

Optical absorption spectrum of nickel antipyrine complex

V L R MURTHY* and S V J LAKSHMAN

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

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Abstract. The optical absorption spectrum of nickel antipyrine complex has been studied both at laboratory and liquid nitrogen temperatures. The spectrum is characteristic of Ni^{2+} in an octahedral crystal field. A good fit between theoretical and experimental band positions is obtained for the following crystal field parameters : $Dq = 940 \text{ cm}^{-1}$, $B = 795 \text{ cm}^{-1}$, $C = 4.7 B$.

Keywords. Optical absorption; crystal field parameters; nickel antipyrine complex; oscillator strengths.

1. Introduction

The molecule 1-phenyl-2,3-dimethyl-5 pyrazolone ($C_{11}H_{12}ON_2$), known as antipyrine or phenazone is a crystalline organic compound and it forms stable crystalline complexes with transition metal chlorates, iodides or nitrates. The optical absorption of some of these complexes have been studied (Ravi *et al* 1967). The metal complexes are isomorphous to the magnesium antipyrine perchlorate single crystals. A detailed crystal structure analysis is carried out for the latter (Vijayan and Viswamitra 1965, 1967). It belongs to the hexagonal crystal system with space group $R\bar{3}$ and cell dimensions $a = 14.00 \text{ \AA}$ and $C = 9.76 \text{ \AA}$, with one molecule per unit cell. The metal is coordinated to six oxygens of the carbonyl group of the antipyrine molecule. Since a detailed study has not been done earlier the nickel antipyrine complex (NAP) is now studied both at laboratory and liquid nitrogen temperatures.

2. Experimental

A crystal of about 2 mm thickness was chosen and its optical absorption spectrum was recorded with a Cary-14 spectrophotometer at laboratory and liquid nitrogen temperatures. The near IR spectrum was obtained with a Carl Zeiss DMR 21 spectrophotometer.

* To whom all correspondence should be made.

3. Theory

The Ni^{2+} ion has eight 3d electrons which give rise to the free ion terms ${}^3\text{F}$, ${}^3\text{P}$, ${}^1\text{D}$, ${}^1\text{G}$ and ${}^1\text{S}$ with ${}^3\text{F}$ being the ground state. In a crystal field of octahedra, symmetry the ${}^3\text{F}$ term splits into ${}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{2g}(\text{F})$ and ${}^3\text{T}_{1g}(\text{F})$ crystal field terms, the ${}^3\text{A}_{2g}(\text{F})$ being the lowest. The ${}^3\text{P}$ term transforms as ${}^3\text{T}_{1g}(\text{P})$ term. Other singlet terms change into the ${}^1\text{E}_g(\text{D}) + {}^1\text{T}_{2g}(\text{D})$, ${}^1\text{A}_{1g}(\text{G}) + {}^1\text{T}_{1g}(\text{G}) + {}^1\text{T}_{2g}(\text{G})$ and ${}^1\text{A}_{1g}(\text{S})$ respectively.

4. Results and discussion

The spectrum recorded at laboratory temperature is shown in figure 1. It consists of three bands centred at 8900, 14595 and 24505 cm^{-1} . Using energy level diagrams (Tanabe and Sugano 1954) these bands are assigned to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ respectively. When the crystal is cooled to liquid nitrogen temperature, a new band centred at 22095 cm^{-1}

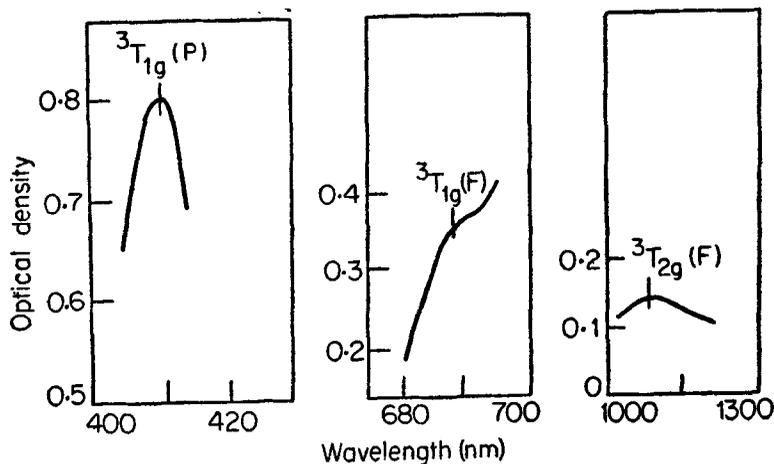


Figure 1. Spectrum of Ni^{2+} in nickel antipyrine complex (1300°K).

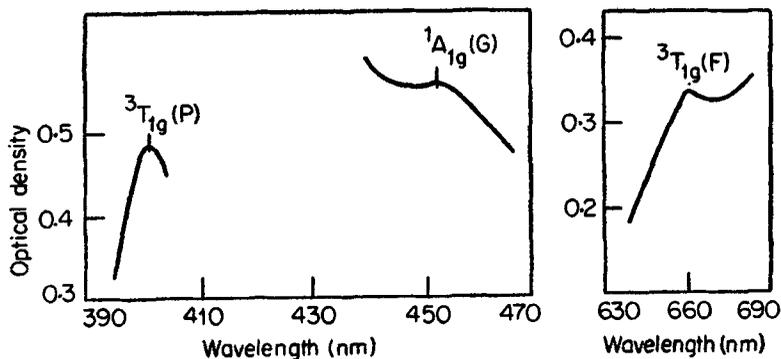


Figure 2. Spectrum of Ni^{2+} in nickel antipyrine complex (80°K).

is recorded. The band originally at 14595 cm^{-1} got shifted to 15150 cm^{-1} and the band at 24505 cm^{-1} to 24930 cm^{-1} as shown in figure 2. The IR band is not recorded because the cryostat could not be used with the Carl Zeiss DMR 21 spectrophotometer.

The absorption band at 22095 cm^{-1} recorded at liquid nitrogen temperature is assigned to the transition ${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$. It could be easily seen from the Tanabe-Sugano energy level diagrams that the transitions ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ have positive slopes and hence these bands, on cooling the crystal to liquid nitrogen temperature should show a blue shift (Dunn 1967) which was experimentally observed in the change of positions of the bands from 14595 to 15150 cm^{-1} and 24505 to 24930 cm^{-1} respectively.

The bands at 15150 cm^{-1} (ν_2) and 24930 cm^{-1} (ν_3), at liquid nitrogen temperature are characteristic of Ni^{2+} ion in octahedral symmetry. Accordingly ν_2 and ν_3 are used to calculate the electron repulsion parameter B and crystal field parameter Dq using the following relations (Underhill and Billing 1966)

$$340 Dq^2 - 18 (\nu_2 + \nu_3) + \nu_2\nu_3 = 0,$$

$$B = (\nu_2 + \nu_3) - 30 Dq/15.$$

The values obtained are : $B = 795\text{ cm}^{-1}$ and $Dq = 940\text{ cm}^{-1}$.

The energies of transitions are calculated using the linear relationships (Lakshman and Rao 1972) and $C = 4.7 B$. The wave numbers, assignments and oscillator strengths both at laboratory and liquid nitrogen temperatures are shown in table 1. The experimental and calculated values of energies show a good agreement, which indicates that Ni^{2+} ion has an octahedral site symmetry.

Table 1. Wave numbers, assignments and oscillator strengths for the bands in nickel antipyrine complex.

$Dq = 940\text{ cm}^{-1}$		$B = 795\text{ cm}^{-1}$	$C = 4.7 B$	
Laboratory temperature	Liquid nitrogen temperature	Calculated	Assignments with ${}^3A_{2g}$ as ground state	Oscillator strengths ($f \times 10^5$)
8900		9400	${}^3T_{2g}(F)$	0.9
14595	15150	15162	${}^3T_{1g}(F)$	1.7
	22095	21960	${}^1A_{1g}(G)$	0.4
24505	24930	24963	${}^3T_{1g}(P)$	1.4

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