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Excitation Profiles of Soret-excited Resonance Raman Spectra of Platinum–Hematoporphyrin Complexes

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Resonance Raman spectra of solid hematoporphyrin-IX [$H_2(Hem)$] *and a series of platinum–hematoporphyrin complexes, the diacid species* [$H_4(Hem)$]CL_2 *and* [$H_4(Hem)$]$PtCl_4$, *and of* cis-$Pt(H_2Hem)Cl_2$ *complexes have been studied. Several bands show intensity changes with excitation wavelengths in the strong Soret and the weak α and β absorption regions. The 4579 Å excitation in the Soret region enhances mainly the totally symmetric modes, whereas excitation in the α and β absorption region enhances the non-totally symmetric modes. New absorption maxima at 4965 and 4658 Å have been revealed from the excitation profiles which were not visible in the absorption spectra of the complexes and which confirm the assignment of the α band near 5190 Å in the* cis-$Pt(H_2Hem)Cl_2$ *and Pt(Hem) complexes.*

Introduction

Earlier, we reported the Raman spectra of a series of platinum(II)–hematoporphyrin complexes [1]. In these spectra it was noticed that resonance enhancement occurred in some vibrations, mainly in the α and β absorption bands of the hematoporphyrin-IX molecule [2], when the spectra were taken with radiation wavelengths in the region 4579–5575 Å. The most intense electronic band ($\epsilon \sim 10^5 M^{-1}\mathrm{cm}^{-1}$) of hematoporphyrin-IX is located near 4030 Å (the Soret or S band). A pair of weaker bands are also observed near 5190 Å (β band) and 5575 Å (α band). Some Raman bands are greatly enhanced in intensity through coupling with the above electronic transitions. The electronic absorption spectra of metalloporphyrins arise from two allowed $\pi \rightarrow \pi^*$ electronic transitions [3] in the visible and near ultraviolet regions due to the π-conjugation in the porphyrin ring which are both of E_u symmetry in the D_{4h} point group. The $\pi \rightarrow \pi^*$ transitions due to strong configuration interactions give rise to the intense Soret absorption band and the two weak α, β bands. For a general discussion of porphyrins and metalloporphyrins and their absorption spectra see the works of P. Hambright [4]. X-ray photoelectron spectra of the above platinum complexes have been published [5]. The resonance Raman spectra in the Soret band are dominated by A-term scattering whereas the α and β bands show B-term scattering [6].

We showed in the previous study [1] that the Raman spectra of the platinum hematoporphyrin-IX complexes are significantly different from those of the free hematoporphyrin and that there is a shift of several bands on complexation in the sequence of reactions $H_2Hem \rightarrow [H_4Hem]Cl_2 \rightarrow [H_4Hem][PtCl_4] \rightarrow$ *cis*-$Pt(H_2Hem)Cl_2 \rightarrow Pt(Hem)$*. The Raman differences have been attributed to nitrogen–proton and nitrogen–platinum binding of the porphyrin tetrapyrrolic skeleton and to crystal packing forces [1]. In addition, some Raman bands which occur from vibrations of the porphyrin ring (1100–1650 cm^{-1}) showed resonance enhancement.

In this paper we analyse the excitation profiles of some Raman bands of the free hematoporphyrin-IX, the protonated porphyrin and the platinated porphyrin complexes [5] by comparing the intensities of the porphyrin ring vibrations in order to obtain a better understanding of the absorption spectra and the electronic properties of these complexes. The understanding of the resonance Raman spectra is important in order to determine the nature and the assignments of some porphyrin ring vibrational modes. Resonance enhancement is observed when approaching the S band. It is found that excitation of the platinum complexes within this band enhances

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*Abbreviations: *cis*-$Pt(H_2Hem)Cl_2$ = *cis*-dichlorohematoporphyrin-IX platinum(II), Pt(Hem = hematoporphyrin-IX platinum(II).

mainly the totally symmetric modes (A) while excitation in the α and β absorption regions [2] shows that the resonance Raman spectra are dominated by the non-totally symmetric modes (B).

Experimental

The free hematoporphyrin-IX was purchased from the National Biochemical Company. Its absorption spectrum corresponds to that published [2]. The platinum complexes studied here were prepared by the method of Macquet and Theophanides [2]. The visible absorption spectra of the complexes were recorded in the solid state as powders in the region 4500–6000 Å.

An Argon ion Laser (Spectra Physics 164) was used for sample illumination with a model 371 tunable dye Rhodamine 6G. Laser Raman spectra of solid samples were run using the rotating cell technique to avoid decomposition of the dark red samples. A 90° scattered light was used and the spectra were obtained with a Coderg triple Monochromator (Model T800). Band intensities were corrected for instrumental response using a calibration curve with a standard tungsten ribbon lamp operated under fixed conditions as well as the $(NH_4)_2SO_4$ band of νSO_4^{2-} at 981 cm^{-1} and the sodium dithionite band at 983 cm^{-1} as internal standards.

Results and Discussion

The resonance Raman spectra of the H_2Hem, $[H_4Hem]Cl_2$, $[H_4Hem][PtCl_4]$, *cis*-$Pt(H_2Hem)Cl_2$ and Pt(Hem) as solids were recorded using several exciting lines shown as vertical lines on the visible spectra in the Figures. Resonance enhancement was shown by the deviation from the (ν^4) law characteristic of resonance scattering. It was observed that excitation inside the absorption bands of the optical spectrum produced enhancement of some vibrational modes. Only the in-plane Raman vibrations are enhanced on resonance [7]. For example, excitation in the Soret band near 4000 Å, enhances mainly the totally symmetric modes, whereas excitation in the maximum of the α (or 0–0) band or inside the β (or 0–1) absorption band in the region 5000–6000 Å theoretically enhances the non-totally symmetric modes $(\rho_{\ell} > \frac{3}{4})$. The excitation profiles are shown in Figs. 1–4. These are corrected for transmission and sensibility due to the setting up of the samples and for the dependence on (ν^4). The assignments of the bands are given in Table I.

The excitation profiles for six of the Raman bands of hematoporphyrin are given in Fig. 1. Four bands are observed in the visible spectrum in addition to

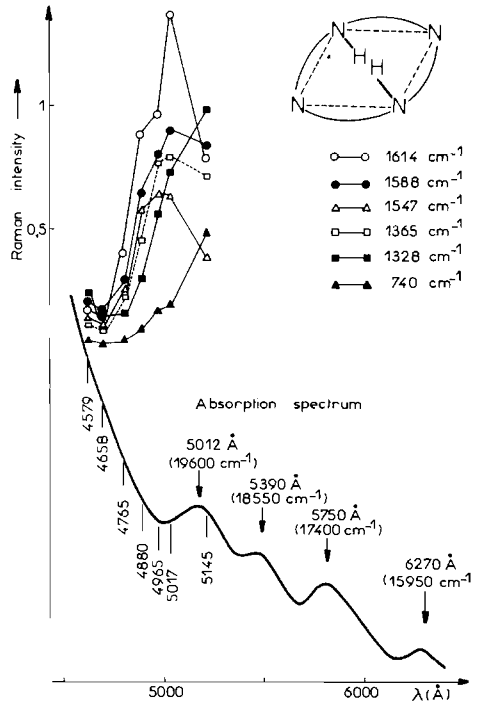

Fig. 1. Visible absorption spectra and excitation profiles for some of the Raman bands of H_2Hem. Vertical lines indicate position of exciting lines as marked. (Slit ≅ 6 cm^{-1}, time constant: 3s; 50 cm^{-1}/min).

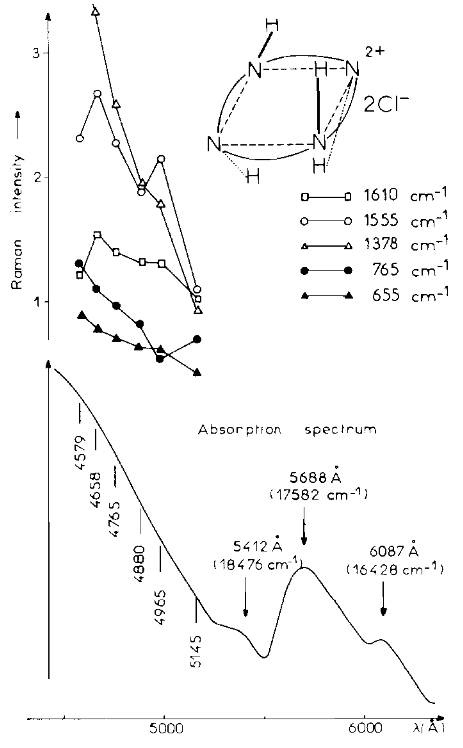

Fig. 2. Visible absorption spectra and excitation profiles for some of the Raman bands of $[H_4Hem]^{2+}$ $2Cl^-$. (Slit ≅ 6 cm^{-1}, time constant: 3s; 50 cm^- /min).

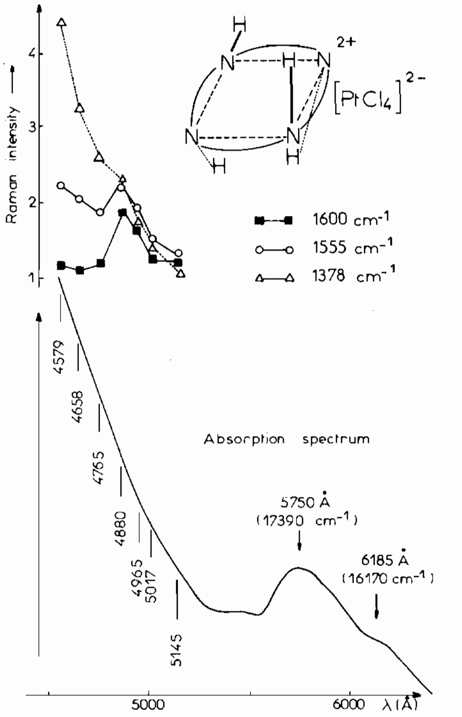

Fig. 3. Visible absorption spectra and excitation profiles of some Raman band of $[H_4Hem]^{2+}[PtCl_4]^{2-}$. (Slit ≅ 6 cm^{-1}, time constant 3s; 50 cm^{-1}/min).

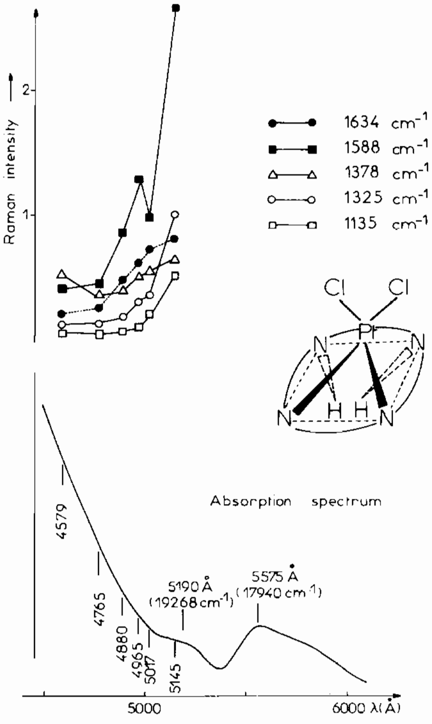

Fig. 4. Visible absorption spectra and excitation profiles of some Raman bands of *cis*-$Pt(H_2Hem)Cl_2$. (Slit ≅ 6 cm^{-1}, time constant 3s; 50 cm^{-1}/min).

the intense Soret band shown only partially in the spectrum peaking near 4500 Å. The Raman spectra of Hem show resonance enhancement of the Raman bands at 1614, 1588, 1547 and 1365 cm^{-1}. The maxima of these bands shift a quantum of vibration as we approach the 0–0 (or α band), which is due to a vibronic coupling. The bands at 1328 cm^{-} and 740 cm^{-1} seem to peak at the 0–1 band or β band. Therefore, these bands are coupled with the β band. Furthermore, a slight upward slope of the profiles towards the Soret band is shown. It is interesting that the excitation profile of the band at 1328 cm^{-1} crosses with those of the bands at 1365, 1547, 1588 and 1614 cm^{-1}. This seems to indicate a mixing of configurations during the excitation of this mode.

The resonance Raman spectra of the diacid chloride salt $[H_4Hem]Cl_2$ were also recorded. The excitation profiles and the absorption spectra are shown in Fig. 2. A general observation in these spectra is that the excitation profiles follow the Soret band. The excitation profiles of the Raman bands at 1610 and 1555 cm^{-1} give two maxima at 4965 and 4658 Å which are not shown in the absorption spectrum. The profile of the band at 765 cm^{-1} seems to rise after 4880 Å in resonance with the maxima at 5412 Å. The excitation profiles for the diacid salt of tetrachloroplatinate, $[H_4Hem][PtCl_4]$ are shown in Fig. 3. The bands at 1600 and 1555 cm^{-1} follow the Soret band with a maximum near 4880 Å. The band at 1378 cm^{-1} also follows the Soret band, but it shows a shoulder near 4880. The symmetry of the diacid cation with a heavy anion ($PtCl_4^{2-}$ as a counterion is higher than that of the free base and the absorption spectrum of the cation becomes simpler [2] with only two well-defined maxima at 5750 and 6185 Å.

The excitation profiles and the absorption spectrum of the sitting-atop complex *cis*-$Pt(H_2Hem)Cl_2$ are shown in Fig. 4. The excitation profiles of this covalently bound platinum to the nitrogens are going up in a reverse fashion as compared to the previous porphyrin cation species. They increase in intensity going towards higher λ and form a small hill near 5190 Å, towards the α or β bands. This intermediate complex of H_2Hem is an interesting compound [1, 2], because it is active against cancer [2] like [9] *cis*-$Pt(NH_3)_2Cl_2$. The Raman band at 1588 cm^{-1} also shows a maximum at 4965 Å. The excitation profile of the band at 1378 cm^{-1} is enhanced towards the Soret band and the α band and again shows a crossing with the bands at 1634, 1588 and 1325 cm^{-1}. The platinum atom and the two chlorides in this sitting-atop complex are assumed to be above the plane of the porphyrin [1, 2, 5]. The resonance Raman spectra of the platinum complex Pt(Hem) in which the Pt(II) is assumed to be in the plane of the Hem could be compared to that of Cu–porphin complexes [10]. However, the platinum

TABLE I. Raman Bands in (cm^{-1}) Observed for Pt(II) Porphyrin Complexes Excited in the Soret Region[a].

[H_4Hem] [$PtCl_4$]	*cis*-Pt(H_2Hem)Cl_2	Pt(Hem)	Assignment and Coupling of Vibrations [8]
	1634 m	1634 m	
1600 m	1610 sh	1614 sh	B_{1g} $C_\alpha C_m + C_\beta C_\beta + C_\alpha C_\beta$
1588 s	1588 s	1588 s	A_{2g} $C_\alpha C_m + \delta CH + C_\alpha C_\beta$
1555 s	1550 s	1556 m	
1470 w	1480 w	1496 w	B_{2g} $C_\alpha C_m + C_\alpha N$
1378 s	1378 m	1378 m	A_{1g} $C_\alpha C_\beta + C_\alpha C_m + C_\beta C_\beta$
1365 m	1365 m	1365 m	B_{1g} $C_\alpha C_\beta + \delta CH$
1328 m	1325 m	1325 w	
1225 w	1230 w	1250 w	
1120 m	1135 m	1135 m	
760 m	760 w	760 w	
730 m	738 w	735 w	$C_\alpha C_\beta + \delta C_\beta C_\alpha + C_\alpha N_\alpha$
670 m	680 w	675 w	

[a]All band positions are accurate to 1–2 cm^{-1}; s = strong, m = medium, w = weak, sh = shoulder. $C_\alpha C_m$, $C_\alpha C_\beta$ and $C_\beta C_\beta$ are carbon–carbon stretches, C_m is methine carbon atom, C_α and C_β are the α- and β-carbon atoms, respectively, of pyrrole [5] and $C_\alpha N$ is a carbon–nitrogen stretching.

atom in the Pt(Hem) complex is inside the plane of the porphyrin but without axial ligands. The excitation profiles for this compound have been published [12]. If we assume a D_{4h} point symmetry in this compound then it is known that both the S and β bands arise from the in-plane electronic π → π* transitions of E_u symmetry [11]. From the selection rules one can predict the Raman active modes capable of vibronically coupling with the two previous electronic transitions of E_u symmetry [10]. These vibrations are of the symmetry types, A_{1g}, A_{2g}, B_{1g} and B_{2g} (the irreducible representations in the direct product of $E_u \times E_u$). The A_{1g} modes are not effective in configuration mixing and should be enhanced by resonance Raman using excitation lines of shorter wavelengths approaching 4579 Å at the maximum of the Soret band producing bond and angle changes in the excited state. The intensity of the A_{2g}, B_{1g} and B_{2g} modes arises from vibronic coupling with the E_u electronic transitions. The band at 1378 cm^{-1} is enhanced in both directions as we move towards the S band and the α band and crosses the profiles of the bands at 1634, 1588 and 1325 cm^{-1}. This is a characteristic of totally symmetric modes (A). The profile of the Raman band at 1588 cm^{-1} reveals again a maximum near 4965 Å, like the diacid salt and the *cis*-Pt(H_2Hem)Cl_2. The non-totally symmetric modes are enhanced in intensity vibronically when the exciting line approaches the maxima of the α and β bands of the absorption spectrum at 5190 and 5579 Å, respectively and the intensity enhancement is more rapid with the 1325 cm^{-1} and 1588 cm^{-1} bands (See Fig. 4).

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