NIR to UV absorption spectra and the optical constants of phthalocyanines in glassy medium

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Abstract

Optical absorption studies of phthalocyanines (Pc-s) in borate glass matrix have been reported for the first time. Measurements have been done corresponding to photon energies between 1.1 and 6.2 eV for free base, manganese, iron, nickel, molybdenum, cobalt and copper phthalocyanines. Several new discrete transitions are observed in the UV–vis region of the spectra in addition to a strong continuum component of absorption in the IR region. Values of some of the important optical constants viz. absorption coefficient (α), molar extinction coefficient (ε), absorption cross-section (σ_a), band width ($\Delta\lambda$), electric dipole strength (q^2) and oscillator strength (f) for the relevant electronic transitions are also presented. All the data reported for Pc-s in the new matrix have been compared with those corresponding to solution, vapor and thin film media.
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Keywords: Optical absorption; Phthalocyanines; Borate glass matrix

1. Introduction

Phthalocyanine (Pc) compounds have attracted a great deal of attention for quite some time because of their unique properties such as semi-conductivity, photoconductivity and chemical stability [1]. In addition to their excellent photoconductive properties, Pc-s have the advantages of being very stable against thermal and chemical decomposition and present very intense optical absorption in the visible region.

These properties together with the structural similarity to chlorophyll have resulted in many investigations directed towards their applications in solar energy conversion [1]. Also they have the potential to serve as active material for molecular electronic devices such as electrochromic displays, chemical sensors [2] and optical data storage [3]. Furthermore, interest in Pc compounds has recently been renewed due to the discovery that they form 'molecular metals' after partial oxidation [4,5].

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Ever since the discovery of Pc-s in 1907 a great deal of effort has been made to study the optical properties of Pc-s and associated compounds. Because of the very good optical absorption of these molecules in the UV–vis region, there is considerable interest in the characterization of the electronic structure of phthalocyanines. The absorption spectra of many metallated as well as free base Pc-s have been reported in the vapor phase [6,7], various solvents [8−11], thin films [12−15], crystals [16] and in thermoplastic media [17]. Since most of the Pc-s are found to exhibit very good optical absorption and emission in the 600−700 nm region, they can be considered as suitable candidates for optical amplification in this region. Thus, for example, Pc-s are today regarded as good nonlinear optical materials, which can be used in organic dye lasers in general. Most of the studies reported so far discuss the application of Pc-s in either solvents, vapors or in thin films. Studies on the optical properties of Pc-s have barely been done in solid matrices except for some reports on thermoplastic media viz. styron, tyril 767 and plexiglass [17]. The objective of this work is to study the optical absorption spectra of metallated as well as free base phthalocynnines in borate glass matrix and to derive the important optical parameters viz. absorption coefficient (α), molar extinction coefficient (ε), absorption cross-section (σ_a), half band width ($\Delta\lambda$), electronic dipole strength (q^2) and oscillator strength (f) of the principal optical transitions in the UV−vis−NIR region. A comparison is also made between the optical absorption data of the newly synthesized Pc-glass matrix and those of the other reported matrices.

2. Experimental

The metal Pc-s used were capable of purification by sublimation without decomposition. They were prepared by the reaction of phthalonitrile with metal dust as metal chlorides [18] and purified by repeated sublimation at 500 °C under a reduced pressure of nitrogen gas flow. The metal free Pc was prepared by decomposition of the dilithium Pc by dispersing in acid and then sublimating repeat-

edly. The glass samples were prepared by rapid quenching technique [19]. Reagent grade boric acid (99.9% purity from BDH) and doubly sublimed Pc's have been used as the starting materials for the preparation of the glass samples. In all the samples boric acid acts as the glass former and phthalocyanines as the network modifiers. To avoid high molecular concentrations all the glass samples were synthesized with 0.002 g of Pc-s in 18 g of boric acid (1.1×10^{-2} mass%). Weighed quantities of the starting materials were mixed homogeneously in an agate mortar. The batch was then placed in a silica crucible and heated at about 120 °C for 1 h so that a homogeneously mixed liquid is obtained. To ensure that the metal-lophthalocyanines did not undergo thermal decomposition the glass forming and processing temperatures were kept well below the thermal decomposition temperature (≥ 450 °C). A slow heating was initially maintained until the temperature reached 80 °C and decomposition of H_3BO_3 to B_2O_3 is complete. The temperature was then rapidly increased to 120 °C so as to obtain a bluish green melt. The melt was retained for about 10 min and then rapidly quenched by placing in between two well polished preheated brass plates so as to obtain glass discs of approximately 3 mm thickness and 2 cm diameter. The glass discs thus obtained were annealed at a temperature of about 60 °C for 1 h and then taken out and polished with water free lubricants. All the glass samples have been obtained with very good transparency and appear to be of good optical quality. The formation of glass was confirmed by recording the X-ray diffraction pattern. The absence of well defined diffraction peaks in the X-ray pattern shows the formation of the glassy phase. The absorption spectra of the samples were recorded on a spectrophotometer (Hitachi model U 2000) in the wavelength region 200−1100 nm. All the spectra were taken at room temperature.

3. Results and discussion

Figs. 1 and 2 show the absorption spectra of H_2Pc, MnPc, FePc, NiPc, CoPc, CuPc, ZnPc and MoOPc doped borate glass samples recorded over

the spectral range 200–1100 nm. The resulting glasses are found to be hygroscopic in nature and they require handling in a dry atmosphere. The samples have been characterized from a structural point of view by recording the FTIR spectra. A representative spectrum of the sample (NiPc) is shown in Fig. 3. The spectrum shows the characteristic peaks of the Pcs in the IR region [20] confirming that the Pcs are intact inside the glass host. The observed transitions, their spectral assignments and the calculated optical constants except the molar extinction coefficient ε (which was directly obtained from the absorption data) are summarized in Tables 1–8. In fact, the actual sample concentrations can be evaluated through the equation [$N = A/\varepsilon l$] with known values of the absorbance A, the molar extinction coefficient ε and the sample thickness l [21]. In order to evaluate the oscillator strengths of the overlapping bands, the fitting procedure described by Medeiros
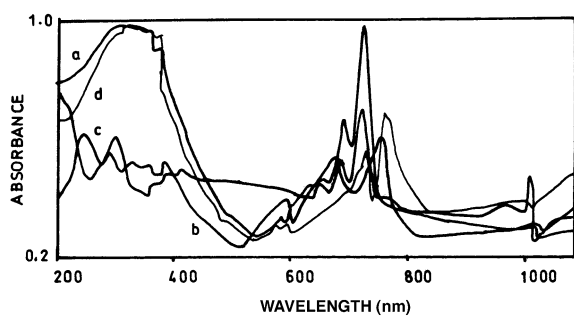

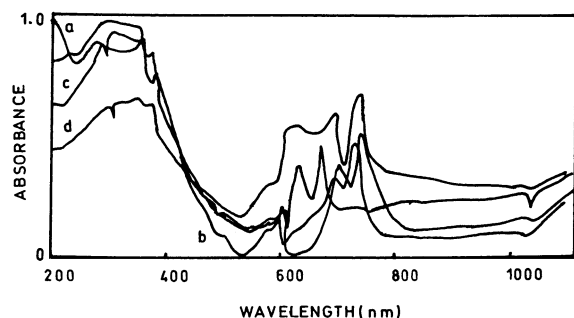Fig. 1. Absorption spectrum of various phthalocyanine molecules in borate glass (a) H$_2$Pc, (b) MnPc, (c) FePc, (d) NiPc.

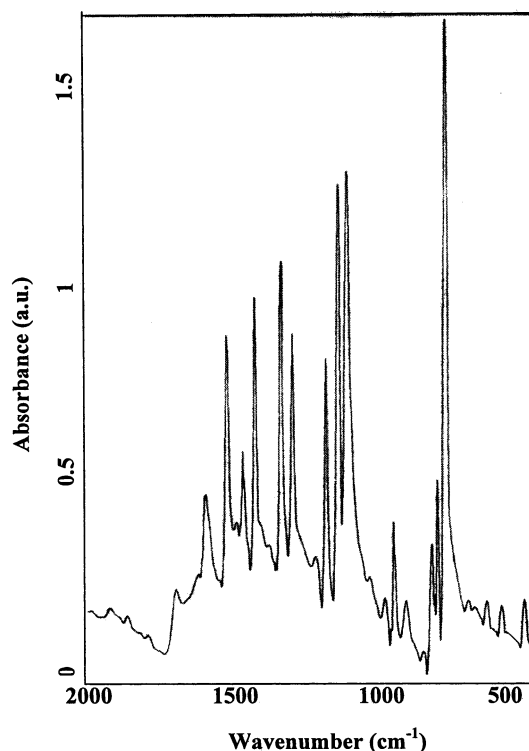Fig. 2. Absorption spectrum of phthalocyanine molecules in borate glass (a) CoPc, (b) CuPc, (c) ZnPc, (d) MoOPc.

Fig. 3. A representative FTIR spectrum of the sample NiPc.

et al. was adopted [22]. A Lorentzian fit was performed to each peak in order to determine the peak position and the area was determined using Simpson's rule for numerical integration. The calculated areas of the individual peaks were then scaled to match the total area of the overlapping bands.

The oscillator strengths have been evaluated using the standard equation (see footnote of Table 1).

3.1. Band assignments and interpretation of the spectra

3.1.1. H$_2$Pc

The absorption spectrum of H$_2$Pc in borate glass does not show any strong transition in the visible region (400–600 nm). However, in the UV region it shows three strong absorption bands. The band at 273.3 nm is the usual N band of the Pc molecule. It results from the molecular transition

$b_{2g}(d_{xy}) \rightarrow b_{1n}(\pi)$. The N band is observed to have high absorption cross-section and extinction coefficient. This band is preceded by a UV continuum which is the characteristic absorption of the glassy matrix. In the region between 400 and 800 nm the spectrum shows a total of five bands of which the band at 693.3 nm is the well known Q_y band occurring due to the transition $b_{1u}(\pi) \rightarrow e_g(\pi^*)$ and the band at 730 nm is the well-known Q_x band. It can be seen from the data summarized in Table 1 that, in all other matrices the Q band exists as a doublet, i.e. it splits into Q_x and Q_y components, the first being the longer wavelength transition. In the present glassy system also, we have observed

Table 1
Optical constants of H_2Pc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm)$^{-1}$	$\Delta\lambda$ (nm)	q (Å)[a]	f[b]	σ (10^{-18}) cm^2[c]	Δv (cm^{-1})
Borate glass	273.3	N	2.99	0.27	–	–	[d]	1.27	–
	355.7	B	3.01	0.77	–	–	[d]	1.28	–
	386.6	–		2.47	0.63	–	[d]	1.05	–
	510	–	0.59	0.15	55.1	6.7	0.94	0.25	–
	566	–	0.56	0.14	20.7	2.0	0.39	0.23	–
	600	–	0.63	0.16	14	1.4	0.27	0.26	–
	693.3	Q_y	0.27	0.07	24.6	1.03	0.15	0.11	505
	730	Q_x	0.31	0.06	28.0	1.09	0.19	0.14	520
CIN[d]	664	Q_y	–	1.51	16.0	–	~0.17	–	966
	698	Q_x	–	1.62	18.5	–	~0.17	–	252
Vapor	624	Q_y	–	–	–	–	–	–	–
	685.9	Q_x	–	–	–	–	–	–	–
Styron	662	Q_y	–	–	10	–	–	–	920
	697	Q_x	–	–	15	–	–	–	232
Tyril	661	Q_y	–	–	–	–	–	–	897
	694.4	Q_x	–	–	–	–	–	–	178
Plexiglas	654.3	Q_y	–	–	–	–	–	–	742
	687.4	Q_x	–	–	–	–	–	–	31

[a] $q = 1/2500(\varepsilon \Delta\lambda/\lambda)$.
[b] $f = 4.32 \times 10^{-9} \int \varepsilon(v)dv$.
[c] Since the bands are all overlapping in this region f is not evaluated.
[d] Chloronaphthalene.

Table 2
Optical constants of MnPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm)$^{-1}$	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	324.1	N	3.33	0.94	–	–	[a]	1.52	–
	365.5	B	3.26	0.92	–	–	[a]	1.49	–
	386.2	–	2.86	0.81	–	–	[a]	1.31	–
	489.6	–	0.36	0.10	34.4	2.8	0.65	0.16	–
	579.3	–	0.4	0.11	10.3	0.8	0.15	0.18	–
	600	–	0.53	0.15	14	1.4	0.25	0.24	**
	696.5	Q_y	1.1	0.31	34.5	6.1	0.95	0.50	708
	737.9	Q_x	1.63	0.46	24.6	8.6	1.3	0.74	451
CIN	654	Q_y	–	–	–	–	–	–	**
	682	Q_x	–	–	–	–	–	–	**

[a] No vapor data available.

Table 3
Optical constants of FePc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm^{-1})	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	283.3	N	2.41	0.68	–	–	–	1.14	–
	309	–	2.23	0.62	–	–	–	1.06	–
	376.7	B	2.33	0.66	–	–	–	1.10	–
	386	–	2.17	0.61	–	–	–	1.02	–
	500	–	0.92	0.12	17.4	1.66	0.72	0.20	–
	580	–	0.37	0.10	17.2	1.18	0.23	0.17	–
	600	–	0.45	0.13	20.9	1.78	0.32	0.21	
	626.7	Q_y	0.48	0.18	26.8	1.92	0.28	0.30	670
	667	Q_x	0.56	0.16	29.1	2.07	0.30	0.26	654
DMSO	320	B	–	–	84.5		$\sim$0.17		
	655.5	Q	–	–	35.5		$\sim$0.17		−475
Vapor	340	B	–	–	–	–	–	–	–
	676	Q	–	–	–	–	–	–	–

Table 4
Optical constants of CoPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm^{-1})	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	293.3	N	2.59	0.74	–	–	–	1.23	–
	353.3	B	2.54	0.72	–	–	–	1.21	–
	379.8	–	2.31	0.66	–	–	–	1.10	–
	506.5	–	0.50	0.14	68.9	7.8	1.74	0.23	
	573.3	–	0.43	0.12	14.0	1.1	0.21	0.20	
	600	–	0.52	0.14	14.0	1.3	0.24	0.24	
	680	Q_y	0.43	0.12	48.2	2.3	0.37	0.20	1042
	747	Q_x	0.52	0.14	45.2	3.6	0.58	0.24	810
Vapor	312.5	B	–	–	74	–	–	–	–
	657.0	Q	–	–	55.5	–	–	–	–
DMSO	329.0	B	–	–	68.0	–	–	–	–
	663.0	Q	–	–	35.5	–	–	–	138

the Q_x and Q_y components. In fact because of the D_{2h} symmetry of H_2Pc, a total of four bands should be observed in the region of Q bands. However, it is interesting to note that no quartet was till observed in the Q band of any H_2Pc based systems [23]. Apparently the slight interaction with the neighboring molecules that occur in the solid is sufficient to broaden these transitions so that only two absorptions are observed. The results summarized in Table 1 also reveal that the oscillator strength of the Q_x and Q_y bands of H_2Pc in borate glass are well in agreement with that of CIN whereas the half width of the bands shows the sequence styron < CIN < borate glass.

3.1.2. MnPc

The MnPc system shows two well resolved transitions in the 600–800 nm region. The Q_x and Q_y transitions are observed, respectively, in the 737.9 and 696.5 nm regions. Also in the visible region oscillator strength is found to be maximum ($f = 1.3$) for the Q_x transition. The other optical parameters viz. absorption coefficient, electric dipole strength, molecular extinction coefficient are also found to be maximum for this band. The spectrum also shows an intense band in the UV region and is usually designated as the B band or Soret band. This band is a result of the molecular transitions $b_{2u}(\pi) \rightarrow e_g(\pi^*)$. Since the absorption

data of MnPc in other matrices are rarely reported, no comparison could be made.

3.1.3. FePc

The spectrum of FePc is fairly resolved so that Q_x and Q_y bands appear as distinct bands. The N band appears at 283.3 nm with an extinction coefficient of 0.68×10^{-6} (ml^{-1} cm)$^{-1}$ and absorption coefficient of 2.41 cm^{-1}. If a comparison of the absorption data of FePc in DMSO solvent with that of borate matrix is made one can clearly notice the fact that the half band width of Q_x and Q_y absorption bands has been considerably reduced in going from DMSO to glass.

Table 5
Optical constants of NiPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm^{-1})	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	320.5	N	1.69	0.48	–	–	–	0.84	–
	355.0	B	1.69	0.48	–	–	–	0.83	–
	379.1	–	1.67	0.47	–	–	–	0.27	–
	482.6	–	0.56	0.16	17.2	2.2	0.90	0.38	–
	572.2	–	0.77	0.22	48.4	7.4	1.39	0.71	–
	624.1	–	0.43	0.40	48.4	12.4	2.28	0.71	–
	693.3	Q_y	1.42	0.40	34.4	8.0	1.26	0.70	715
	726.7	Q_x	1.42	0.40	41.3	9.1	1.38	–	782
CIN	671	Q	–	1.26	18.0	–	0.2	–	453
			–	–	–	–	–	–	–
Styron	668	Q	–	1.30	15.0	–	0.18	–	386
			–	–	–	–	–	–	–
Tyril	668.4	Q	–	1.4	–	–	0.16	–	395
			–	–	–	–	–	–	–
Plexiglas	662.0	Q	–	0.51	–	–	0.12	–	250
			–	–	–	–	–	–	–
Vapor	651.2	Q	–	–	31	–	–	–	–
			–	–	–	–	–	–	–

Table 6
Optical constants of CuPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm^{-1})	$\Delta\lambda$ (nm)	Q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	275.7	N	1.35	0.38	–	–	–	1.27	–
	289.5	–	1.52	0.43	–	–	–	1.28	–
	330.9	B	1.38	0.39	–	–	–	1.05	–
	361.9	–	1.35	0.38	-	–	–	0.25	–
	386.0	–	1.38	0.39	–	–	–	–	–
	431	–	0.69	0.19	–	–	–	0.23	–
	600	–	0.83	0.23	48.5	7.4	1.45	0.26	
	634.4	–	1.04	0.29	30.2	5.5	0.9	0.11	
	662.0	–	1.14	0.32	24.2	4.7	0.7	–	–
	700	Q_y	1.97	0.56	40.2	15.5	2.4	–	880
	740	Q_x	3.3	0.95	34.6	14.3	2.1	–	1558
CIN	678	Q	–	2.15	20.0	–	0.23	–	490
Styron	675.8	Q	–	1.4	21	–	0.20	–	442
Tyril	675.3	Q	–	1.34		–	0.18	–	431
Plexiglas	667.9	Q	–	0.48		–	0.14	–	267
Vapor	656.2	Q	–	–	57	–	–	–	–
	325	B	–	–	–	–	–	–	–

Table 7
Optical constants of ZnPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm)$^{-1}$	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	251.6	L	1.70	0.49	48.2	4.3	18.1	1.27	–
	303.3	B	1.60	0.47	–	2.9	11.4	1.28	–
	372.2	–	1.00	0.28	–	–	–	1.05	–
	399.8	–	1.10	0.33	–	–	–	0.25	–
	417.2	–	1.10	0.33	–	–	–		–
	662.0	–	0.90	0.26	41.3	6.4	1.06	0.23	–
	693.0	Q_y	1.30	0.37	27.6	5.8	0.9	0.26	574
	730.9	Q_x	2.0	0.16	38.8	1.8	0.2	0.11	862
DMSO	672	Q	–	2.15	20.0	–	–	–	248
	346	B	–	–	60.5	–	–	–	–
Vapor	661	Q	–	–	40.5	–	0.4	–	–
	326.5	B	–	–	56.5	–	1.2	–	–

Table 8
Optical constants of MoOPc doped borate glass matrix

Matrix	λ (nm)	Bands	α (cm^{-1})	ε (10^6) (mol l^{-1} cm)$^{-1}$	$\Delta\lambda$ (nm)	q (Å)^2	f	σ (10^{-18}) (cm^2)	Δv (cm^{-1})
Borate glass	330.9	B	3.23	1.0	–	–	–	1.68	–
	358.4	–	3.16	0.98	–	–	–	1.64	–
	379.1	–	3.06	0.95	–	–	–	1.59	–
	489.5	–	0.51	0.16	68.9	8.9	1.0	0.26	–
	579.1	–	0.46	0.14	13.8	1.3	0.24	0.23	–
	600.0	–	0.53	0.16	14.0	1.5	0.27	0.27	–
	733.3	Q_y	1.30	0.40	36.2	19.4	0.58	0.67	668
	766.7	Q_x	1.49	0.77	44.2	24.7	0.92	0.77	882

3.1.4. CoPc

The Q band of CoPc is much more resolved in borate glass matrix than that of FePc. The Q_x band appears at 747 nm with oscillator strength of 0.58 whereas the Q_y band appears at 680 nm with oscillator strength of 0.37. Both the bands appear to be superimposed each other over the region extending from 600 to 800 nm. The Soret band appears at 293.3 nm with an extinction coefficient of 0.74×10^{-6} (ml^{-1} cm)$^{-1}$ which is comparatively higher than that of all other bands. On comparing the present halfwidth data with that of DMSO and vapor medium the general tendency observed is DMSO < glass < vapor.

3.1.5. NiPc

Unlike the cases of H$_2$Pc, MnPc, FePc and CoPc, NiPc absorption spectrum shows three intense bands in the 600–800 nm region. In addition to the Q_x and Q_y bands another band also appears at 624.1 nm as in the case of CIN and styrone. The Q_x band is the strongest among the Q band system and is having an oscillator strength of 1.38. The nearby Q_y band is also equally strong with an oscillator strength of 1.26. Another important observation of the NiPc based borate glass is that, the new band at 624.1 nm appears with an oscillator strength which is nearly double that of the Q band. It should be noted that in other matrices such as CIN and styron this tendency was not observed. On comparing the Q band data of NiPc based borate glass with that of other matrices viz. CIN, styron, plexiglas, tyril and vapor phase data, it can be noticed that the Q band oscillator strength is maximum in the former whereas the half band width is minimum in styron medium.

3.1.6. CuPc

Among all other Pc based borate matrices CuPc doped sample exhibits the most interesting spectra. The spectrum altogether shows 12 transitions with a new band in the NIR region. The Q_x band is very sharp and has oscillator strength of 2.1 and half bandwidth 34.6 nm. The Q_y band is also equally sharp with oscillator strength slightly higher than that of the Q_x band. Another interesting observation is that the B band appears with a comparatively smaller extinction coefficient than the Q band. The spectrum also shows the characteristic N band at 275.1 nm. Comparison of the half band width of the Q band with the other matrices shows the tendency CIN < styron < borate glass < vapor. The appearance of the 1024.1 nm band in the NIR region is a characteristic feature of CuPc spectra and the appearance of similar band can be seen in other matrices also [14–16].

3.1.7. ZnPc

The spectrum of ZnPc is also characterized by the well resolved transitions in the UV–vis and the NIR regions. The Q_x and Q_y bands are, respectively, located at 730.9 and 693 nm with oscillator strength 0.2 and 0.9 and is preceded by a new band at 251.6 nm and is usually designated by the L band of Pc molecule. The L band is the result of the molecular transition $2a_{1u}(\pi) \rightarrow 8e_g(\pi)$ and is usually characterized by the extremely high oscillator strength in comparison with the other visible bands. The half bandwidth of this band is also maximum whereas it is approximately three times smaller than that of the Q_x band. Here also the absorption spectrum is characterized by the more pronounced NIR band at 1024.1 nm and its nature clearly shows that the oscillator strength of the transition is many times that of CuPc. Comparison of half bandwidth of Q band with other reported matrices shows that it is much less in comparison with vapor phase whereas it is more in line with that of DMSO solvent.

3.1.8. MoOPc

In the case of MoOPc both the Q_x and Q_y bands appear to be resolved with oscillator strengths 0.58 and 0.92, respectively. The Soret band appears at 330.9 nm with its characteristic features.

3.2. Appearance of new bands

The appearance of the general Q, B, L, and N bands are typical features of a phthalocyanine absorption spectrum in free or metallated derivative forms. Also the basic features of the electronic spectra of many differently substituted Pc-s are quite similar. Major difference in the spectrum between various matrices is attributed to the effect of the surrounding matrix upon the energy levels of Pc molecules. In our experimental observation, we have noticed a number of such 'extra' transitions in the entire UV–vis region in the spectra. It is well established that the free and metallated phthalocyanine molecules have very rich molecular orbitals and available vibronic energy levels [24]. The appearance of such weak 'extra' bands have already been noticed in vapor spectra and are due to the vibronic transitions associated with the phthalocyanine molecule [25]. In the present study, CuPc based borate glass matrix shows the maximum of nine extra bands whereas in all other matrices five to six extra bands are observed. Our experimental results show that except for the 600 nm band all other extra bands are metal dependent. A detailed molecular orbital calculations by Eastwood et al. [6] show the presence of some $\sigma \rightarrow \pi$ transitions in the $300 \rightarrow 700$ nm region. Some of the identified transitions are $e_u'(\sigma) \rightarrow 6e_g(\pi)$ (at $\sim$ 579 nm), $e_u''(\sigma) \rightarrow 6e_g(\pi)$ (at ~ 480 nm) and $a_{1u}(\sigma) \rightarrow 6e_g(\pi)$ (at ~ 355 nm). Eventhough these are forbidden transitions the ligand field surrounding the Pc molecule can mix these transitions with the nearly allowed transitions and thereby relax the forbiddenness of the $\sigma \rightarrow \pi$ transitions. These transitions could account for the bands at approximately 579,480 and 355 nm of the present glassy system. Interpretation of the other 'extra' bands require further molecular orbital calculations on the particular metal Pc.

The origin of the NIR band at 1024 nm can be accounted as arising due to the spin-forbidden $S \rightarrow T$ transition from a bonding to antibonding level. The strong spin-orbit coupling due to the heavy central metal ion relieves the spin-forbid-

denness of the $S \rightarrow T$ transition. Based on the above analysis a schematic energy level diagram showing the normal as well as the extra absorption transitions of free base and metal derivatives of Pc molecules in borate glass matrix is shown in Fig. 4.

3.3. Variation of Q, B band energies and oscillator strength with metals

It is noted from the Tables 1−8 that except for some minor changes the position of B and Q band are almost the same irrespective of the central metal ion. The plot between the B band energy (E_B) and the Q band energy (E_Q) for the various Pc doped samples does not ensure a correlation between the energies of the B and Q transitions Fig. 5. The energy difference between B and Q bands is found to lie in the wavelength range 370–440 nm.

The study of the dependence of Q band energies on the oscillator strengths for various Pc doped glasses shows that the interaction of the metal ion with Pc−π system is quite strong for FePc while the interaction is very weak for MoOPc. The extent of interaction is controlled by a combination of several factors including the size of the metal ion, the geometry of the Pc-s and electrostatic and inductive effect. However in the case of MoOPc the planar geometry of the Pc molecule is perturbed by the presence of the oxygen ion in the axial direction. The perturbation leads to the weakening of the overall π−π interaction and bonding between the Mo ion and the nitrogen ring system. It is reported earlier that the $[MoO]^{2+}$ ion is bound to a single Pc ring and the molybdenum atoms sit above the Pc plane [26]. Thus the aforesaid type and geometry of the bonding, accounts for the weak interaction in the case of MoOPc. The magnitude of the upper Q band energy provides a useful fingerprint for comparison of relative efficiency with which orbitals of the metal ion interact with the Pc−π system.

3.4. Effect of metals and red shift

The introduction of metals into the Pc molecule has a variable effect on the intensity and spacing but on the whole does not alter the general type.
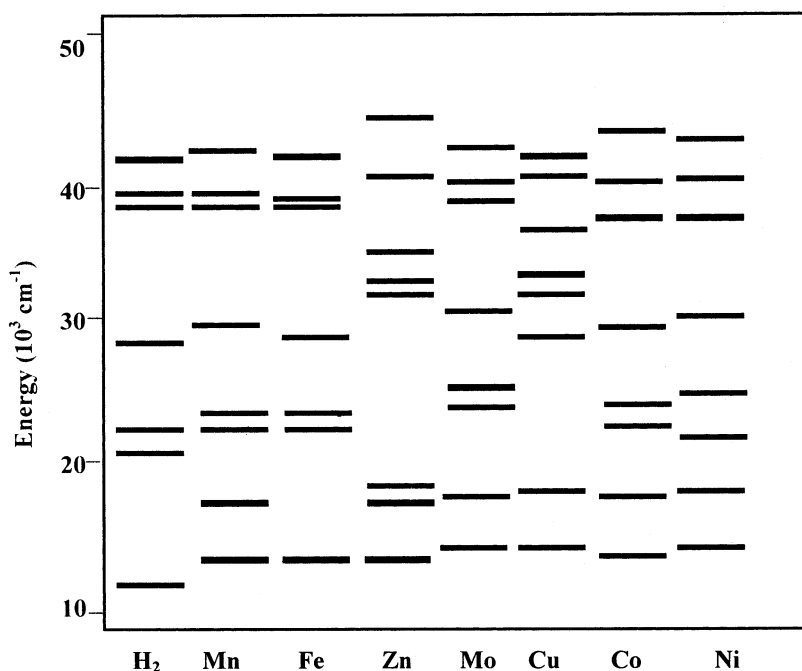

Fig. 4. Energy level diagram of the possible electronic transitions of Pc-molecules in the glass samples.
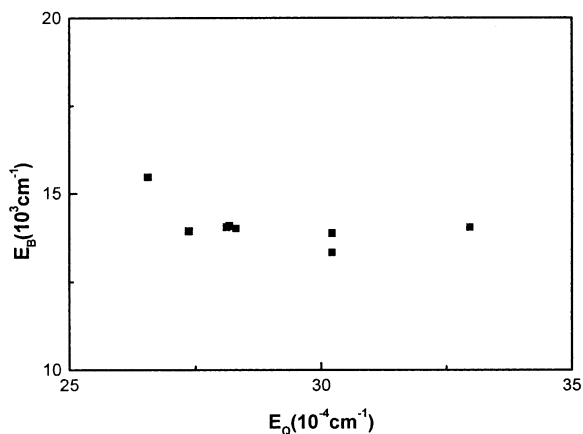
Fig. 5. Plot of B-band energy (E_B) vs. Q-band energy (E_Q) for various Pc doped samples.

The band positions of each of the Pc's in the borate glass are found to be smoothly varying functions of the atomic size of the metal ions with the displacement reaching a maximum for nickel ($Z = 28$). A similar tendency of the bands have already been reported by Anderson et al. in chloronaphthalene [27]. In view of the fact that the tendency to form planar four coordinate compounds reaches its maximum with Ni, it is possible that the magnitude of the shift in the absorption spectrum can be correlated with the strength of the co-ordinate links of the central metal ion.

The amount of Q band splitting (Davydov's splitting) of various Pc's does not show any linear relationship with the atomic number of the central metal ion. It can be seen that Davydov's splitting in the present system is maximum for the MnPc (822 cm^{-1}) whereas it is least in MoOPc (546 cm^{-1}). Usually the metal Q band shows a shoulder to the blue, however in the present glassy matrix we observed an enhancement of the shoulder band. This is tentatively attributed to the orbitally degenerate Q band state formed due to the strong ligand field effects of the environment. In fact, Lucia et al. [17] have already observed a Davydov's splitting in various disordered media. A comparison of the present values with other reported values clearly shows that the splitting in glassy matrix is considerably reduced whereas in the former the splitting observed was of the order of $1350–2230$ cm^{-1} [25]. According to Davydov's theory the amount of splitting is a measure of the interaction energy between molecules having different site symmetries. The bands split into as many components as there are nontransitionally equivalent molecules in the unit cell. Also there exists, a correlation between the tendency of the central metal ion to form out of plane bonding and the magnitude of the Davydov's splitting [28]. Thus the observed weak splitting confirms the out of plane bonding in MoOPc as discussed earlier.

Another important observation of the Q_x band of the Pc in the present glassy system is the linear relationship between the atomic number of the central metal ion and the red shift ($\Delta\nu$) from vapor to glass of the band. The red shifting of the Q_x transition in glassy matrix can be explained on the basis of electrostatic effect of the matrix on the transition dipole moment. The results summarized in Tables 1–8 clearly show that the red shift is matrix dependent being maximum for the present glassy system and minimum for the plastic medium. The comparatively large value of red shift in glassy medium is attributed to the higher value of dielectric constant of glass as well as the comparatively higher value of oscillator strength of the Q_x band consistent with the predictions of Chako [29].

4. Conclusions

We have successfully incorporated free base as well as metallated Pc molecules in inorganic borate glassy matrices and determined the various spectroscopic parameters. These Pc based glass systems show extra absorption bands in the UV–vis region apart from the well known Q, B, L and N bands. The present analysis shows that the 'extra' bands are matrix dependent except for the 600 nm band. It has also been shown that the interaction of the orbitals of the metal ion with the Pc–π system is weak for MoOPc while it is quite strong for the FePc. It is also observed that the present glassy system shows larger red shift as compared with the thermoplastic matrix which is the only solid medium studied earlier. The Davydov's splitting is much reduced in the present system and this

shows that the interaction energy between molecules having different site symmetries is comparatively weak. In conclusion, the smaller value of the half band width of the Q band in comparison with those reported for other matrices clearly indicates that this band can be exploited for better optical amplification.

Acknowledgements

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