Indian J. Phys. **54B**, 132–136 (1980)

Laser induced fluorescence and absorption in neodymium formate

V B Kartha and S Venkateswaran

Spectroscopy Division, Bhabha Atomic Research Centre
Trombay, Bombay-400 085

Abstract. The absorption spectra of Nd $(HCOO)_3$ obtained by absorption from a fluorescence continuum produced with He-Cd laser excitation are presented. The observed absorption bands are assigned to various transitions between the crystal field levels under C_{3v} symmetry. An estimate of the Stark splitting of the $^4I_{9/2}$ ground state configuration is obtained.

1. Introduction

During the investigation of the laser Raman spectra of rare earth formates using He-Cd and Ar^+ ion lasers (Kartha and Sugandhi 1976, 1978) in several cases an intense continuum fluorescence background is observed. The fluorescence radiation is often reabsorbed due to transitions of the rare earth ions between the ground and higher electronic levels giving sharp absorption peaks in the continuum. In this paper we present the absorption spectra of $Nd(HCOO)_3$, observed in the laser-induced continuum fluorescence of this compound

2. Experimental

Spectra of powdered samples in capillary tubes were obtained using a He-Cd laser at 4416 Å, operating at about 15 mW power. A Spex 1401 double monochromator and an RCA-C-31034 cooled photomultiplier with photon counting were used to record the spectra. The fluorescence and absorption bands are shown in Figure 1. The frequencies of the absorption peaks observed in the

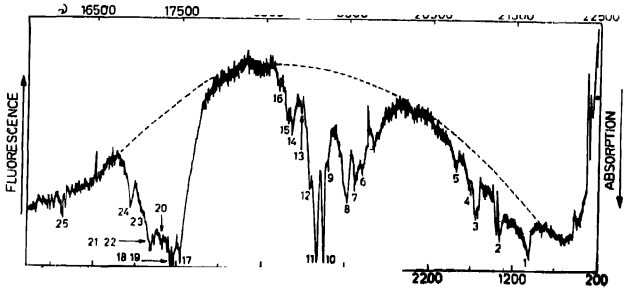

Figure 1. Absorption and Fluorescence Spectra of $Nd(HCOO)_3$ with He-Cd Laser.

present work are given in Table 1, together with the calculated values (Wybourne 1960).

Table 1. Absorption frequencies in $Nd(HCOO)_3$

No.	ν cm^{-1}	Term	Calculated values*
1	21639 (m)	$^4G_{11/2}$	21826
2	21285 (m)	$^2G_{9/2}$ $^2D_{3/2}$	21255, 21247
3	21009 (m)	$^2K_{15/2}$	21027
4	20929 (w)	—	
5	20757 (w)	—	
6	19652 (w)	$^4G_{9/2}$	19720
7	19564 (w)	—	—
8	19475 (s)	$^4G_{7/2}$ $^2K_{13/2}$	19320, 18974
9	19235 (sh)	—	—
10	19179 (vs)	—	—
11	19079 (vs)	—	—
12	19015 (sh)	—	—
13	18903 (w)	—	—
14	18615 (m)	—	—
15	18735 (w)	—	—
16	18645 (vw)	—	—
17	17457 (vs)	$^2G_{7/2}$	17354
18	17365 (vs)	$^4G_{5/2}$	17356
19	17315 (s)	—	—
20	17224 (s)	—	—
21	17137 (s)	—	—
22	17082 (s)	—	—
23	16995 (sh)	—	—
24	16851 (m)	—	—
25	16015 (w)	$^2H_{11/2}$	15985
26	15921 (vw)	—	—
27	15881 (vw)	—	—

* Calculated Values (Wybourne 1960)

3. Discussion

The observed absorption peaks should arise due to transitions from the $^4I_{9/2}$ ground state to the upper states since the other ^4I levels are too high to be populated at room temperature. There are a number of low lying vibrational levels for the rare earth formates (Kartha and Sugandhi 1978) which will be populated at room temperature, and absorption can take place from these levels also

The site symmetry of Nd^{3+} in the formate crystal is C_{3v} (Turcotte *et al* 1970) and each level with a given J will be split into $(2J+1)/2$ levels due to the crystal field. The $^4I_{9/2}$ ground state is thus split into 5 components with similar splittings for the other levels

The observed absorption bands can be separated into groups of closely spaced band systems The strongest of these come into the 17000 cm^{-1} region and are normally assigned to transitions to the $^2G_{7/2}$ and $^4G_{5/2}$ levels (Johnson 1963) Eight bands could be definitely identified in this region, all of them except one, quite strong The frequency differences of the bands of this group are characterised by the fact that those differences which repeat a large number of times in this group, do not exist in the other groups. Hence these differences should arise from the upper state splittings Those frequency differences which are observed only a few times here, and at the same time are also observed in the other groups, should correspond to the splittings of the $^4I_{9/2}$ ground state The splittings and assignments for this group can thus be satisfactorily explained by the energy level scheme shown in Figure 2. The fact that all the 28 observed frequency differences agree with the calculated values within an experimental error of ± 2 cm^{-1}, as shown in Table 2, confirms the present assignment to be correct

Table 2.

Line	18	19	20	21	22	23	24
17	92 (90)	142 (142)	233 (233)	320 (320)	375 (373)	462 (462)	606 (605)
18		50 (52)	141 (143)	228 (230)	283 (283)	370 (372)	514 (515)
19			91 (91)	178 (178)	233 (231)	320 (320)	464 (463)
20				87 (87)	142 (140)	229 (229)	373 (372)
21					55 (53)	142 (142)	286 (285)
22						87 (89)	231 (232)
23							144 (143)

Values in parentheses are those calculated from the assignments shown in Fig. 2.

The assignment of the $^2G_{7/2}$–$^4I_{9/2}$ group has been facilitated by the large number of strong bands observed in this region For the other groups of bands such detailed assignment is difficult since only few bands are observed, and that also mostly weak. Only moderately strong single bands are observed in the

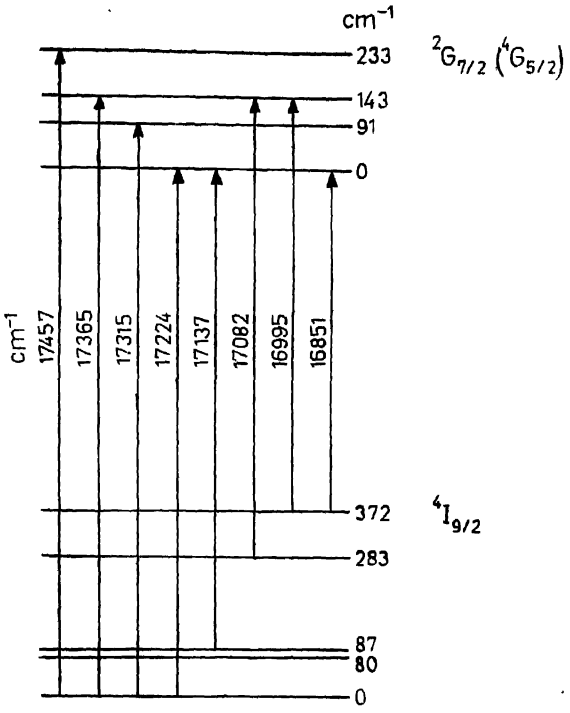

Figure 2. Crystal Field Splittings and Assignments for $^4I_{9/2}$, $^2G_{7/2}$, $^4G_{5/2}$ Transitions.

$^4G_{11/2}$ and $^2G_{9/2}$ transitions and no stark level assignments are thus possible for these bands. In the $^2K_{15/2}$ region we observe a moderately strong band and two weak bands. Because of the large number of levels in the upper state, it is not possible to make any detailed assignments. However, the relative intensities of the bands suggest that the frequency difference of 80 cm^{-1} observed between the stronger and weaker bands could correspond to the only remaining unassigned level in the ground state. The next group of moderately strong bands come around 19500 cm^{-1}. Both the $^4G_{9/2}$ and $^4G_{7/2}$ levels are expected in this region

and because of the complexity of levels no detailed assignments have been attempted.

The remaining group of strong bands in the 19000 cm^{-1} region can belong to the $^2K_{13/2}$ and $^4G_{7/2}$ levels. Previous workers (Dieke and Heroux 1956) have assigned strong absorption in this region to transitions to the $^4G_{7/2}$ state

Frequency differences corresponding to the ground state splittings of 80, 87, 283 and 372 cm^{-1} are observed in this group also confirming the assignments from the other strong absorption group.

It should be pointed out that the assignments made here give ground state splittings comparable to values observed by earlier workers (Satten 1953, Dieke and Heroux 1956). Also the splittings of the $^2G_{7/2}$, $^4G_{5/2}$ state could be unambiguously obtained from the present work

References

Dieke G H and Heroux L 1956 *Phys Rev.* **103** 1227
Johnson L F 1963 *J. Appl. Phys.* **34** 897
Kartha V B and Sugandhi R S 1976 *Indian J. Phys.* **50** 115.
Kartha V B and Sugandhi R S 1978 *Proc. VIth Int. Conf. Raman Specy.* Vol. II P 50, Bangalore
Satten R A 1953 *J. Chem. Phys.* **21** 637
Turcotte R P, Huschke J M, Jenkins M S and Eyring L 1970 *J. Solid State Chem.* **2** 593
Wybourne B G 1960 *J. Chem Phys.* **32** 639