our magnet. The perpendicular component (in near axial field) is expected at $g = 2.72$ and this agrees with the value 2.716 obtained in our experiment.

3.2.2 Effect of CVL illumination: From the experimental results it is observed that EPR of Nd^{3+} shows remarkable changes under CVL illumination. The lasing lines of CVL at 510.5 nm and 578.2 nm overlap with the known absorption bands of Nd^{3+} in condensed matter. The yellow line coincides with $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition of Nd^{3+} and the upper state with long lifetime is known to take part in frequency upconversion due to excited state absorption [11–14]. Therefore CVL is very effective for excitation of Nd^{3+} ions. The near absence of EPR signal of Nd^{3+} on CVL illumination can be due to one or more of the following: (i) purely thermal effects due to laser illumination, (ii) significant changes in the valence of Nd^{3+} , (iii) significant depletion of the population of the ground state, i.e. highly efficient population inversion due to optical pumping with CVL and (iv) optically induced equalization of the population of $|+\rangle$ and $|-\rangle$ spin states, which has the same effect as that of completely saturating the EPR signal. Before discussing these aspects, it may be re-emphasized that the microwave cavity is at room temperature and only the sample tem-

perature is varied. The temperature induced changes are not artifacts of changes in cavity dimensions. In addition to these, there may be yet another possible reason for the disappearance of EPR signal. On excitation with CVL the sample becomes photoconducting and interaction between mobile conduction electrons and local moment on Nd^{3+} would wash out the EPR signal. The PAS studied have not given any indication of photoconductivity, and only the other possibilities mentioned are discussed below.

(i) *Possible thermal effects:* The temperature rise during the laser illumination could be very precisely determined from the temperature dependence of an impurity resonance in the sapphire rod used for loading the sample in closed cycle helium refrigerator. The EPR spectrum of sapphire rod has shown a signal at $H = 2976$ G at 15 K. The position of this resonance was found to be highly temperature dependent. The temperature dependence of this EPR signal was studied in 15–300 K range. This is shown in figure 3. The origin of this line could not be identified. However, the asymmetric line shape, strong temperature

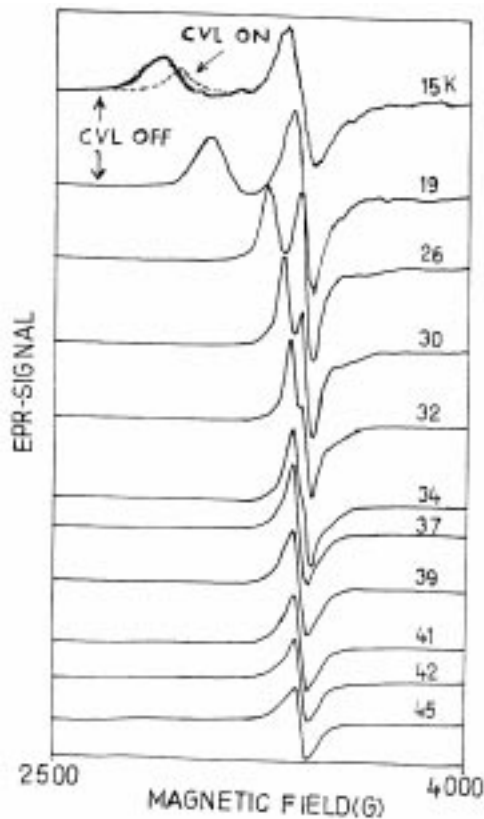


Figure 3. The temperature dependence of the EPR of impurity ion in the sapphire rod of APD cryogenics closed cycle refrigerator. The strong temperature dependence of line around 2976 G can be noted. The dashed curve shows the shift in position of this line on CVL illumination.

dependence and its g value of 2.38 suggest that it is possibly due to the non-Kramers ion Ni^{2+} [10]. On laser illumination, this EPR line shifted towards higher magnetic field. From the plot of resonance field versus temperature, the temperature rise on CVL illumination was determined to be of the order of 2 K. (This rise in temperature corresponds to the change in the physical temperature of the sample. The excitation temperature or electronic temperature at Nd^{3+} center could be quite different.) The reduction in intensity of EPR of Nd^{3+} with laser illumination was found to be significantly more than what can be expected for an estimated increase of 2 K in the temperature of the sample. Further, we have done several measurements on PVA with Tb^{3+} , Er^{3+} dopants in the same temperature region. EPR of these ions are observable only below 40 K and they are more strongly temperature dependent than that of Nd^{3+} . However, the extent to which EPR signals of Tb^{3+} and Er^{3+} got reduced on CVL illumination was only to the order of 10–20%. This is shown in figure 4. Near 100% changes were observed only in Nd^{3+} -doped PVA. This clearly suggests that the observed changes in EPR intensities are not due to *bulk thermal effects*. The results on Er- and Tb-doped PVA will not be discussed here, with the view of focusing the present paper on results obtained on Nd^{3+} -doped PVA.

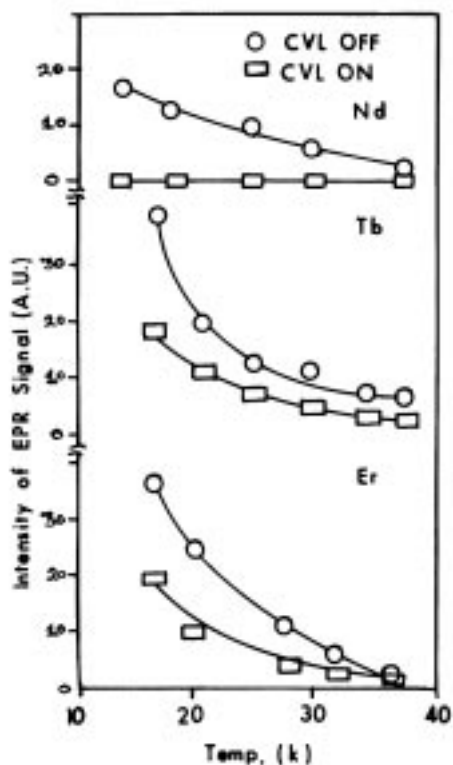


Figure 4. The temperature dependence of intensity of EPR signals due to Nd^{3+} , Tb^{3+} and Er^{3+} ions without and with *in situ* CVL illumination. It can be seen that the reduction in intensity with laser illumination is >90% for Nd^{3+} -doped PVA film.

(ii) *Possible valence changes/depletion of ground state population*: The possible change of valence and/or depletion of the ground state can be ascertained by conducting an electronic absorption spectral measurement under the condition of *in situ* CVL pumping. Under these conditions, a convenient way of obtaining the absorption spectrum is by photoacoustic spectroscopy under a pump-probe type of measurement where the pump is CVL and the probe is the output of scanning monochromator with entrance slit illuminated by white light from a high pressure xenon lamp.

The PA spectra of Nd³⁺:PVA were obtained without and with CVL illumination (510.5 nm and 578.2 nm). The features of the absorption spectrum under these conditions (shown in figure 5) clearly suggest that neither valence change nor complete depletion of the ground state occurs under CVL pumping. (Under both these scenarios, the PA spectra would have disappeared.) However, there are some important findings. These are: (i) near continuum extra absorption at wavelengths greater than 500 nm and (ii) additional absorption features between 700–800 nm (shown in the inset of figure 5).

Klintonberg *et al* [15] have calculated the energy levels and oscillator strengths of different transitions of Nd³⁺ in Nd₂O₃ and Nd³⁺:LiYF₄ using 20 parameter fitting. Their results have clearly shown that there are close lying energy levels between 19,000 cm⁻¹ to 22,300 cm⁻¹, and also the low lying excited states ⁴I_{11/12}, ⁴I_{13/2} and ⁴I_{15/2} have their stark components separated from the ground manifold by 2000, 4000 and 6000 cm⁻¹ respectively. In view of these, it is easy to see that if the low lying excited states are sufficiently populated, one would observe continuum absorption between 500 to 750 nm (or 20,000 cm⁻¹ to 13,000 cm⁻¹). It may be pointed out that ⁴I_{9/2} → ⁴G_{5/2} transition occurs resonantly at the yellow line of CVL. The ion in excited ⁴G_{5/2} relax to ⁴F_{3/2} (around 11,000 cm⁻¹) which is known to have long lifetime. There are a number of reports for frequency upconversion in Nd³⁺ containing crystals [11–14]. This arises due to excited state absorption from ⁴F_{3/2}. Due to relaxation to low lying ⁴I_{11/2,13/2,15/2} states, these states also get populated. The extra absorption seen at 13,000 cm⁻¹ on CVL pumping coincides with the absorption for excited ⁴F_{3/2} → ²P_{1/2}, ²D_{5/2} transition. Furthermore, the absorption line around 11,000 cm⁻¹ corresponding to ⁴I_{9/2} → ⁴F_{3/2} transition enhances in intensity when the sample is exposed to 578.2 nm light of CVL. This increase, we believe, is due to additional absorption from excited ⁴F_{3/2} → ⁴G_{11/2} + ²K_{15/2}, which also occurs [16] around 11,000 cm⁻¹.

Therefore, it appears that the illumination with CVL resulted in the creation of non-equilibrium population distribution rather than in valence change or in complete depletion of the ground state. The population redistribution is most effective with yellow line of CVL, despite its lesser intensity than green line, which coincides with the ⁴I_{9/2} → ⁴G_{5/2} transition. This gives further proof that the observed effects are not associated with mere laser heating.

(iii) *Equalization of population among Zeeman components*: The EPR signal being proportional to difference in population between |−⟩ and |+⟩ states of the Kramers' doublet, its disappearance can imply zero population difference between Zeeman components.

In this scenario, the excitation with CVL essentially has the effect of saturating the EPR line and the recovery time should be closely related to spin-lattice relaxation time T_1 of

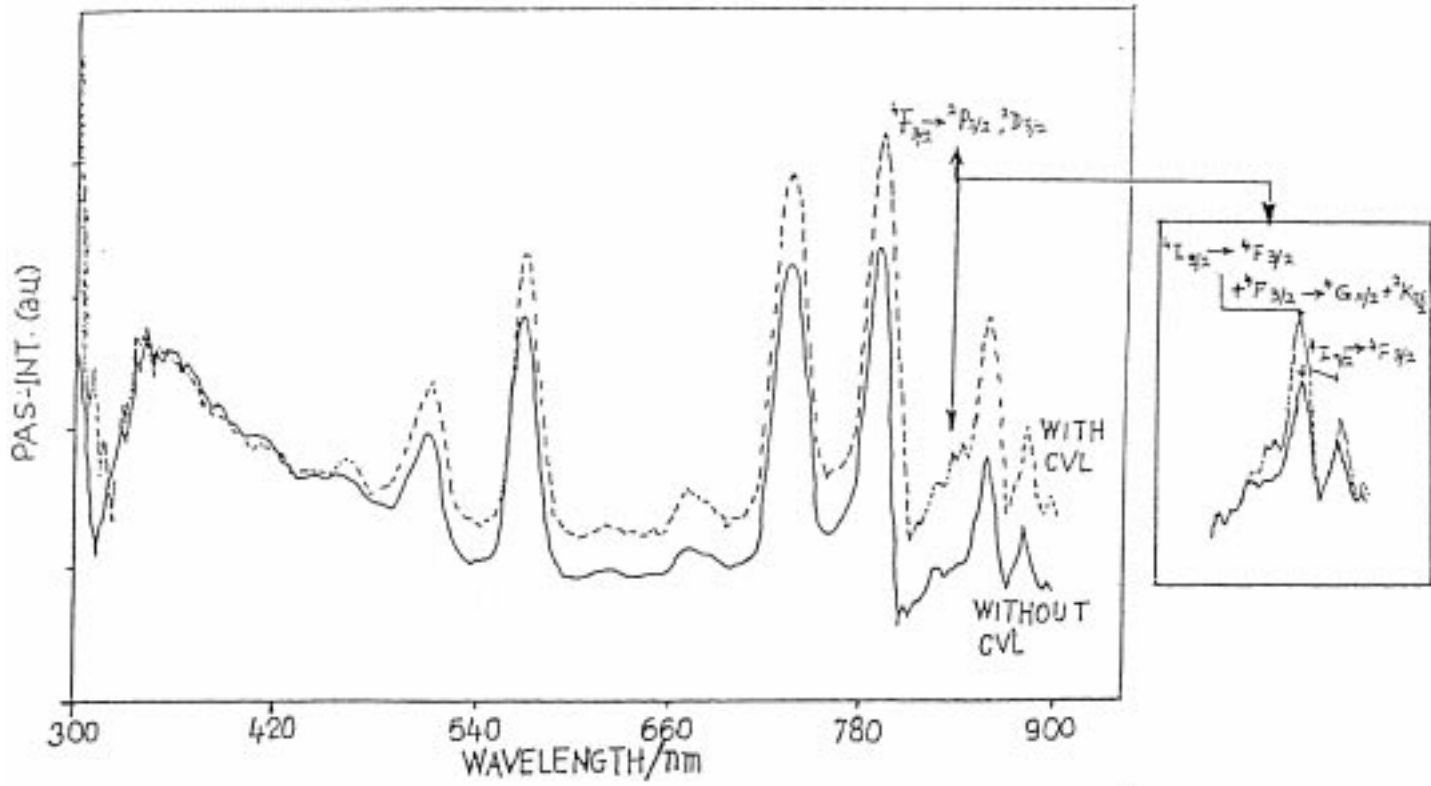


Figure 5. PAS spectra of $\text{Nd}^{3+}:\text{PVA}$ obtained at room temperature without CVL (—) and under CVL pump conditions (- - -).

Nd^{3+} . It is well known [10] that the values of spin-lattice relaxation T_1 of Nd^{3+} are very much smaller ($\sim 10^{-8}$ s) compared to the values of time constants obtained in the present experiment. The long time scales observed cannot be realistically associated with spin-lattice relaxation. At this point, it should be mentioned that CVL is a pulsed laser with 5 kHz frequency. Therefore, the CVL illumination and associated electronic absorption by Nd^{3+} , generates acoustic waves at that frequency. This input into phonon bath can create a bottleneck situation and can increase the spin-lattice relaxation, leading to equalization of population in $|+\rangle$ and $|-\rangle$ Zeeman states. However, it is rather unlikely that this process could increase the value of T_1 by almost 7 orders of magnitude (from 10^{-8} s to a fraction of a second).

These PA-spectral findings have given direct evidence for the role of CVL excitation in populating the ${}^4F_{3/2}$ excited state thereby facilitating the excited state absorption. The physics involved in this experiment is somewhat similar to that in non-photochemical hole burning (NPHB), studied using double resonance techniques [17–21]. The types of hole burning experiment are normally classified according to population reservoirs into which ions are being removed from the ground state [18]. In the case of rare earths, the most efficient population reservoirs were provided by the hyperfine splittings (for $I \neq 0$ and for experiment with r.f.) of the ground electronic state. In such cases the lifetime of the hole (characteristic time required for the system to come back to equilibrium) is determined by spin-relaxation among hyperfine levels. Macfarlane *et al* [19], have reported hole lifetimes in the order of milliseconds to minutes. These authors also reported unusually long hole lifetimes, greater than hours, in rare earth-doped glasses and photo ionizing compounds. These were referred to as cases of persistent hole burning.

The mechanism for this is likely to involve small photoinduced changes in the configuration of ions surrounding the rare earth. As Macfarlane and Shelby [17] pointed out, there are many almost equienergetic positions for the constituent ions in glassy matrices. Such a scenario was indeed reported by Fearey *et al* [22] in glassy matrix of PVA doped with Nd^{3+} and Pr^{3+} . These authors have reported NPHB only when the excitation coincided with absorption to 4G state of Nd^{3+} and the hole burning efficiencies are 2 to 3 orders of magnitude higher than in inorganic glasses. The laser power used was $\sim 0.5 \text{ W/cm}^2$ at the wavelength of excitation. These configuration changes associated with NPHB can change the crystal field at the rare earth site thereby shifting electronic resonance frequency. In optical cases, persistent hole burning was reported to shift the rare earth transition [20,21], the shifts being of the order of GHz. The configurational changes can also arise due to the changes in chemical bonding of rare earth ion (on electronic excitation) or due to electronic excitation of stable organic ligands themselves. Even though the shifts in optical absorption are rather small to be observable in PAS using a low resolution monochromator, the changes in EPR line position would be observable if the changes at all Nd^{3+} centers are identical and coherent. As there can be many equienergetic positions for constituent ions of PVA matrix and the g values of Nd^{3+} being highly anisotropic ($g_{\parallel} = -0.34$ and $g_{\perp} = 2.72$), the EPR spectrum would be smeared out over a wide magnetic field range of 2.4 kG to 20 kG. Furthermore, due to the population redistribution in different electronic excited states, there would be additional spread in effective g -values contributing to the spread in resonance fields. Such a spread in resonance fields would not make it possible to observe the EPR in derivative form. The time constants associated with the disappearance and recovery of EPR may be characteristic of configurational relaxation of the medium and kinetic data of photo-EPR appears to yield this information.

These findings have relevance to the original problem that was addressed, viz., the mechanism of photorefraction/grating formation in this system. In Nd³⁺-doped PVA films the grating formation at the CVL wavelengths does not appear to take place through photoinduced electron transfer or photoconductivity, but occurs more as a population grating or thermal grating if one considers the excitation as an effective increase in local temperature. The formation of such a grating will be highly efficient in Nd³⁺:PVA when excited by the yellow line of CVL.

4. Conclusions

Photo-EPR and PAS studies of Nd³⁺-doped PVA under CVL illumination have given evidence for significant population in the electronic excited states. The long lifetime suggests that it is likely to be a case similar to that of persistent hole burning. The Nd³⁺:PVA is shown to be a suitable system for efficient creation of population grating.

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