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Probing vacuum ultraviolet energy levels of trivalent gadolinium by two-photon spectroscopy

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Abstract

The energy levels of lanthanide ions have been studied in great detail in the energy range up to 40 000 cm^{-1} (250 nm). Recently, an increased interest in the high-energy levels between 40 000 and 70 000 cm^{-1} has emerged, partly triggered by the need for new luminescent materials for vacuum ultraviolet (VUV) excitation. Using synchrotron radiation many new energy levels have been discovered for many lanthanide ions. However, the spectral resolution of a synchrotron is limited and to resolve the complete energy level structure higher-resolution tunable lasers are required. Unfortunately no tunable lasers are available in the VUV. To overcome this problem two-photon spectroscopy may be applied. In this contribution the use of resonant and non-resonant two-photon spectroscopy is applied to measure the energy level structure of Gd^{3+} in fluorides. Non-resonant two-photon excitation and resonant excited state absorption from the $^6P_{7/2}$ level is shown to provide high-resolution spectra of the high-energy levels of Gd^{3+}. The extension of the energy level structure may be beneficial for energy level calculations, especially for Gd^{3+} where only a limited number of energy levels is available from conventional laser spectroscopy.

Keywords: VUV; Lanthanides; Excited state absorption

1. Introduction

In the last decades, the spectroscopy of the trivalent gadolinium ion has been studied extensively using one-photon techniques. As a result of that, the positions of the energy levels up to 40 000 cm^{-1} in several host-lattices are known very accurately nowadays [1,2]. Also some two-photon excitation (TPE) spectra have been measured for Gd^{3+} [3]. The parameters required for energy level calculations are obtained by fitting the calculated levels to experimental values. This works well for the lower-energy levels, but to accurately calculate the higher-energy levels of gadolinium situated in the vacuum ultraviolet (VUV) ($>50\,000\,cm^{-1}$) experimental values from that region are required. Recently, many of the VUV levels of gadolinium have been measured using synchrotron radiation [4] but the resolution of these experiments is not high enough to observe the splitting of several multiplets and therefore does not allow unambiguous assignment of measured energy levels to the calculated levels.

To obtain higher-resolution spectra in the UV and VUV a laser is required, but unfortunately no

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tunable VUV lasers exist at the moment. To overcome this problem, TPE or excited state absorption (ESA) measurements can be used to probe the VUV levels with the high accuracy required.

Using two tunable lasers simultaneously, the gadolinium ion is excited in two steps. The first excitation is at a fixed energy exciting the Gd^{3+} ion into the $^6P_{7/2}$ level at about 32 200 cm^{-1}, while the second tunable laser is used to excite the Gd^{3+} ion from the $^6P_{7/2}$ state to a higher-energy state. Using the laser dyes commercially available at the moment this allows excitation to levels up to approximately 62 000 cm^{-1} for the trivalent gadolinium ion.

For a high-resolution measurement in the (V)UV region of the spectrum, also TPE can be used, where the energy of two (visible) photons is absorbed simultaneously to excite into the (V)UV levels of gadolinium. The disadvantage of this technique is that it is very sensitive for impurities in the samples. The probability for resonant one-photon absorption involving an impurity ion is several orders of magnitude higher than the probability of TPE. The method of ESA does not suffer from this problem since the first excitation step is very specific for the ion to be probed.

In this article we present our results using the techniques of TPE and ESA to measure high-energy levels of Gd^{3+} in LaF_3.

2. Experimental

A single crystal of LaF_3 doped with 0.5% Gd^{3+} was grown in a Philips PH 1006/13 high-frequency furnace using the vertical Bridgman method. A slice of approximately 7 mm in diameter and a thickness of 2 mm was cut and polished and glued to a copper sample holder. Measurements were performed at approximately 10 K using an Oxford Instruments liquid helium flow cryostat fitted with quartz windows. TPE experiments were performed using a Lambda Physik LPD 3002 Dye laser which was pumped with a Lambda Physik LPX100 XeCl excimer laser. The experimental setup for ESA consisted of two tunable lasers. The first was a Spectra-Physics PDL3 dye laser pumped by a frequency-doubled Spectra-Physics Quanta Ray Nd:YAG laser operating at 15 Hz. A Rhodamine B laser dye solution was used to obtain a laser tunable around 620 nm. This red laser beam was led into a Spectra-Physics wavelength extender with KDP crystals, where it was frequency doubled to an UV laser with a wavelength of approximately 310 nm. The second laser used was a Lambda Physik LPD 3002 Dye laser which was pumped with a Lambda Physik LPX100 XeCl excimer laser. The excimer laser was triggered by the YAG laser. Both laser beams were focussed on the same spot in the crystal using a series of mirrors and lenses. For both the techniques, the emission from the crystal was collected using a cooled Hamamatsu R7154 solar blind photomultiplier tube. Various band and interference filters were used to block any light within the wavelength range of the excitation sources. The obtained spectra were corrected for the dye output using dye output spectra recorded with a power meter.

3. Results and discussion

3.1. Two-photon excitation

TPE spectra for LaF_3:Gd^{3+} 0.5% and GdF_3 (powder) were recorded in the wavelength region

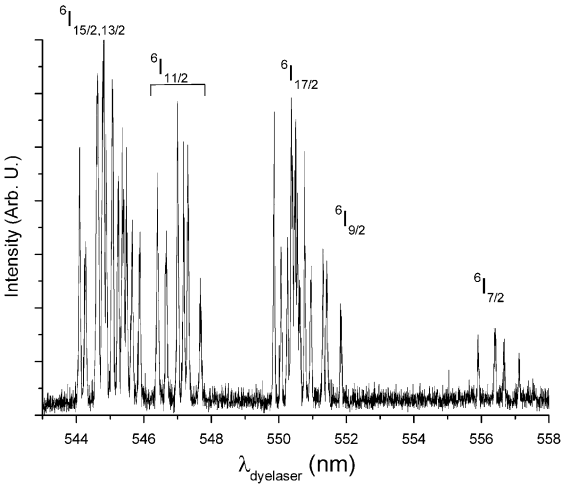

Fig. 1. TPE spectrum of GdF_3 monitoring $^6P_{7/2}$ emission at 4 K.

of the ^6P_J, ^6I_J, ^6D_J and ^6G_J levels. For the ^6P_J and ^6I_J levels high-resolution excitation spectra were obtained. As an example, Fig. 1 shows the TPE spectrum for the ^6I_J levels of GdF_3 in the wavelength region 270–280 nm (dye laser scanned between 540 and 560 nm). In the spectrum 36 of the 39 expected energy levels are observed. The line widths of the excitation lines are about 1 cm^{-1}, corresponding to the inhomogeneous line width of the transitions. From this high-resolution excitation spectrum the positions of the ^6I_J can be determined with great accuracy. Attempts to measure the TPE spectra for the higher-energy ^6D_J and ^6G_J levels were not successful. Possibly,

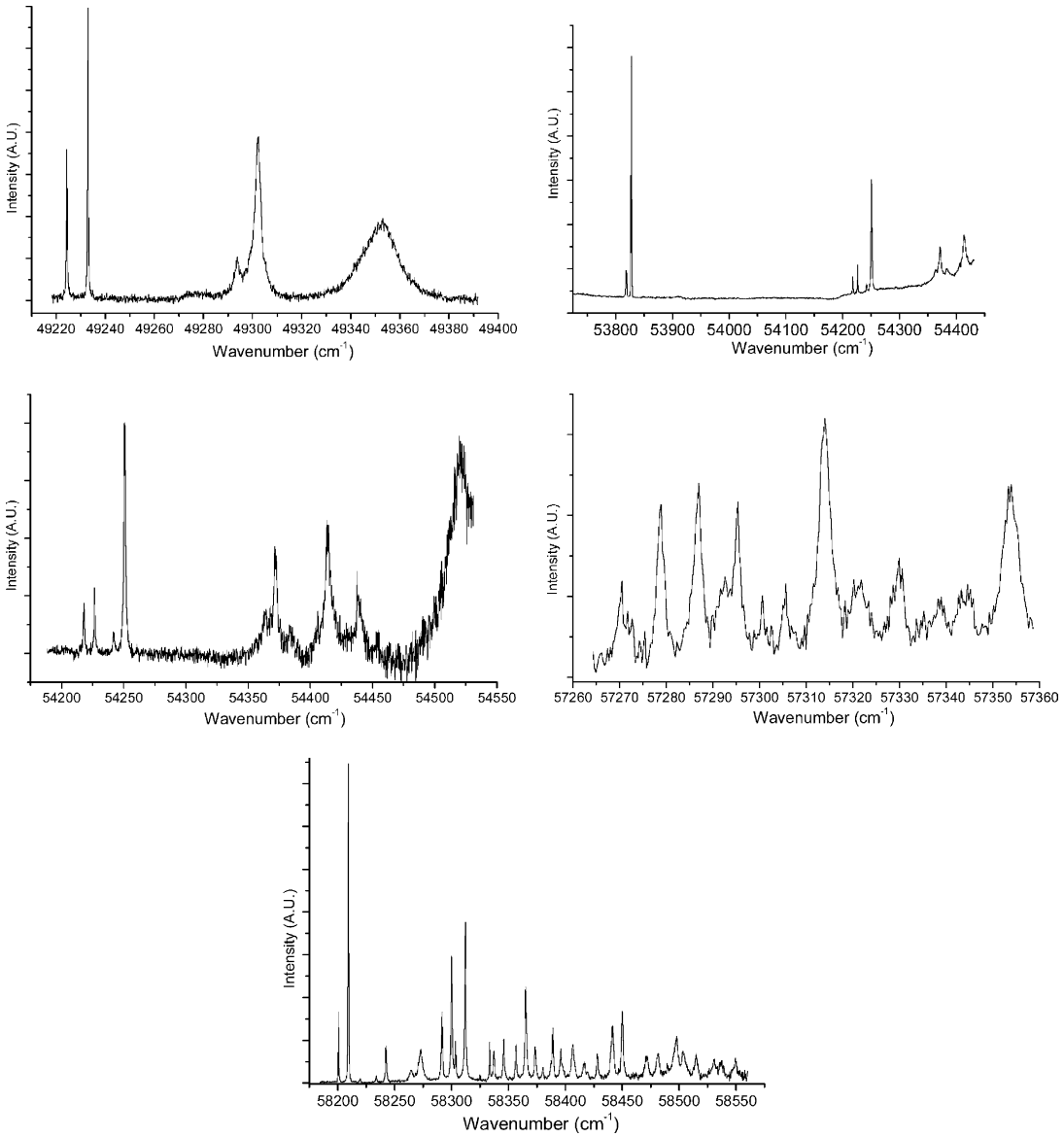

Fig. 2. ESA spectra of LaF_3:Gd^{3+} crystal monitoring $^6I_{7/2}$ emission at 10 K.

the lower oscillator strengths hamper the observation of TPE. For the ^6G_J (situated around 200 nm) also the presence of trace amounts of Eu^{3+} ions, which absorb excitation light in the wavelength region around 400 nm, interfered with the observation of TPE for Gd^{3+}. Further experiments on crystals with higher Gd^{3+} concentrations may be used to measure the higher-energy levels of Gd^{3+} by TPE.

3.2. Excited state absorption

ESA spectra have the advantage of a greater sensitivity (higher oscillator strength since resonant absorption occurs) and greater selectivity (due to selective excitation in the first excitation step). For the LaF_3:Gd^{3+} 0.5% crystal, the high-energy levels in the VUV were probed by exciting with one laser in the third crystal field component of the $^6P_{7/2}$ level at 310.24 nm and scanning with a second dye laser over various wavelength intervals between 365 and 608 nm using different types of dyes. Emission was recorded around 280 nm, where the $^6I_{7/2}$ emission is located. Only after a two-step excitation process this anti-Stokes emission may be observed. In Fig. 2, a number of ESA spectra is shown. The energy scale along the x-axis corresponds to the position of the VUV energy levels. The value is obtained by adding the energy of the photon from the tunable dye laser to the energy of the lowest $^6P_{7/2}$ crystal field component of Gd^{3+} from which ESA occurs. The second crystal field level of the $^6P_{7/2}$ level is situated 7.4 cm^{-1} above the lowest level and at 10 K this level will be thermally populated. As a result, weaker satellite peaks are observed at 7.4 cm^{-1} lower energies from the main ESA peaks.

From the ESA spectra the positions of many VUV levels of Gd^{3+} can be determined with great accuracy. In Fig. 3, an overview of the measured energy levels is given together with the energy levels calculated using the parameters for Gd^{3+} in LaF_3 as reported in the literature [2]. At this point, still many levels are missing and more ESA spectra in various wavelength regions need to be recorded to obtain the full picture. When this is done a careful analysis of the energy level structure is expected to provide more data which will help in obtaining better parameters for the energy level calculations of Gd^{3+}.

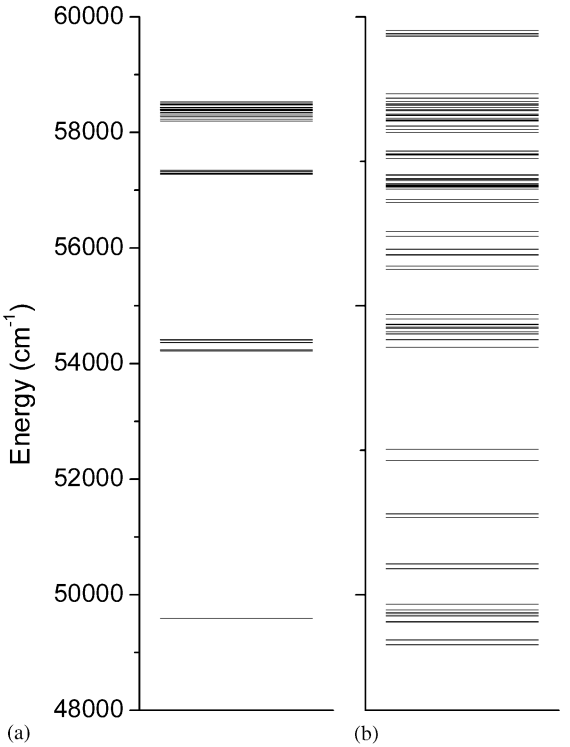

Fig. 3. Measured energy levels (a) and calculated values (b) for LaF_3:Gd^{3+} between 48 000 and 60 000 cm^{-1}.

4. Conclusions

Two-photon excitation and excited state absorption techniques have been used to probe high-energy levels of the trivalent gadolinium ion with a high resolution. Further measurements using different dyes is required to give a complete and accurate picture of the energy level scheme up to 62 000 cm^{-1}. The various energy levels measured can then be used as a basis for finding more accurate parameters used for energy level calculations of Gd^{3+} in LaF_3.

References

[1] G.H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, Interscience Publishers, New York, 1968.
[2] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, A Systematic Analysis of the Spectra of the Lanthanides Doped into Single Crystal LaF_3, Argonne National Laboratory, Argonne, IL, 1988.
[3] M. Dagenais, M. Downer, R. Neumann, N. Bloembergen, Phys. Rev. Lett. 46 (1981) 561.
[4] R.T. Wegh, H. Donker, A. Meijerink, R.J. Lamminmäki, J. Hölsä, Phys. Rev. B 56 (1997) 13841.