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Zinc phthalocyanine thin film and chemical analyte interaction studies by density functional theory and vibrational techniques

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Abstract

Thin films of zinc phthalocyanine have been deposited on KBr and glass substrates by the thermal evaporation method and characterized by the x-ray diffraction, optical, infrared and Raman techniques. The observed x-ray diffraction and infrared absorption spectra of *as-deposited* thin films suggest the presence of an α crystalline phase. Infrared and Raman spectra of thin films after exposure to vapours of ammonia and methanol have also been recorded. Shifts in the position of some IR and Raman bands in the spectra of exposed films have been observed. Some bands also show changes in their intensity on exposure. Increased charge on the phthalocyanine ring and out-of-plane distortion of the core due to interaction between zinc phthalocyanine and vapour molecules involving the fifth coordination site of the central metal ion may be responsible for the band shifts. Changes in the intensity of bands are interpreted in terms of the lowering of molecular symmetry from D_{4h} to C_{4v} due to doming of the core. Molecular parameters and Mulliken atomic charges of zinc phthalocyanine and its complexes with methanol and ammonia have been calculated from density functional theory. The binding energy of the complexes have also been calculated. Calculated values of the energy for different complexes suggest that axially coordinated vapour molecules form the most stable complex. Calculated Mulliken atomic charges show net charge transfer from vapour molecules to the phthalocyanine ring for the most stable complex.

1. Introduction

The phthalocyanine (Pc) compounds are suitable for thin film deposition by thermal evaporation due to their chemical and thermal stability. Thin films of Pc are sensitive to strong electron acceptor gases, such as nitrogen oxide, halogens and hydrogen chloride, and show moderate response to donors, such as ammonia and hydrogen sulfide [1]. Adsorption of gases on the surface of Pc thin films induces changes in

the electrical conductivity of Pc films [2, 3]. Hence, the sensing properties of Pc films have been extensively studied by electrical conductivity measurements. In order to understand the mechanism of the sensing action, various spectroscopic techniques have also been employed [4–10]. Jones *et al* [11] have shown that the p-type metallo-phthalocyanine (MPc) films of cobalt, copper, iron, zinc and nickel could be used to discriminate between different electron-accepting and electron-donating gasses at low ppm concentrations.

A number of articles in the literature explain the sensor activity of Pcs in terms of the charge transfer interaction

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between Pc (electron donor) and the electron acceptor nitrogen dioxide [1, 12, 13]. However, even in the case of strong electron acceptor gases, the inferred structure of charge transfer complexes remain a subject of discussion [8, 9, 14, 15]. Moderate sensitivity of the CuPc towards methanol is also suggested to be a result of very little charge transfer/interaction between CuPc and methanol [1]. In earlier studies, we have also reported the possibility of electron transfer from methanol and ammonia to CuPc in order to explain the decreased conductivity of CuPc in the presence of these vapours [10, 16]. However, except for the decreased conductivity, there is no other supporting evidence of the charge transfer from methanol/ammonia in the literature according to the best of our knowledge. A conclusive molecular level understanding of the interaction between Pc and chemical vapour molecules is, therefore, a critical element required for optimizing their use as a sensor. It is also important to investigate the nature of bonding between the Pc and vapour molecules as reflected in the electronic charge distribution and the geometric configuration of the Pc–chemical vapour entity. Both of these issues, in principle, can be addressed by the density functional theory (DFT) and vibrational spectroscopy, namely infrared (IR) absorption and Raman scattering. These spectroscopic techniques provide valuable information about the interaction between chemical analytes and Pc on the molecular level, as the vibrational frequency positions are sensitive to the sub-ångström changes in bond length. Changes in the intensity of vibrational bands provide information about the orientational changes due to the distortions in molecules caused by the analytes. Another advantage of using the IR absorption spectroscopy is that it can also be used to identify the crystalline nature of Pc [17, 18]. In the recent past, the DFT has been used to accurately calculate the vibrational frequencies of the Pc molecules [19–21]. An additional advantage of the DFT methodology is that the equilibrium geometry of a molecule and interacting molecules are predicted [22], which can be tested against experiment.

In the present work, we analyse the IR and Raman spectra of ZnPc thin films before and after exposure to vapours of ammonia and methanol to investigate the effect of vapours on the ZnPc molecule by monitoring the changes in the spectra. DFT calculations have been performed to calculate the probable structure of the analyte–Pc complex, their bond formation energies and electronic charge transfer between ZnPc and methanol/ammonia. The thin films are also characterized by the x-ray diffraction (XRD) and optical absorption techniques.

2. Experimental details

In the present study, ZnPc powder (dye content 97%) from Aldrich is used without further purification. Methanol and ammonia from Qualigens Fine Chemicals, India, are used without further purification. Thin films of ZnPc have been deposited on the KBr and Corning 7059 glass substrates by the vacuum evaporation technique by keeping the substrates at room temperature and base pressure $\approx 2 \times 10^{-5}$ mbar, using a molybdenum boat. The deposited films have been

kept in the deposition chamber in the dark for 24 h to attain thermodynamic equilibrium [23]. The thickness of the film, used in the present study, is found ≈ 256 nm with a Surface Profiler Decktak 3030 ST. The IR spectra of the films deposited on the KBr substrate are recorded with a Perkin Elmer PE-R $\times 1$ FTIR Spectrophotometer having a spectral resolution of 1 cm^{-1} . The Raman spectra are recorded on a LabRam JY HORIBA HR 800 spectrograph equipped with the Olympus B $\times 41$ microscope and an ANDOR Model DU 420-0E-323 CCD detector. The measurements are carried out in a backscattering geometry with the incident light linearly polarized and scattered light was detected unpolarized. The excitation line at 488.0 nm is provided by an air-cooled Ar⁺ laser. The UV–visible spectra are recorded on a Hitachi 330 UV–vis–NIR Spectrophotometer having a resolution of 0.07 nm. The crystalline nature of the thin films is characterized by using the x-ray diffraction technique (Model: Philips, Goniometer: PW3050/60, geometry configuration: θ – θ , detector: Cu K α). Thin films are first placed in a desiccator under vacuum and then exposed to each analyte vapour for 20 min by introducing them into the desiccator.

3. Results and discussion

3.1. DFT calculations

DFT calculations to optimize the molecular structure of ZnPc and to analyse the interaction between ZnPc and vapours of methanol and ammonia are carried out using the B3LYP functionals [24, 25] with the basis set of 6-31G. These calculations are performed using the Gaussian 03 Revision D.01 program package [26]. In the process of geometry optimization of ZnPc for the D_{4h} point group, convergence of all the calculations and the absence of imaginary values in the wavenumbers confirmed the attainment of local minima on the potential energy surface. Selected optimized structural parameters of the molecule are listed in table 1. These values match well with the reported molecular structure data of ZnPc [21]. The optimized structure of ZnPc is shown in figure 1. This figure also shows the atom numbering and labelling scheme of the molecule. The calculated bond lengths, given in table 1, show an average error of 0.02 Å. After accounting for this error due to the selected basis set, the bond lengths correlate well with the structure in the crystal [27, 28]. However, DFT calculations of Tackley *et al* [20] without any symmetry constraints resulted in the C_{4v} point group with the zinc ion lying almost 0.07 Å above the plane of the Pc core. We have observed a few weak IR and Raman bands which are forbidden under the D_{4h} but allowed under the C_{4v} point group. This also suggests that the zinc ion is slightly displaced out of the core.

In order to monitor the effect of methanol and ammonia vapours on ZnPc thin films, the binding of vapour molecules at the different sites of ZnPc are considered by assuming that the binding may lead to the formation of stable complexes. The energy-minimized structures of these complexes without any symmetry restrictions have been calculated and reported in figure 2. We have also calculated the molecular parameters

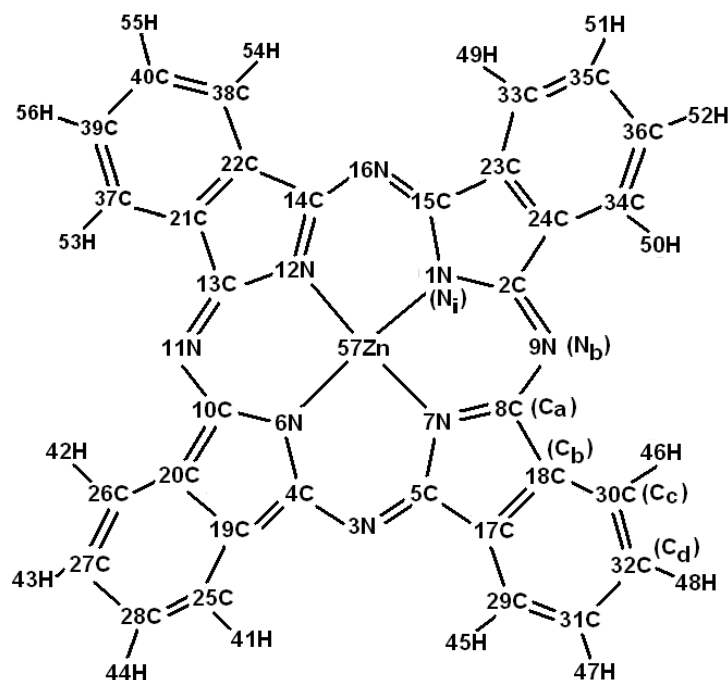


Figure 1. Structure, atom numbering and labelling scheme of zinc phthalocyanine.

Table 1. Calculated molecular parameters of ZnPc molecule.

Parameter ^a	ZnPc	ZnPc–methanol			ZnPc–ammonia	
		a	b	c	d	e
Zn–N _i	2.002	2.040	2.004	2.002	2.052	2.004
C _a –N _i	1.387	1.384	1.386	1.387	1.384	1.387
C _a –N _b	1.335	1.336	1.336	1.335	1.337	1.336
C _a –C _b	1.461	1.463	1.461	1.461	1.463	1.461
C _b –C _b	1.417	1.417	1.417	1.417	1.417	1.417
C _b –C _c	1.396	1.396	1.397	1.397	1.396	1.397
C _c –C _d	1.399	1.399	1.399	1.399	1.399	1.399
C _d –C _d	1.411	1.411	1.410	1.411	1.410	1.410
C _c –H	1.084	1.084	1.084	1.084	1.084	1.084
C _d –H	1.085	1.085	1.085	1.085	1.085	1.085
Zn–N _i –C _a	125.4	125.3	125.5	125.4	125.3	125.5
N _i –C _a –N _b	127.0	127.1	126.8	126.9	127.1	126.9
C _a –N _i –C _a	109.1	109.0	109.0	109.1	109.0	109.1
N _i –C _a –C _b	108.7	108.8	108.8	108.7	108.9	108.7
C _a –C _b –C _b	106.8	106.6	106.7	106.8	106.6	106.7
C _b –C _b –C _c	121.0	121.0	121.0	121.0	121.0	121.0
C _b –C _c –C _d	117.9	117.9	117.8	117.9	117.9	117.9
C _c –C _d –C _d	121.1	121.1	121.2	121.1	121.1	121.1
Zn–O _m		2.152				
N _b –H _m			1.868			
H–O _m				2.585		
Zn–N _{am}					2.177	
N _b –H _m						2.299

^a Bond lengths and bond angles are given in Å and degrees, respectively. Subscripts m and am refer to methanol and ammonia, respectively.

of these complexes. The average values of the parameters are reported in table 1. The calculated structures of ZnPc–analyte complexes represent the ZnPc and analyte molecules in the gas phase, whereas ZnPc is in the solid phase in the thin films. Therefore, calculated structures of these complexes may be

considered an approximation to the actual complexes formed in the thin films. It can be seen from figure 2 that the methanol and ammonia molecules bind with the zinc metal ion, bridge nitrogen atoms and/or the peripheral hydrogen atoms. The binding of methanol or ammonia vapours with ZnPc induces the out-of-plane distortion in the Pc ring, especially when the vapour molecules bind with the zinc ion (figures 2(a) and (d)) and form five-coordinated ZnPc species. This distortion is caused by the out-of-plane displacement of zinc ions on binding of the vapour molecules on its fifth coordination position (see figure 3).

We have also calculated the binding energy (E) of methanol and ammonia with ZnPc. The values of E for different ZnPc–analyte complexes are given in table 2. From this table, it is clear that methanol and ammonia molecules bind strongly with ZnPc when they are coordinated to the central zinc ion compared to other sites. On the basis of the calculated values of E , it can be inferred that the bonding between peripheral hydrogen and vapour molecules is very weak and hence need not be considered for the discussion of IR and Raman data. Moreover, the chosen standard B3LYP functionals inadequately describe weak van der Waals interactions [29]. It is interesting to note that the binding energy of ammonia is more than for methanol, if the zinc ion takes part in the bonding. On the other hand, calculated values of E show that methanol binds more strongly than ammonia at the N_b atoms. The out-of-plane displacement of the zinc ion leads to the increase in the Zn–N_i bond length by 0.038 Å for the methanol complex and 0.050 Å for the ammonia complex with a slight decrease in the C_a–N_i bond lengths. Other calculated molecular parameters do not show significant changes on complex formation.

The calculated values of Mulliken atomic charges suggest that, when the methanol molecule interacts with the ZnPc, the

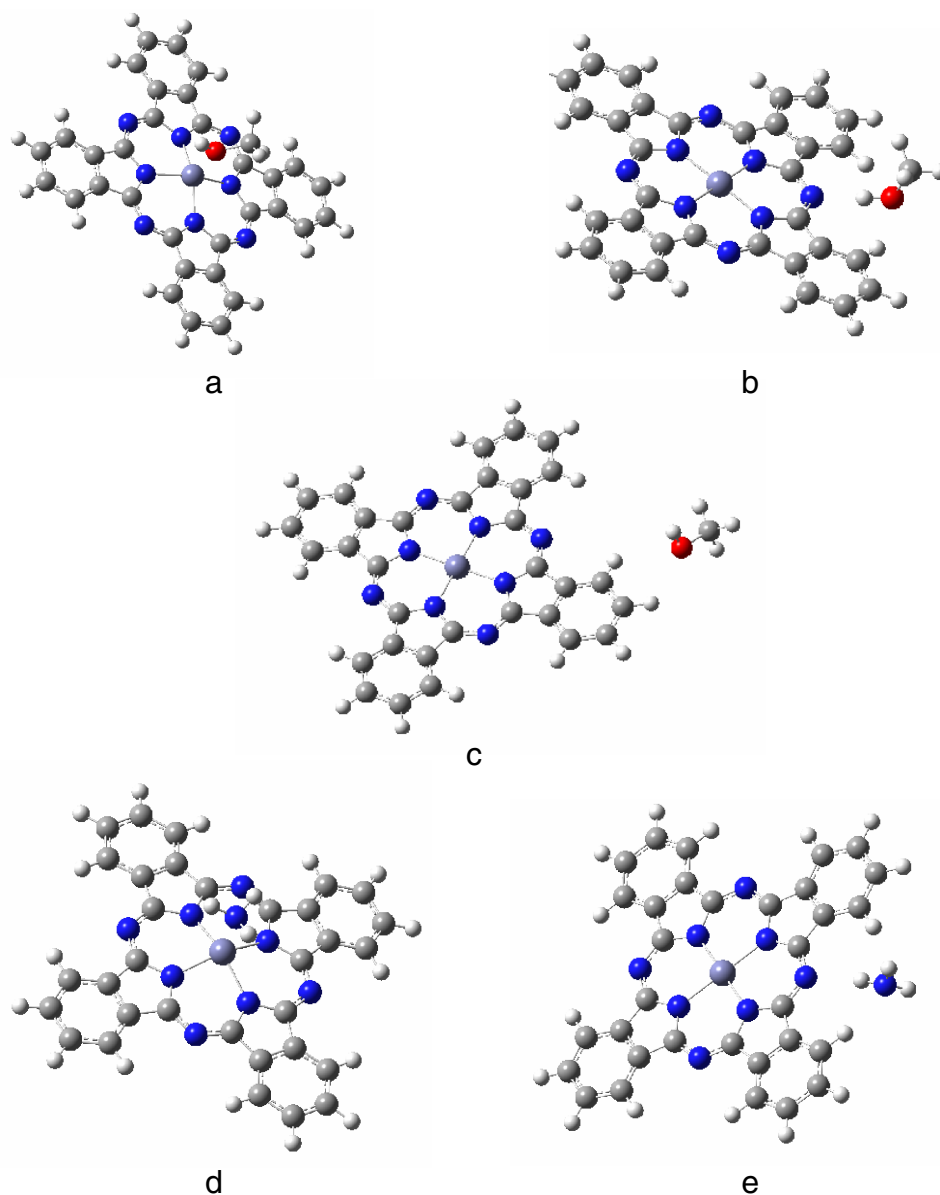


Figure 2. Calculated structure of the ZnPc and vapour complexes; (a) methanol bonded to the zinc ion, (b) methanol bonded to the N_b of Pc, (c) methanol bonded with the peripheral H atoms of the Pc, (d) ammonia molecule bonded to the zinc ion and (e) ammonia bonded to the N_b of Pc.

(This figure is in colour only in the electronic version)

Table 2. Binding energy between ZnPc and methanol/ammonia.

ZnPc–analyte complex (see figure 2)	Binding energy (E) kcal mol ⁻¹
a	-16.36
b	-12.21
c	-3.23
d	-20.27
e	-6.45

atomic charge is increased on the O_m atom of methanol for complexes a and b. The charge on the H atoms of methanol is also changed in both the complexes in comparison with the isolated methanol molecule, whereas the charge on the O_m

atom, which does not directly interact with ZnPc, remains unchanged for complex c. For complex a, Zn and N_i atoms of the core, designated as 57Zn, 1N, 6N, 7N and 12N (see figure 1), show a decrease in the Mulliken charge, while C_a atoms of the pyrrole rings designated as 2C, 4C, 5C, 8C, 10C, 13C, 14C and 15C show an increase in the charge. The pattern of changes in the atomic charges for complex a seems to contradict the fact that methanol transfers some of its electronic charge to the ZnPc. However, if the change in the atomic charge on the entire molecules of ZnPc and methanol are considered, we found that the ZnPc and methanol, respectively, are negatively and positively charged compared to neutral isolated molecules due to 0.12 (au) of charge transfer from methanol to ZnPc. This suggests the partial charge transfer

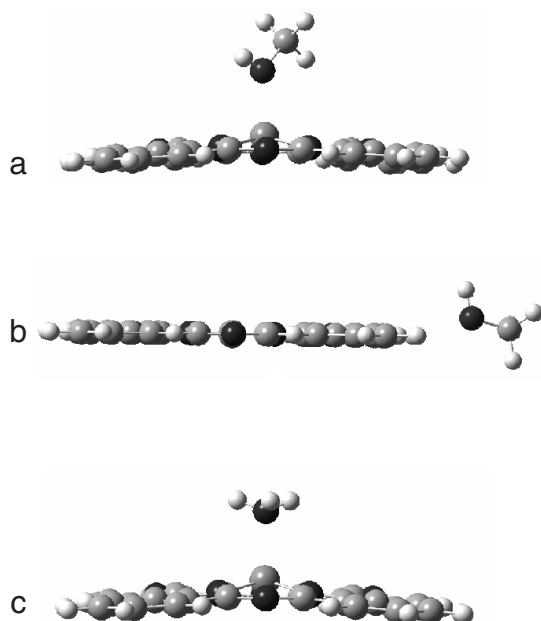


Figure 3. Calculated out-of-plane distortion in the ZnPc ring due to binding between ZnPc and methanol/ammonia molecules; (a) distorted and (b) planar ZnPc after interaction with methanol at different sites, (c) distorted ZnPc with zinc ion displaced out of the Pc plane on bond formation with ammonia molecule.

from methanol to ZnPc when the former interacts with the Zn atom of the latter molecule, since the O_m atom has a lone pair of electrons. The Zn atom further donates charge to the π electron system of the ZnPc molecule; similar to the π back donation observed in the porphyrin molecules, involving electron donors and metal ions [30]. Calculations indicate a similar charge transfer of 0.16 (au) from ammonia to ZnPc in the ZnPc–ammonia complex d involving the N atom of ammonia.

For the ZnPc–methanol complex b our calculations show the charges on the 2C and 8C atoms of ZnPc are decreased and on the 9N atom is increased, whereas in the methanol molecule, the charge on the O_m and H_m atoms of the OH group is increased and decreased, respectively. However, no net charge transfer from the methanol to ZnPc is observed. Hence, the changes in local atomic charge in complex b may be termed as the intramolecular rearrangement of electronic charges. Calculations indicate negligibly small charge transfer in ZnPc–ammonia complex e. The net charge transfer from methanol and ammonia to ZnPc for complexes a and d further justifies the values of binding energies for the above complexes.

3.2. Optical absorption characterization

In the visible region of the absorption spectrum of the as-deposited ZnPc thin film, we observe a broad Q band doublet at 613 and 673 nm (figure 4). The intensity of the former band is more than the latter band. This intensity pattern correlates well with the spectra of α -crystalline ZnPc thin films reported in the literature [31]. However, in the literature the higher wavelength Q band for α ZnPc thin films is reported around 700 nm [31]. The origin of electronic absorption bands of

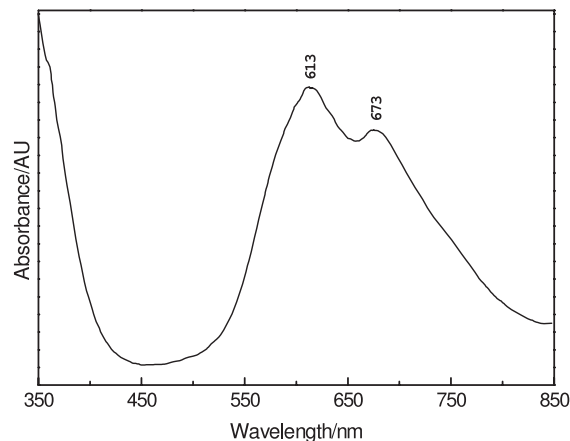


Figure 4. Optical absorption spectrum of the as-deposited ZnPc thin film in 350–850 nm region.

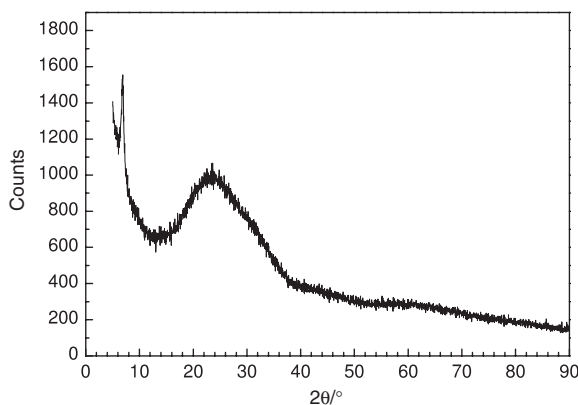


Figure 5. XRD spectrum of the as-deposited ZnPc thin film.

the ZnPc can be explained on the basis of π – π^* excitation from HOMO, a_{1u} and a_{2u} , to LUMO, $2e_g$. The broadening of the absorption bands is caused by the aggregation of the molecules [32]. Observation of more than one band in the Q spectral region is due to the exciton formation [33]. The lower energy Q band at 613 nm is due to the monomer and the higher energy Q band at 673 nm is the Q band of the dimer or higher aggregates [34].

3.3. XRD study

Figure 5 shows the XRD pattern of as-deposited ZnPc film on a glass substrate at room temperature. We observe a broad diffraction band between 16° and 36° , suggesting, thereby, that most of the composition of the thin film is amorphous. However, a peak at an angle of 6.912° corresponding to d value = 12.778 \AA is also observed. It arises due to the (2 0 0) plane of α -crystallites belonging to the monoclinic symmetry [35, 36]. The observed XRD pattern, therefore, suggests that in the as-deposited thin film ZnPc is present with an α -crystallites unit cell. The spacing of lattice planes of the crystallites and b axes are arranged parallel to the surface of the ZnPc layer. Further evidence of the presence of α crystalline

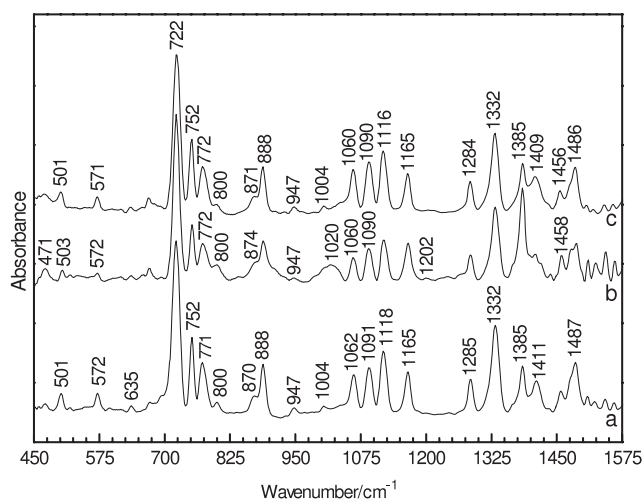


Figure 6. IR spectra of the ZnPc thin films: (a) *as-deposited*; (b) exposed to methanol; and (c) exposed to ammonia in 450–1575 cm^{-1} region.

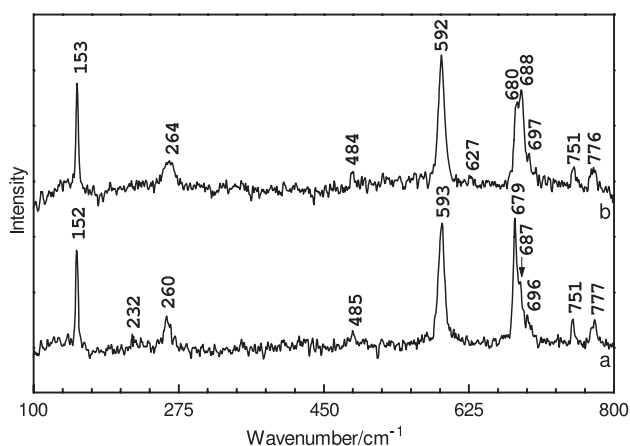


Figure 7. Raman spectra of the ZnPc thin films: (a) *as-deposited* and (b) exposed to methanol in 60–800 cm^{-1} region.

ZnPc in the thin film is provided by the IR absorption study as discussed in the next sections.

3.4. Vibrational study

The IR and Raman spectra of ZnPc thin films under different experimental conditions are shown in figures 6–8. In order to simplify the interpretation of vibrational spectra we assume that the film consists of ZnPc molecules, since the ZnPc crystal is a molecular solid. The molecule belongs to the D_{4h} point group symmetry with 165 normal modes of vibrations. These vibrations can be broadly divided into two groups: one consisting of the in-plane vibrations of symmetry A_{1g} , A_{2g} , B_{1g} , B_{2g} and E_u and the other consisting of the out-of-plane vibrations of A_{1u} , A_{2u} , B_{1u} , B_{2u} and E_g symmetry. Out of these, the vibrational modes of symmetry A_{1g} , B_{1g} , B_{2g} and E_g are Raman-active and the vibrational modes of symmetry species A_{2u} and E_u are IR-active. Therefore, its IR spectra consist of a few intense out-of-plane bands of the A_{2u} symmetry and in-plane bands of the E_u symmetry. In the Raman spectra,

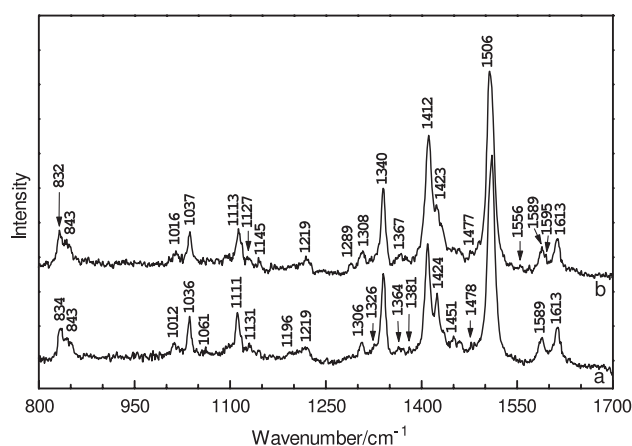


Figure 8. Raman spectra of the ZnPc thin films: (a) *as-deposited* and (b) exposed to methanol in 800–1700 cm^{-1} region.

we observe an intense band of B_{1g} symmetry. Bands, which belong to the A_{1g} , B_{2g} and E_g symmetry, are also observed. We have utilized a simpler, qualitative approach to interpret the vibrational data of the ZnPc thin film on the basis of recently reported normal coordinate calculations [19–21]. These calculations, along with the reported resonance Raman and IR studies of these complexes [17, 18, 37–40], considerably simplify the assignment of vibrational bands of ZnPc.

3.4.1. IR spectra. The observed IR bands and their assignments are listed in table 3. The IR bands of Pcs in the 700–800 cm^{-1} region are also used to identify different crystallites because of their sensitivity to the crystal packing arrangements in thin films [41–43]. In the spectrum of *as-deposited* ZnPc thin films (figure 6(a)), we observe bands at 722, 752 and 771 cm^{-1} with a shoulder at 780 cm^{-1} . The 722 and 771 cm^{-1} bands can be assigned to the out-of-plane wagging of C–H bonds [19]. The band at 752 cm^{-1} has been assigned to the out-of-plane wagging motion of C–H and the out-of-plane bending motion of $C_a-N_b-C_a$ and $C_a-N_i-C_a$ [21]. The observed wavenumbers of these IR bands are in complete agreement with the reported positions of the bands of α -crystallites [17]. Therefore, ZnPC is present in the α phase in the thin film. Thus, the observed IR band positions are in agreement with the XRD data.

In the IR spectra of the ZnPc thin film exposed to methanol and ammonia vapours (figures 6(b) and (c)), we observe C–H bending modes at 722, 753/752 and 772 cm^{-1} with a shoulder at 780/781 cm^{-1} . The positions of these bands match well with the corresponding bands of the *as-deposited* ZnPc thin film in the α phase, indicating that the crystalline form of the thin film does not change on exposure to the vapours. In the spectra of thin films exposed to methanol vapours, relative intensity of the bands at 1062, 1091, 1118, 1285, 1332, 1411 and 1487 cm^{-1} are decreased with respect to the band at 722 cm^{-1} . The relative intensity change can be explained on the basis of deviation of the ZnPc structure from the planarity which decreases the symmetry of exposed ZnPc molecules from ideal D_{4h} . This distortion is caused by the vapour molecules when they attach to the fifth coordination site of the zinc ion as

Table 3. Position and assignment of some observed IR bands of ZnPc thin film before and after exposure.

Thin film On KBr	Band (cm ⁻¹)		Mode no. and assignment ^{a,b}
	Thin film exposed to CH ₃ OH	NH ₃	
472	472	470	B _{2g} (B ₂); δ (iso)
501	503	501	E _u (E); c ring rot. + δ (C _a -N _i -C _a) + δ (Zn-N _i)
572	572	571	E _u (E); δ (iso) + ν (Zn-N _i)
635	636	634	E _u (E); δ (iso) + ν (Zn-N _i)
692	693	694	E _g (E); ρ (C-H) + ρ (C _a -N _i -C _a)
722	722	722	A _{2u} (A ₂); ρ (C-H) + ρ (C _a -N _i -C _a)
752	753	752	E _u (E); ρ (C-H) + ρ (C _a -N _i -C _a) + ρ (C _a -N _b -C _a)
771	772	772	A _{2u} (A ₁); ρ (C-H)
780	780	781	B _{1g} (B ₁); ν (Zn-N _i) + ν (C _b -C _b) + δ (C-H)
800	800	800	E _u (E); ν (Zn-N _i) + iso bre
870	874	871	E _g (E); ρ (C-H)
888	888	888	E _u (E); δ (iso) + δ (C _a -N _b -C _a) + ν (Zn-N _i)
947	947	947	A _{2u} (A ₂); ρ (C-H)
1004	1005	1004	E _u (E); δ (C-H) + ben exp
	1020		Methanol ν (C-O)
1062	1060	1060	E _u (E); ben def + δ (C-H) + ν (C _a -N _b) + ν (C _a -C _b)
1091	1090	1090	E _u (E); ν (C _a -N _i) + ν (C _a -N _b) + δ (C-H) + δ (Zn-N _i)
1118	1117	1116	E _u (E); δ (C-H) + ν (C _a -C _b)
1165	1166	1165	E _u (E); δ (C-H)
	1202		B _{2g} (B ₂); δ (C-H) + δ (Zn-N _i) + ν (C _a -N _i -C _a)
1285	1285	1284	E _u (E); ν (Zn-N _i -C _a -N _b) + δ (C _b -C _b) + δ (C-H)
1332	1332	1332	E _u (E); ν (ben) + ν (C _a -N _b -C _a) + δ (C-H)
1385	1385	1385	A _{1g} (A ₁); ν (Zn-N _i) + δ (C _a -N _b -C _a) + δ (C-H) + ν (C _a -N _b)
1411	1409	1409	E _u (E); δ (py) + ν (C _c -C _c) + δ (C-H)
1460	1458	1456	E _u (E); ν (C _b -C _b) + ν (C _c -C _c) + δ (py) + δ (C-H)
1477	1477	1474	E _u (E); ν (C _b -C _b) + ν (C _c -C _c) + δ (py) + δ (C-H)
1487	1486	1486	E _u (E); py exp + δ (C _a -N _i -C _a) + ν (C _a -N _b) + δ (C-H)

^a Assignments are based on [19–21].

^b The ν , δ and ρ denote stretching, in-plane bending and out-of-plane bending, respectively. The symbols iso, ben, def, exp, bre and rot represent the isoindole, benzene, deformation, expansion, breathing and rotation, respectively.

predicted by the DFT calculations for ZnPc–analyte complexes a and d (figure 3). In fact, there is evidence of the coordination of ammonia molecules with the central copper ion of the CuPc thin films in the literature [8, 10, 44]. The attachment of methanol molecules at the ZnPc thin film is evident from the observation of a band at 1020 cm⁻¹ in the spectrum of exposed films (figure 6(b)). This band can be assigned to the C–O stretching motion of the methanol molecule. Interaction between the Zn ion and methanol results in the displacement of zinc ions out of the mean Pc plane. The displacement of the Zn metal ion from the mean plane of the Pc leads to the doming of Pc macrocycles with decrease in overall molecular symmetry from D_{4h} to C_{4v}.

The 1383 cm⁻¹ band in the IR spectrum of ZnPc exposed to methanol shows intensity enhancement (figure 6). This band is assigned to the symmetric Zn–N_i stretching and in-plane C_aN_bC_a bending motion [19, 21]. It belongs to the IR-forbidden and allowed modes of A_{1g} and A₁ symmetries, respectively, in D_{4h} and C_{4v} point groups. Therefore, the presence of this band with the enhanced intensity in the spectrum of the exposed thin film relative to the *as-deposited* also supports the coordination of vapour molecules on the Zn ion. The non-presence of other bands of A_{1g} symmetry species also suggests that the distortion in the core or inner part of the ring of ZnPc of the exposed film is more than the outer part of the ring. The intensity of the 888 cm⁻¹ band, which is assigned

to the Zn–N_i and benzene ring breathing vibration [21], is also reduced in the spectra of exposed film. This observation also suggests the conformational change in the ZnPc molecule in the presence of vapours. Similar observations of the intensity change in surface-enhanced Raman spectra (SERS) of NO₂ exposed Langmuir–Blodgett films of cerium bisphthalocyanine (CePc₂) are reported by Aroca *et al* [4].

3.4.2. Raman spectra. The Raman spectra of ZnPc thin films under different experimental conditions are shown in figures 7 and 8. The observed bands and their assignments are listed in table 4. There are few differences in the spectra of ZnPc thin films before and after exposure to the methanol vapours. Some bands show a shift in their positions after exposure. Intensity of some bands also changes on exposure. Bands observed at 832, 1111, 1306 and 1410 cm⁻¹ in the spectra of *as-deposited* ZnPc thin films (figures 7(a) and 8(a)) show small but important upward shifts of 2 cm⁻¹ on exposure to the methanol vapour (figures 7(b) and 8(b)). This shift indicates a slight increase in the bond order of the ZnPc molecule due to the π back donation of electron density to the ring when methanol interacts with the zinc metal through its fifth coordination site. Our calculations also suggested that the net charge transfer takes place only for complexes a and d. Therefore, it is more likely that interaction between ZnPc and

Table 4. Position and assignment of observed Raman bands of ZnPc thin film before and after exposure.

Band (cm ⁻¹)		Mode no. and assignment ^{a,b}
As-deposited on KBr	Exposed to CH ₃ OH	
152	153	B _{1g} (B ₁); ring + ν (Zn-N _i)
232		B _{2g} (B ₂); δ (Zn-N _i) + ring def
260	264	A _{1g} (A ₁); ring bre
485	484	B _{2g} (B ₂); δ (iso)
593	592	A _{1g} (A ₁); ring bre + ν (Zn-N _i) + ben exp
	627	E _g (E); iso twi
679	680	A _{1g} (A ₁); δ (C _a N _b -C _a) + iso exp
687	688	B _{2g} (B ₂); ben def
696	697	E _g (E); ρ (C-H) + ρ (py)
751	751	B _{1g} (B ₁); δ (C _a -N _b -C _a) + ν (Zn-N _i) + py exp
777	776	B _{1g} (B ₁); ν (Zn-N _i) + ν (iso)
832	834	A _{1g} (A ₁); ν (Zn-N _i) + ben exp + δ (C _a -N _b C _a)
843	843	E _g (E); ρ (C-H)
1012	1016	A _{1g} (A ₁); δ (C-H) + ben exp
1036	1037	B _{2g} (B ₂); δ (Zn-N _i) + ν (ring) + ben def
1061		E _u (E); ben def + δ (C-H) + ν (C _a -N _b) + ν (C _a -C _b)
1111	1113	E _u (E); δ (C-H) + ν (iso) + ν (Zn-N _i)
1131	1127	B _{1g} (B ₁); δ (C-H)
1145	1145	A _{1g} (A ₁); δ (C-H)
	1165	B _{1g} (B ₁); δ (C-H) + ν (Zn-N _i)
1196		E _u (E); δ (C-H) + iso def
1219	1219	B _{2g} (B ₂); δ (C _c -H) + δ (Zn-N _i) + ν (C _a -N _i -C _a)
	1289	B _{2g} (B ₂); δ (C-H)
1306	1308	B _{1g} (B ₁); ν (iso) + ν (Zn-N _i) + δ (C-H)
1326		A _{1g} (A ₁); ν (iso) + ν (Zn-N _i) + δ (C-H) + δ (C _a -N _b -C _a)
1340	1340	B _{1g} (B ₁); ν (C _c -C _c) + δ (C-H)
1364	1367	E _u (E); ν (C _c -C _c) + ν (C _b -C _b) + δ (C-H) + ν (C _a -N _b)
1381		A _{1g} (A ₁); ν (C _d -C _d) + ν (Zn-N _i) + δ (C _a -N _b -C _a) + δ (C _c -H)
1410	1412	A _{1g} (A ₁); ν (C _a -N _b -C _a) + py exp + δ (C-H)
1424	1423	B _{2g} (B ₂); δ (C-H) + ν (Zn-N _i) + ν (ring)
1451	1451	B _{1g} (B ₁); δ (C-H) + ν (C _b -C _b)
1460	1459	B _{2g} (B ₂); δ (C-H) + iso def
1478	1477	A _{1g} (A ₁); ν (C _a -N _b -C _a) + py exp + δ (C-H)
1510	1506	B _{1g} (B ₁); ν (C _a -N _b -C _a) + py exp + δ (C-H)
	1556	E _u (E); ν (ben) + δ (C-H)
	1568	B _{1g} (B ₁); ν (ben) + δ (C-H)
1589	1589	A _{1g} (A ₁); ν (ben) + δ (C-H)
	1595	E _u (E); ν (ben) + δ (C-H)
1613	1613	B _{2g} (B ₂); ν (C _b -C _c) + δ (C-H)

^a Assignments are based on [19, 20].

^b The ν , δ and ρ denote stretching, in-plane bending and out-of-plane bending, respectively. The symbols iso, py, ben, def, exp, bre and twi represent the isoindole, pyrrole, benzene, deformation, expansion, breathing and twist, respectively.

methanol/ammonia is taking place through the central metal ion.

The relative intensity of bands at 679 and 687 cm⁻¹ are increased and decreased, respectively, on exposure. The bands at 232, 1061, 1196 and 1326 cm⁻¹ disappear after exposure. On the other hand, new bands at 627, 1165, 1289, 1556, 1568 and 1595 cm⁻¹ appear in the spectra of exposed ZnPc. The appearance and disappearance of these bands and changes in the relative intensity of the observed bands once again confirm the distortions in the Pc molecule induced by the interaction of methanol vapours with the ZnPc.

The most important change in the spectrum of exposed compared to the as-deposited ZnPc spectrum is the downshift of 4 cm⁻¹ in the position of a band at 1510 cm⁻¹. This band arises due to the large displacement of C_a-N_b-C_a bridge bonds of the Pc ring. In Raman spectra of metal-Pc, this band has

been identified as highly sensitive to the core size of the Pc ring [45]. The core size variations correlate well with the metal ion size and structural distortions to some extent [46]. This band is observed at higher positions for the Pc, which have a smaller core [19, 20, 46]. Since the zinc ion has a large size, therefore, the core expands in order to accommodate the zinc ion at the centre. The zinc ion, therefore, lies almost in the plane of the Pc ring. On the other hand, in PbPc the corresponding band is observed at 1498 cm⁻¹ due to nonplanarity and doming of the core [46]. As predicted by the DFT calculations (see figure 3) the nonplanar distortions are induced in the Pc ring due to doming of the core on methanol coordination at the zinc ion. The doming of the core is mainly responsible for the downshift in the band at 1510 cm⁻¹ as the calculated value of N_b-N_b separation show only a negligible change of 0.001 Å.

In short, a small upward shift in the wavenumbers of Raman bands after exposure is due to the charge transfer from vapour molecules to the ring. Changes in the intensity of vibrational bands are due to the out-of-plane distortion of the ring, when vapour molecules attach to the metal ion as suggested by DFT calculations and a core-sensitive Raman band around 1510 cm^{-1} .

4. Conclusions

Zinc phthalocyanine thin films, deposited on the KBr and glass substrates, have been characterized by the UV-visible, IR, Raman and XRD spectroscopic techniques. Observed IR and XRD spectra show the presence of α -crystalline ZnPc in the *as-deposited* thin films. When these films are exposed to methanol and ammonia vapours, changes in the wavenumbers and intensity of some IR and Raman bands are observed. These changes arise due to binding of vapour molecules at the axial coordinate site of the zinc ion. The axially coordinated vapour molecule donates some of its charge to the Pc ring via the zinc ion. This charge transfer is responsible for most of the changes in the wavenumbers of the IR and Raman bands. The axial coordination of vapour molecules also induces an out-of-plane distortion in the Pc ring by moving the zinc ion out of the mean Pc plane. Displacement of the zinc ion lowers the symmetry of ZnPc from D_{4h} to C_{4v} , which accounts for the intensity changes in the vibrational bands and the downward shift in the core-sensitive Raman band of Pc observed around 1510 cm^{-1} . DFT calculations of the binding energies of methanol and ammonia with ZnPc also support the axial coordination of these vapour molecules. Calculations further indicate towards a partial charge transfer from axially coordinated vapour molecules to the Pc ring with concomitant out-of-plane distortion in the Pc ring, in complete agreement with the vibrational studies.

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