# Resonance Raman Investigation of the Electronic Transitions of some Iron(II) and Copper(II) α-Di-imine Complexes

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The electronic, i.r., Raman, and resonance Raman spectra of [Fe(phen)$_2$(CN)$_2$] (phen = 1,10-phenanthroline), [Cu(bq)Br$_2$] (bq = 2,2′-biquinolyl), and [Fe(bipy)$_3$][BF$_4$]$_2$ (bipy = 2,2′-bipyridyl) have been studied. Excitation within the contours of the strong visible charge-transfer bands in the electronic spectra of these complexes leads to the resonance enhancement of many of the $a_1$ modes of the α-di-imine ligands. The electronic shoulders (present for all three complexes) have their origin in vibronic coupling for [Fe(bipy)$_3$][BF$_4$]$_2$ and [Cu(bq)Br$_2$]. The electronic side-band for [Fe(phen)$_2$(CN)$_2$], however, arises from a second electronic transition. The presence of more than one ν(C≡N) mode in the Raman spectrum of [Fe(phen)$_2$(CN)$_2$] dissolved in 1 mol dm$^{-3}$ $H_2SO_4$ has been explained in terms of protonation of the phenanthroline ligand.

This paper extends the use of resonance Raman (r.R.) spectroscopy to study the electronic profiles of the α-di-imine systems [Cu(bq)Br$_2$] (bq = 2,2′-biquinolyl), [Fe(phen)$_2$(CN)$_2$] (phen = 1,10-phenanthroline), and [Fe(bipy)$_3$][BF$_4$]$_2$ (bipy = 2,2′-bipyridyl). Resonance Raman investigations have been carried out previously[1] for [Fe(bipy)$_3$]I$_2$·5H$_2$O. Solutions of the latter dissolved in water show an intense visible band at 530 nm which has been attributed to an electronic dipole-allowed 3*d* to ligand π charge-transfer (c.t.) transition[2] ($^1E \longleftarrow {}^1A_1$). This intense visible band exhibits a high energy shoulder (~1 600 cm$^{-1}$ separation from the main peak) which may be due to either an additional c.t. transition or a vibrational coupling in the excited electronic state. Clark *et al.*[1] observed up to 13 intensity-enhanced vibrational fundamentals in the r.R. spectrum and a study of the excitation profile indicates that the ν(C–N) mode of the ligand at ~1 600 cm$^{-1}$ possesses the greatest intensity enhancement. Thus, they explained the high energy shoulder in terms of vibronic coupling.

We have carried out an analogous r.R. study of [Fe(bipy)$_3$][BF$_4$]$_2$ dissolved in water to check our own data against the published results and to verify that the counter ion is totally independent of the complex cation in solution, with respect to its electronic and vibrational characteristics.

Metal complexes with 2,2′-biquinolyl have not been studied as extensively as their bipyridyl analogues but both Cu$^{II}$ and Cu$^{I}$ adducts with biquinolyl have been prepared.[3-6] The complex [Cu(bq)Br$_2$] is considered to have a distorted tetrahedral geometry on the basis of electronic spectra and magnetic susceptibility measurements,[7] but no *X*-ray data are available. The electronic spectrum of the complex dissolved in methanol shows an intense visible band at ~540 nm together with a high frequency shoulder. The latter may again be due to a second allowed electronic transition or to vibronic coupling.

Crystalline [Fe(phen)$_2$(CN)$_2$] possesses a pseudo-octahedral geometry and two isomeric forms, *cis* and *trans*, have been proposed.[8] The particular isomeric form produced is thought to be dependent upon the solvent used for the preparation, recrystallisation of the sample, or the solvent used during the spectroscopic investigations. The i.r. results for the solid state have been interpreted in terms of a *cis* structure for samples recrystallised from water or aqueous acid while a *trans* structure is suggested for samples prepared from non-aqueous media. The electronic spectrum of [Fe(phen)$_2$(CN)$_2$] in solution consists of one intense visible band with a high frequency shoulder. The position of the main band and shoulder move to higher wavenumber positions as the solvent is changed from CHCl$_3$ to 1 mol dm$^{-3}$ $H_2SO_4$. We have examined the r.R. spectra of the complex dissolved in several solvents in order to determine the origin of the electronic shoulder. We have also re-examined the apparent presence of *cis* or *trans* isomers in different solvents by Raman spectroscopy in the ν(C≡N) region.

## Experimental

*Preparation of Samples.*—The complex [Fe(bipy)$_3$][BF$_4$]$_2$ was prepared electrochemically[9] in 100 cm$^3$ of a solvent consisting of 60% anhydrous methanol and 40% anhydrous benzene. Iron wire (0.5 g, 99.5% purity) was cleaned in hot KOH solution and then anodically dissolved (using a platinum flag cathode) in the presence of 0.2 mol dm$^{-3}$ bipy and 0.05 mol dm$^{-3}$ NaBF$_4$. The latter acted as an electrolyte during the anodic dissolution. A current density of 50—75 mA cm$^{-2}$ was used for 3 h and a deep red crystalline product (1.0 g) was obtained after a small reduction in solvent volume. The product was not recrystallised (Found: C, 51.4; H, 4.4, N, 11.4. $C_{30}H_{24}B_2F_8FeN_6$ requires C, 51.2; H, 4.3; N, 11.9%).

The complex [Cu(bq)Br$_2$] was prepared by the electrochemical oxidation of copper in a cell containing 0.2 mol dm$^{-3}$ Br$_2$ and 0.05 mol dm$^{-3}$ NEt$_4$Br dissolved in anhydrous methanol (100 cm$^3$). A deep green solution containing 0.43 mol dm$^{-3}$ Cu$^{2+}$ was produced and addition of bq (1 mol) yielded deep red crystals of [Cu(bq)Br$_2$] (Found: C, 45.6; H, 2.8; N, 6.2. $C_8H_{12}Br_2CuN_2$ requires C, 45.1; H, 2.5; N, 5.8%).

The complex [Fe(phen)$_2$(CN)$_2$] was also prepared by the electrochemical oxidation of iron wire in a methanol–water (2 : 1) solvent medium containing a 1 : 1 mol ratio of KCN and phen. The phen (Aldrich Chemicals) was recrystallised from methanol prior to use.

*Instrumental Details.*—The Raman spectra were recorded using a Cary model 81 instrument converted to 90° operation by Anaspec Ltd. This incorporated a triple premonochromator which removed extraneous emission lines, a Brookdeal 9511 quantum photometer, and a cooled photomultiplier tube. The spectra were excited using lines of a Coherent Radiation model CR3 argon ion laser and the latter was also used or pump a Coherent model 590 dye laser filled with eithte Rhodamine 6G or sodium fluorescein. The spectra were calibrated by reference to the positions of well documented solvent bands. Band intensities were measured relative to

**Table 1.** Electronic absorption maxima and associated absorption coefficients for the complexes studied [a]

| Complex | Solvent | $\lambda_{max.}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|---|
| $[Fe(bipy)_3][BF_4]_2$ | $H_2O$ | 524, 485 (sh) (8.3 × 10$^3$) |
| $[Fe(phen)_2(CN)_2]$ | $CHCl_3$ | 595, 530 (sh) (~6 × 10$^3$) |
| | $CH_3CN$ | 590, 520 (sh) |
| | MeOH | 554, 490 (sh) |
| | $H_2SO_4$ [b] | 487, 442 (sh) |
| $[Cu(bq)Br_2]$ | MeOH | 546, 500 (sh) |

[a] sh = shoulder. [b] 1 mol dm$^{-3}$.

**Table 2.** Resonance Raman spectrum of $[Fe(bipy)_3][BF_4]_2$ [a] in aqueous solution; exciting frequency = 514.5 nm

| Fundamentals | | | |
|---|---|---|---|
| $\nu$/cm$^{-1}$ | $\rho$ | Intensity | Assignment [b] |
| 767 | 0.11 | w | Ring-H bend |
| 1 026 | 0.55 | m | Ring breathing |
| 1 036 | 0.13 | w | Ring stretch and bend and C–H bend |
| 1 069 | 0.21 | w | |
| 1 108 | 0.23 | w | Ring-H in-plane bend |
| 1 180 | 0.36 | m | |
| 1 282 | 0.29 | m | Ring stretch |
| 1 328 | 0.32 | s | Ring stretch and ring-H bend |
| 1 496 | 0.47 | vs | |
| 1 566 | 0.41 | s | Ring stretch (C=N and C=C) |
| 1 613 | 0.31 | s | |

[a] No $BF_4$ bands observed. [b] See J. S. Strukl and J. L. Walter, *Spectrochim. Acta, Part A*, 1971, **27**, 209.

internal standards {$\nu_1$ mode of potassium perchlorate for $[Fe(bipy)_3][BF_4]_2$ and $\nu(CS)$ of KSCN for $[Cu(bq)Br_2]$ and $[Fe(phen)_2(CN)_2]$} and then corrected for the $\nu_4$ dependence. Solution measurements were made at room temperature on *ca.* $10^{-4}$ mol dm$^{-3}$ solutions using the spinning-cell technique.

The sample of $[Fe(phen)_2(CN)_2]$ exhibited a strong fluorescence band in the region 540—515 nm which severely hampered the recording of the r.R. spectrum in this region. The extent of the fluorescence was drastically reduced by washing the solid complex with diethyl ether prior to the preparation of each solution.

Infrared spectra were recorded on a Perkin-Elmer model 598 spectrometer. Electronic spectra of the complexes dissolved in various solvents were recorded using a Perkin-Elmer model 402 spectrometer. Curve resolution of the shoulders which are present on the side of the visible absorption bands was carried out using a Du Pont 3100 Curve Resolver.

## Results

*Electronic Spectra.*—The data obtained from solution electronic spectra are shown in Table 1. The absorption coefficients of *ca.* $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ and the solvent dependence of the electronic absorption maximum for $[Fe(phen)_2(CN)_2]$ are characteristic of c.t. bands. The solvent shifts for the latter are large and readily observable by eye (deep blue in $CHCl_3$, red-orange in 1 mol dm$^{-3}$ $H_2SO_4$). The splitting between the main and shoulder bands is largely independent of solvent.

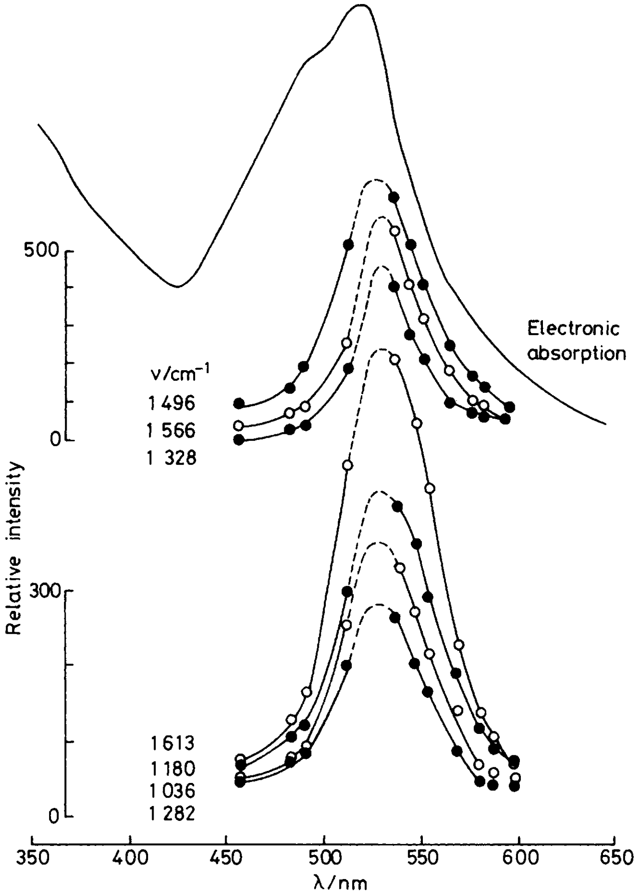

**Figure 1.** Excitation profiles of $[Fe(bipy)_3][BF_4]_2$ in aqueous solution

*Resonance Raman Spectra.*—The spectra of $[Fe(bipy)_3][BF_4]_2$ were recorded in aqueous solution at several different exciting frequencies. Table 2 reports band positions, depolarisation ratios, intensities, and assignments for some resonantly enhanced bipyridyl modes. The excitation profiles for the bipy fundamentals are shown in Figure 1. The intensity values given are relative to $\nu_1$ of $ClO_4^-$ used as the internal standard. The depolarisation ratios were found to be independent of the exciting radiation frequency. The bands at 1 496, 1 566, and 1 613 cm$^{-1}$ were observed to exhibit the greatest intensity enhancements as the frequency of the exciting line was tuned across the electronic absorption maximum at 524 nm. The band at 1 613 cm$^{-1}$ showed the largest intensity increase of all, but it should be noted that it is not the most intense band in the spectrum. It is largely attributable to a ligand $\nu$(C=N) mode.[1] The excitation profiles are incomplete in the region 515—535 nm due to the lack of exciting lines; however, the different degrees of enhancement are still clearly demonstrated.

The excitation profiles for $[Cu(bq)Br_2]$ dissolved in methanol are shown in Figure 2 and the positions, relative intensities, and depolarisation ratios of the resonantly enhanced ligand modes are given in Table 3. The depolarisation ratios indicate that only the symmetric ligand modes are resonantly enhanced and the ratios are approximately constant for different exciting lines. The vibration occurring at 1 571 cm$^{-1}$ gives the greatest intensity enhancement on approaching resonance; this position should be compared with the value of the curve-resolved peak-to-shoulder separation of the visible band (*ca.* 1 685 cm$^{-1}$). The measured excitation profiles have symmetrical contours. No resonance enhancement is observed for vibrations assigned to either benzene ring modes of the ligand or $\nu(CuBr_2)$.

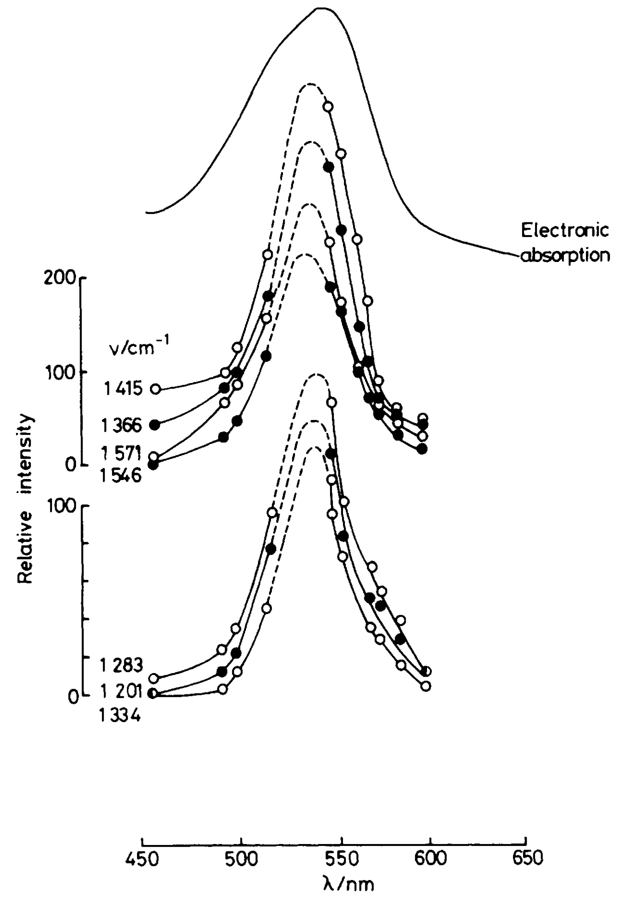

**Figure 2.** Excitation profiles of [Cu(bq)$Br_2$] in methanol

**Table 3.** Resonance Raman bands of [Cu(bq)$Br_2$] in methanol; exciting frequency = 542 nm

| Fundamentals | | |
|---|---|---|
| v/cm$^{-1}$ | ρ | Intensity |
| 1 163 contains solvent component | | |
| 1 201 | 0.32 | m |
| 1 283 | 0.51 | m |
| 1 334 | * | w |
| 1 366 | 0.45 | s |
| 1 415 | 0.27 | vs |
| 1 546 | 0.37 | m |
| 1 571 | 0.31 | s |

* Too weak to estimate value of ρ accurately.

The spectra of [Fe(phen)$_2$(CN)$_2$] were recorded for both chloroform and methanol solutions. The resonantly enhanced modes lie in the region 1 200—1 650 cm$^{-1}$ and they are assigned to fundamentals of the phen ring [10] (see Table 4). The excitation profiles for the complex dissolved in both solvents are shown in Figures 3 and 4. The ring stretching mode at 1 637 cm$^{-1}$ exhibits the maximum intensity enhancement calculated as a percentage increase in intensity on reaching resonance.

*Infrared and Normal Raman spectra of* [Fe(phen)$_2$(CN)$_2$].—Infrared spectra of samples, recrystallised both from aqueous and chloroform solutions, have been recorded as KBr discs.

**Table 4.** Resonance Raman spectrum of [Fe(phen)$_2$(CN)$_2$] in chloroform; exciting frequency = 549.3 nm

| Fundamentals | | | |
|---|---|---|---|
| v/cm$^{-1}$ | ρ | Intensity | Assignment |
| 738 | * | w | Ring-H bend |
| 810 | * | w | |
| 882 | 0.13 | m | |
| 1 141 | 0.38 | m | Ring-H in-plane bend |
| 1 256 | 0.55 | w | Ring stretch |
| 1 307 | 0.38 | m | Ring stretch and ring-H bend |
| 1 325 | * | w | |
| 1 456 | 0.31 | vs | Ring stretches (C=C and C=N) |
| 1 512 | 0.35 | s | |
| 1 586 | 0.30 | vs | |
| 1 608 | 0.29 | w | |
| 1 637 | 0.23 | s | |

* Too weak to determine ρ accurately.

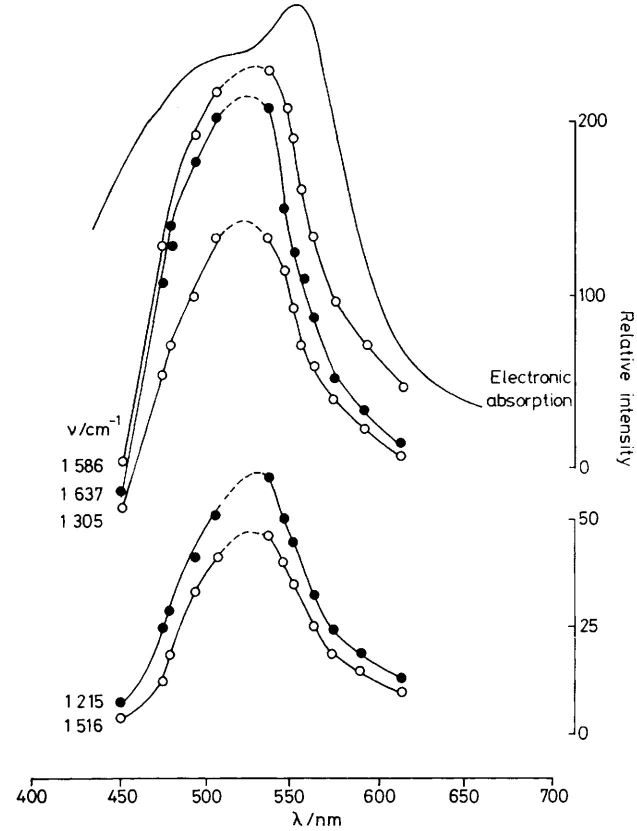

**Figure 3.** Excitation profiles of [Fe(phen)$_2$(CN)$_2$] in methanol

The region 2 000—2 100 cm$^{-1}$ is of particular interest because of the *cis–trans* interpretation given by previous workers.[8] Our solid state spectra, obtained for this region, are shown in Figure 5.

Since crystalline state effects may well account for one or more of the bands present in the spectrum of the complex recrystallised from water, we have also examined the Raman-active ν(C≡N) modes in solution. These were recorded for saturated solutions of [Fe(phen)$_2$(CN)$_2$] dissolved in $CH_3OH$, $CHCl_3$, and 1 mol dm$^{-3}$ $H_2SO_4$; the complex is insufficiently soluble in aqueous solution at room temperature

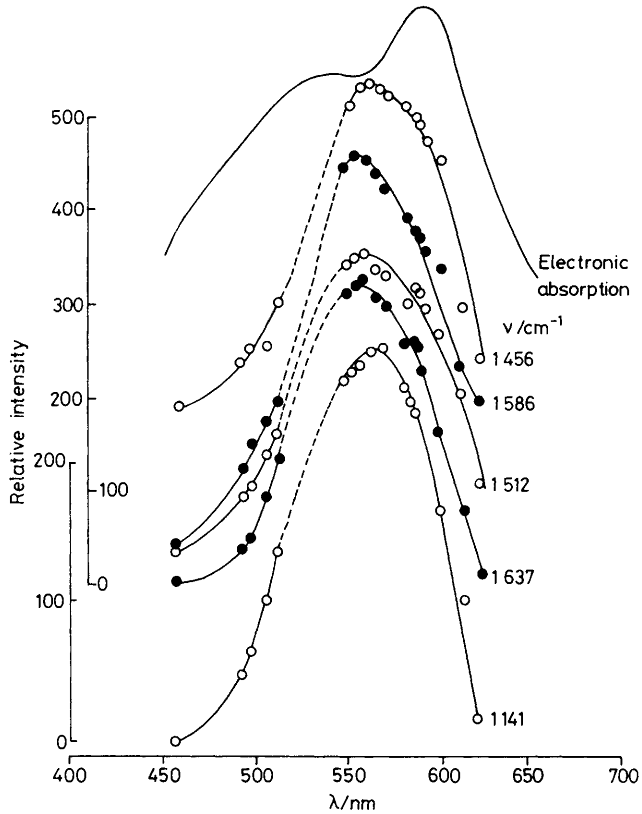

**Figure 4.** Excitation profiles of [Fe(phen)$_2$(CN)$_2$] in chloroform

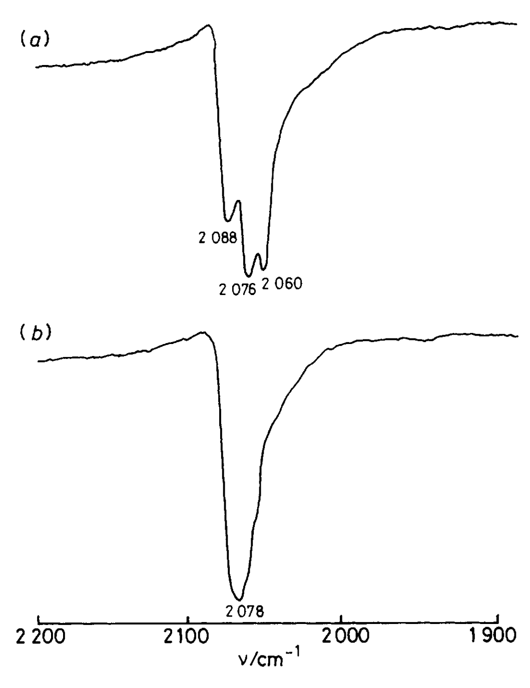

**Figure 5.** The solid state i.r. spectra showing the ν(CN) modes of [Fe(phen)$_2$(CN)$_2$] recrystallised from aqueous solution (*a*) and chloroform (*b*)

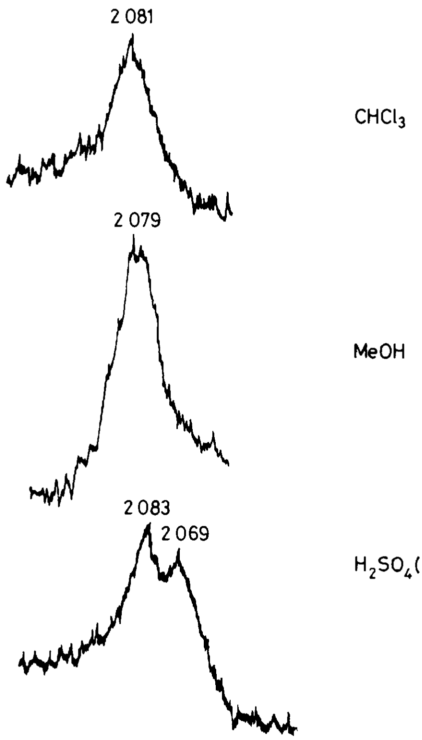

**Figure 6.** Cyanide stretching modes of [Fe(phen)$_2$(CN)$_2$] in various solvents; excitation frequency = 620.3 nm

to observe ν(C≡N) modes in the Raman spectrum. Raman spectra were recorded in a rotating cell and with an incident wavelength of 620.3 nm to minimise the possibility of photodecomposition. The spectra are shown in Figure 6 and the band positions lie at 2 081 (CHCl$_3$), 2 079 (CH$_3$OH), and 2 083 and 2 069 cm$^{-1}$ (1 mol dm$^{-3}$ H$_2$SO$_4$). The peaks do not exhibit resonance enhancement.

The Raman spectrum of K$_4$[Fe(CN)$_6$] dissolved in water shows a single ν(C≡N) band at 2 067 cm$^{-1}$. The band lies at 2 091 cm$^{-1}$ in 1 mol dm$^{-3}$ H$_2$SO$_4$.

## Discussion

[Fe(bipy)$_3$][BF$_4$]$_2$.—As is usual for α-di-imine complexes, the strong visible absorption is assigned to an electric dipole-allowed metal 3*d* to ligand π c.t. transition. Under the $D_3$ symmetry of the complex, the degeneracies of the Fe$^{2+}$ *d* orbitals and the ligand π orbitals are split, hence enabling the possibility of ${}^1E \longleftarrow {}^1A_1$ or ${}^1A_2 \longleftarrow A_1$ transitions. Calculations indicate that only a transition of the type ${}^1E \longleftarrow {}^1A_1$ will contribute significantly to the visible region.[11,12] Thus it appears reasonable to assign the accompanying shoulder to a vibronic interaction.

The r.R. spectrum is dominated by bands arising from totally symmetric fundamentals. The values of ρ are *ca.* $\frac{1}{3}$ (see Table 2) and these remain approximately constant, on varying the exciting line. If the shoulder on the side of the visible absorption band was due to a second electronic transition, then non-totally symmetric as well as totally symmetric modes would be brought into resonance by a variation of the exciting frequency.[13] Calculated as a percentage increase in intensity on reaching resonance, the band at 1 613 cm$^{-1}$ exhibited the maximum enhancement. This band, largely attributable to a ligand ν(C=N) mode, is thus expected to contribute most to the vibronic side-band, and the peak-to-shoulder separation in the electronic spectrum of 1 577 cm$^{-1}$ is in reasonable correspondence with this interpretation.

The absence of resonance bands below 700 cm$^{-1}$ indicates that the ring in-plane bends and ring torsion modes do not affect those parts of the ligand which contain most electronic density on charge transfer. Moreover the absence of $BF_4^-$ fundamentals in the r.R. spectrum implies that the anion does not contribute to the electronic spectrum. Our results correspond closely to those obtained by Clark *et al.*[1] for $[Fe(bipy)_3]I_2 \cdot 5H_2O$.

$[Cu(bq)Br_2]$.—The correspondence between the position of the most resonantly enhanced vibrational mode (1 571 $cm^{-1}$) and the value of the peak-to-shoulder separation from the electronic absorption (1 685 $cm^{-1}$) leads us to conclude that the shoulder is vibronic in origin. The lack of resonant enhancement of the $\nu(CuBr_2)$ modes implies that this part of the complex is not involved in the electronic c.t. transition.

$[Fe(phen)_2(CN)_2]$.—The visible absorption spectrum is found to be strongly solvent dependent,[8] and it varies according to the hydrogen bonding and acidic properties of the solvent. The main visible absorption has been assigned to an iron 3*d* to phen $\pi^*$ c.t. transition.[14] Iron complexes of the type $[FeL_2(CN)_2]$ (L = bipy or phen) have been used as acid–base indicators.[15] The complexes react rapidly and reversibly with strong acids to yield mono- and di-protonated species. A blue shift in the visible c.t. absorption is observed on protonation of the species, and this is reported to bring about an increase in the $\pi$-acceptor ability of the cyanide ligand, and to stabilise the complex correspondingly. This stabilisation of the ground state results in a blue shift in the c.t. iron–phen spectrum.[14] The splitting between the main and shoulder bands (*ca.* 60 nm) is largely independent of solvent, which strongly implies that the absorbing species retains the same structure in all solvents; it does not favour an explanation involving structural changes between *cis* and *trans* isomers.[8]

We have further examined the Raman spectrum of the complex in several solvents and compared our results with the aqueous solution data for $K_4[Fe(CN)_6]$. The Raman spectrum of the latter shows a single $\nu(C{\equiv}N)$ vibration at 2 067 $cm^{-1}$. In 1 mol $dm^{-3}$ $H_2SO_4$ the vibration occurs at 2 091 $cm^{-1}$, clearly indicating that an interaction between cyanide and acid results in a wavenumber shift to higher values. Our evidence from solution Raman spectra of $[Fe(phen)_2(CN)_2]$, where no shift in the $\nu(C{\equiv}N)$ mode is observed, implies that the centre of protonation is not the cyanide ligand, and is therefore most probably at the site of the phen species. The evidence obtained from solid i.r. studies reflects these results as the band positions are likewise identical. The presence of additional bands in the solid i.r. spectra obtained from aqueous-recrystallised samples may be misleading due to possible crystalline effects. The presence of a further band at 2 069 $cm^{-1}$ in the Raman spectrum of the species in acidic solution may be due to a decomposition product containing cyanide. The evidence hence implies that $[Fe(phen)_2(CN)_2]$ is affected by acidic solvents and the interaction occurs at the $\alpha$-di-imine moiety, causing large shifts in the position of the electronic absorption. This may be rationalised as a protonation on the bidentate ligand which lowers its capacity to back-bond and thus increases the energy of the charge-transfer process.

A r.R. study of the complex in solution was carried out to determine which parts of the complex are responsible for the visible absorption(s) occurring at 480—600 nm, as only vibrations due to these moieties exhibit enhancement. Since the visible absorption exhibits an acid effect, that same moiety will be most affected by the acidity of the solvent.

The r.R. spectra of $[Fe(phen)_2(CN)_2]$ in both chloroform and methanol show that the band at 1 637 $cm^{-1}$ (coincident in both solvents) exhibits maximum intensity enhancements, calculated as a percentage increase in intensity on reaching resonance. The peak-shoulder separation in the electronic spectrum of the sample in chloroform is calculated as 2 063 $cm^{-1}$ (2 357 $cm^{-1}$ in methanol). These values clearly do not correspond to any vibrations observed, even considering the somewhat large errors incurred in the estimation of peak positions. These considerations imply that the electronic side-bands occurring in both solvents are not vibronic in nature, and may then reasonably be assigned to a second electronic transition. Such a transition would bring the vibrations associated with the moiety producing it into resonance, and although no vibrations achieve a clear second maximum beneath the shoulder, the asymmetries of the excitation profiles show that a second electronic transition may well occur (see Figures 3 and 4). No cyanide modes are observed at all in the region of wavelengths studied, and hence both electronic transitions are associated with the phen ligands.

The tris(1,10-phenanthroline) complex has been studied by r.R. spectroscopy,[16] and the coincidence of the splitting in its electronic spectrum with the C=N ring vibration is taken as a clear indication of the vibronic nature of the side-band. The substitution of cyanide ligands for a phen moiety greatly alters the nature of the complex in solution, as the r.R. data indicate. Moreover, the change in symmetry, *i.e.* $D_3$ to $D_{4h}$, which occurs as a result of this substitution may account for the two electronic transitions which then occur.

The excitation profiles obtained for samples in both solvents exhibit the same basic structure, although shifted. Indeed, such a solvent-shifted absorption spectrum may be employed as an alternative to changing the exciting frequency, and the profiles obtained in this study illustrate the equivalence of the two methods.

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