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# Electronic, Raman and resonance Raman spectroscopy of $[NBu_4][RuBr_4(MeCN)_2]$

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Raman spectra taken at resonance with the $e_u(\mathrm{Br}\ p\pi) \longrightarrow b_{2g}(\mathrm{Ru}\ d\pi)$ charge-transfer (CT) transition of the *trans*-$[RuBr_4(MeCN)_2]^-$ ion, as its $[NBu_4]^+$ salt at *ca.* 80 K, consist of long overtone progressions in $\nu_1(a_{1g})$, the symmetric RuBr stretch (at 188.5 $\mathrm{cm}^{-1}$), together with combination band progressions in which $\nu_1$ is the progression-forming mode and the enabling modes include $\nu_2(b_{1g})$, $\nu_{as}(\mathrm{RuBr})$, and $\nu_4(b_{2g})$, $\delta_s(\mathrm{BrRuBr})$. The excitation profile of the $\nu_1$ band approximately follows the contour of the $e_u \longrightarrow b_{2g}$ CT transition referred to above, consistent with the operation of the A-term scattering mechanism. The spectroscopic data allow the determination of the harmonic wavenumber ($\omega_1$) and anharmonicity ($x_{11}$) of the $\nu_1(a_{1g})$ mode to be 188.8 $\mathrm{cm}^{-1}$ and $-0.15$ $\mathrm{cm}^{-1}$, respectively. Some comparative data on the analogous chloride ion, *trans*-$[RuCl_4(MeCN)_2]^-$, are also given.

## Introduction

The colours of 4d and 5d transition metal complexes frequently arise, at least in part, as a consequence of electron transfer from the metal to the ligand, or the converse, from the ligand to the metal. An understanding of electronic transitions of this kind, commonly termed charge transfer (CT) transitions, can provide considerable insight into the electronic structure of the complex under examination. As part of an on-going study devoted to understanding the electronic spectra of mixed halide (X)–neutral donor ligand (L) complexes, $[MX_{6-n}L_n]^z$, the chloride and bromide complexes of *trans*-$[RuX_4(MeCN)_2]^-$ have been studied by Raman and resonance Raman spectroscopy.

The electronic spectra of *trans*-$[MX_4L_2]^z$ complexes, where M is a 4d$^n$ or 5d$^n$ transition metal element with $n < 6$, tend to be very similar in profile, particularly in the case of d$^5$ complexes. For example, the visible spectra of *trans*-$[RuCl_4(Im)_2]^-$ (Im = imidazole),[1] *trans*-$[OsCl_4(CO)_2]^-$ and *trans*-$[IrCl_4(PPh_3)_2]$ all consist of a weak leading band, followed by two intense, closely spaced bands.[2–4] The wavenumbers of these bands all differ but the overall similarity in the spectral profile is unmistakeable, an observation that has ultimately led to the assignment of the characteristic bands as halide-to-metal charge-transfer transitions.[5] The electronic spectra of other related complexes can, however, be considerably more complicated. For instance mixing of the appropriate X and L orbitals may occur in complexes of lower symmetry, *e.g.* *mer*-$[MX_3L_3]$.[3,6] Alternatively, the presence of different ligands with donor orbitals of similar energy can result in quite complicated electronic spectra, *e.g.* in the case of *trans,trans,trans*-$[MX_2L_2L'_2]^+$.[7] The *trans*-$[RuX_4(MeCN)_2]^-$ species therefore provide an ideal starting point for a systematic study of $[MX_{6-n}L_n]$ complexes,[8] the purpose of the work being to confirm the assignment of the visible spectra of $[NBu_4][RuX_4(MeCN)_2]$ (X = Cl or Br) by resonance Raman spectroscopy and, in so doing, to test the efficacy of this method for making assignments of more complicated electronic spectra.

## Experimental

The complexes $[NBu_4][RuX_4(MeCN)_2]$ (X = Cl or Br) were prepared according to literature procedures,[5] or minor variations thereof, by heating acetonitrile solutions of $[NBu_4]_3[Ru_2X_9]$ overnight under an atmosphere of nitrogen.[9] $[NEt_4][RuCl_4(MeCN)_2]$ was prepared as described previously.[10] Electronic spectra were measured on a solution of the ruthenium complex in dichloromethane using a Cary 5 spectrometer. (Spectra measured on a solution in acetonitrile are essentially identical.) Raman spectra were excited with argon ion and krypton ion lines (457.9, 476.5, 488.0, 496.5, 501.7, 514.5, 530.9, 568.2 and 647.1 nm) from Coherent I70 and I301 lasers. Samples of $[NBu_4][RuBr_4(MeCN)_2]$ were prepared as pellets of concentration ≈10% in KBr and held at liquid nitrogen temperature. Spectra were recorded on a Spex 1401 double grating spectrometer in the 90° scattering configuration, the monochromator being coupled to an RCA C31034 photomultiplier tube used in the photon counting mode. Slit widths of 150–200 μm were employed, depending on wavelength, to keep the spectral resolution to between 2 and 3 $\mathrm{cm}^{-1}$. Acquisition times varied between 1 and 4 s. Wavenumber calibration was achieved by superimposing neon emission lines on the spectra. Post-acquisition linear or quadratic interpolation was performed on the data, the calibration lines generally being fitted with r.m.s. residues which were <0.2 $\mathrm{cm}^{-1}$. The Raman band wavenumbers determined using this procedure are, of course, also dependent upon the band definition; the wavenumbers of well defined bands are typically accurate to better than ± 0.5 $\mathrm{cm}^{-1}$.

## Results and discussion

### Electronic spectra

The electronic spectrum of purple $[NBu_4][RuBr_4(MeCN)_2]$ in dichloromethane (Fig. 1) is closely similar to that of $[NBu_4][RuBr_4(PhCN)_2]$,[5] the most intense pair of bands at 17950 and 20000 $\mathrm{cm}^{-1}$ being assigned to the $e_u(\mathrm{Br}\ p\pi)$ to $b_{2g}(\mathrm{Ru}\ d\pi)$ transition. This is a halide-to-metal CT transition which is electric dipole allowed (the only one to be fully so) and split by 2050 $\mathrm{cm}^{-1}$ by bromide-centred spin–orbit coupling. The other features in the spectrum can also be assigned by comparison with those for the analogous benzonitrile complex,[5] *viz.* the

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**Table 1** Electronic spectra of $[NBu_4][RuX_4(MeCN)_2]$ complexes (X = Cl or Br)[a]

| Complex | Wavenumber/cm$^{-1}$ | $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ |
|---|---|---|
| X = Cl | 21000 | 760 |
| | 24200 | 6500 |
| | 25000 | 6000 |
| | 32800 | 2000 |
| | 40300 | 10500 |
| X = Br | 15380 | 570 |
| | 17950 | 6900 |
| | 20000 | 6400 |
| | 27200 | 2100 |
| | 32150 | 8500 |

[a] Measured as dichloromethane solutions at room temperature.

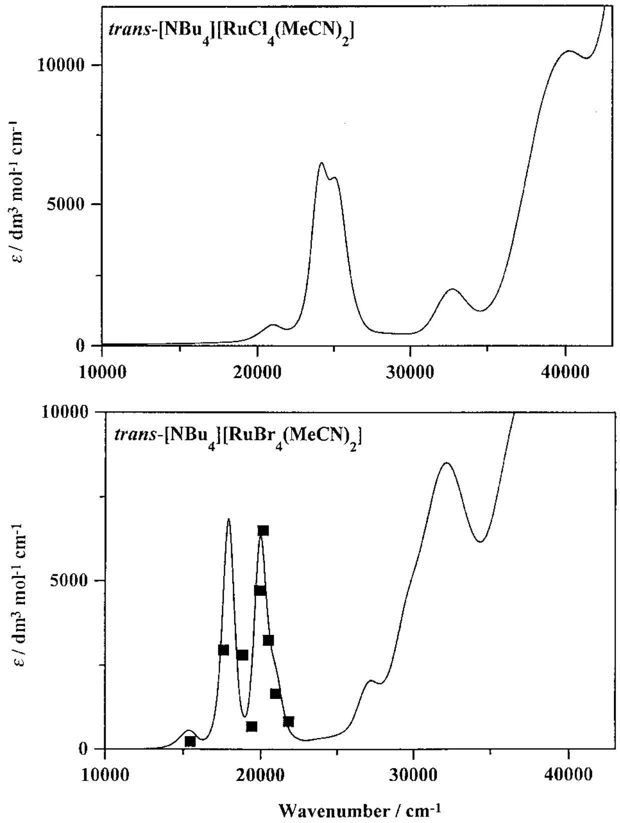

**Fig. 1** Electronic spectra of $[NBu_4][RuCl_4(MeCN)_2]$ and $[NBu_4]$-$[RuBr_4(MeCN)_2]$ in dichloromethane. Included in the latter are suitably scaled intensities (■) found for the $\nu_1(a_{1g})$, $\nu_s$(RuBr) band as a function of excitation line wavelength.

weaker one at lower wavenumber to the parity-forbidden $a_{2g}$(Cl π) to $b_{2g}$(Ru dπ) transition, and that in the near ultra-violet to the $e_u$(Br σ) to $b_{2g}$(Ru dπ) transition (Table 1).

The electronic spectrum of yellow $[NBu_4][RuCl_4(MeCN)_2]$ is clearly related to that of the analogous bromide complex when one considers the reduced splitting of the $e_u$(Cl pπ) to $b_{2g}$(Ru dπ) transition on account of the smaller spin–orbit coupling constant of chloride as compared to bromide.[11] As expected, all bands of the chloro-complex are shifted substantially to higher wavenumber than those of the analogous bromo-complex, in consequence of the higher optical electronegativity of chloride than bromide.[12] In particular the midpoint of the intense doublet, the $e_u$(X pπ) to $b_{2g}$(Ru dπ) transition, is shifted by *ca.* 6000 cm$^{-1}$ to higher wavenumber. Shifts of similar magnitude have been noted in the halide-to-metal CT spectra of related complexes.[5,13,14]

## Raman and resonance Raman spectra

**Table 2** Wavenumbers/cm$^{-1}$ of bands assigned to fundamentals observed in the Raman spectra of $[NBu_4][RuBr_4(MeCN)_2]$[a]

| $[RuBr_4(MeCN)_2]^-$ | $[AuBr_4]^-$ [b] | MeCN[c] | Assignment | |
|---|---|---|---|---|
| 188.5 | 213.3 | — | $\nu_1(a_{1g})$ | $\nu_s$(MBr) |
| 158.9 | 197.0 | — | $\nu_2(b_{1g})$ | $\nu_{as}$(MBr) |
| 110.6 | 106.9 | — | $\nu_4(b_{2g})$ | $\delta$(BrMBr) |
| 2303 | — | 2249 | $\nu_2(a_1)$ | $\nu$(CN) |
| 1375 | — | 1376 | $\nu_6(a_1)$ | $\delta(CH_3)$ |
| 963.6 | — | 918 | $\nu_4(a_1)$ | $\nu$(CC) |

[a] KBr pellet, *ca.* 80 K. [b] Ref. 15. $[NEt_4]^+$ salt, spinning disc, *ca.* 300 K. [c] Ref. 18. Gas phase results.

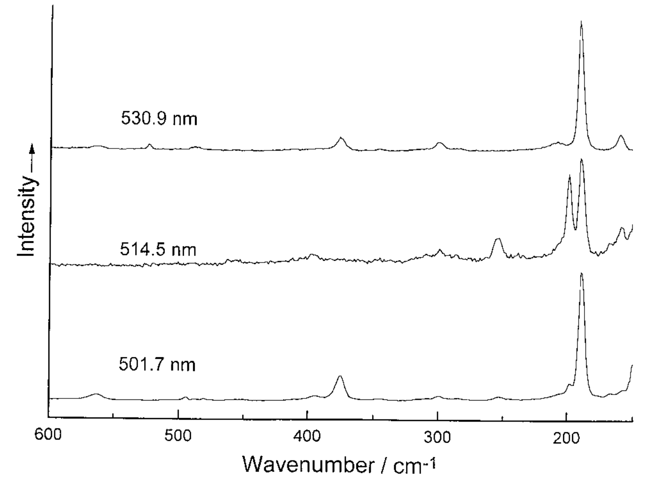

**Fig. 2** Raman spectra of $[NBu_4][RuBr_4(MeCN)_2]$ as a KBr disc at *ca.* 80 K taken with 501.7, 514.5 and 530.9 nm radiation. The spectra have been scaled so that the $\nu_1$ band is approximately the same size in each spectrum. An indication of the relative band intensities is given by the signal to noise ratio on each spectrum.

The Raman spectra of $[NBu_4][RuBr_4(MeCN)_2]$ as a KBr disc at *ca.* 80 K is strongly dependent on the wavelength of the excitation line used to obtain the spectrum (Fig. 2). The most intense band in all the spectra, at 188.5 cm$^{-1}$, is assigned to $\nu_1(a_{1g})$, $\nu_s$(RuBr), the totally symmetric RuBr stretching mode, by analogy with the corresponding mode (at 213.3 cm$^{-1}$)[15] of the square planar $[AuBr_4]^-$ ion as its $[NEt_4]^+$ salt ($D_{4h}$ nomenclature). The other RuBr modes *viz.* $\nu_2(b_{1g})$, $\nu_{as}$(RuBr), at *ca.* 159 cm$^{-1}$ and $\nu_4(b_{2g})$, $\delta$(BrRuBr), at 110.5 cm$^{-1}$ are assigned similarly by analogy with the corresponding ones of the $[AuBr_4]^-$ ion (Table 2).

In the Raman spectrum of the corresponding chloride[16] $[NEt_4][RuCl_4(MeCN)_2]$ ($\lambda_0$ = 514.5 nm), the strongest band occurs at 310 cm$^{-1}$, clearly assignable to $\nu_1(a_{1g})$, $\nu_s$(RuCl), *cf.* the corresponding mode of $[NEt_4][AuCl_4]$ occurs at 349.5 cm$^{-1}$.[17,18] The significant observation is that the ratio of wavenumbers of the totally symmetric MBr to MCl stretching modes is the same for each pair of anions: thus $\nu_s(RuBr)/\nu_s(RuCl) = \nu_s(AuBr)/\nu_s(AuCl) = 0.61$, so confirming the band assignments.

The bands attributable to co-ordinated acetonitrile are (in $C_{3v}$ nomenclature) assigned by comparison with those of free acetonitrile[18] (Table 2), and with the knowledge that both $\nu_2(a_1)$, $\nu$(CN) and $\nu_4(a_1)$, $\nu$(CC) are likely to increase in wavenumber on co-ordination to a ruthenium(III) ion. The change in $\nu$(CN) on co-ordination of acetonitrile depends principally on the oxidation state and hence the d-electron configuration of the metal ion to which it is co-ordinated.[19] For nitrile complexes of ruthenium(III), $\nu$(CN) is typically found at higher wavenumber than that for the free ligand.[19]

The $[RuBr_4(MeCN)_2]^-$ ion displays a spectacular resonance Raman (RR) spectrum when excited with 488.0 nm radiation (Fig. 3). Harmonics of the $\nu_1(a_{1g})$ band dominate the low wavenumber region of the spectrum, reaching $8\nu_1$. Combination bands of the type $\nu_2 + n\nu_1$ (to $n = 3$) and $\nu_4 + n\nu_1$ (to $n = 6$) are

**Table 3** Wavenumbers and assignments of bands observed in the resonance Raman spectra of $[NBu_4][RuBr_4(MeCN)_2]$[a]

| Wavenumber[b]/cm$^{-1}$ | Assignment |
|---|---|
| 110.6 m | $\nu_4$ |
| 158.9 w | $\nu_2$ |
| 188.5 vs | $\nu_1$ |
| 198 vw | ? |
| 208 vw | ? |
| 255 vvw | ? |
| 286 vvw | ? |
| 299.8 w | $\nu_1 + \nu_4$ |
| 318.7 vw | $2\nu_2$ |
| 347.7 vw | $\nu_1 + \nu_2$ |
| 376.6 s | $2\nu_1$ |
| 464 vvw | ? |
| 474 vvw | $\nu_1 + \nu(286)$ or $3\nu_2$ |
| 489.1 w | $2\nu_1 + \nu_4$ |
| 505 vw | $\nu_1 + 2\nu_2$ |
| 536 vw | $2\nu_1 + \nu_2$ |
| 564.9 m | $3\nu_1$ |
| 600 vvw | ? |
| 677.6 w | $3\nu_1 + \nu_4$ |
| 724 vvw | $3\nu_1 + \nu_2$ |
| 752.8 ms | $4\nu_1$ |
| 865 w | $4\nu_1 + \nu_4$ |
| 912 vw | ? |
| 941 m | $5\nu_1$ |
| 963.6 m | $\nu(CC)$ |
| 1054 vw | $5\nu_1 + \nu_4$ |
| 1099 vvw | $\nu_1 + \nu(912)$ |
| 1126 m | $6\nu_1$ |
| 1151.4 w | $\nu_1 + \nu(CC)$ |
| 1313 vw | $7\nu_1$ |
| 1338 vw | $2\nu_1 + \nu(CC)$ |
| 1375 vvw | $\nu(CH_3)$ |
| 1499 vw | $8\nu_1$ |
| 2302.5 w | $\nu(CN)$ |
| 2492 vw | $\nu_1 + \nu(CN)$ |

[a] KBr disc, *ca.* 80 K, 488.0 nm excitation. [b] One place of decimals is given for bands with a wavenumber accuracy of ±0.5 cm$^{-1}$ or better. All bands listed are accurate to ±1.5 cm$^{-1}$. s = strong, m = medium, w = weak, v = very.

also evident. This rich RR spectrum is reminiscent of those seen for a wide range of compounds containing metal–halogen bonds when recorded with an excitation line at resonance with a halide-to-metal CT band.[20–24] No overtones of $\nu_4$ are seen, but the first and possibly the second overtone of $\nu_2$ can be detected. The combination band $\nu_1 + 2\nu_2$ is also seen, as well as (understandably) weak bands arising from combinations of the chromophore-localised mode $\nu_1(a_{1g})$, with the orthogonal ligand-localised modes $\nu(CN)$ and $\nu(CC)$ (Table 3). Several weak features in the RR spectrum are not enhanced by excitation near to the bromide-to-metal CT transitions and therefore probably arise from ligand-localised modes; the bands at 198, 255 and 464 cm$^{-1}$ fall into this category. Other weak features to the high wavenumber side of $\nu_1$ (notably that at 208 cm$^{-1}$) are enhanced at resonance with the CT band and probably arise from crystal field splitting of the $\nu_1$ band. There is no apparent enhancement to any of the Raman bands at resonance with the parity-forbidden transition at *ca.* 15400 cm$^{-1}$.

The observation of a large number of overtones of a fundamental, *viz.* $n\nu_1$, makes possible by standard procedures[20–23] the determination of the harmonic wavenumber $\omega_1$ and the anharmonicity constant $x_{11}$; thus $\omega_1$ was determined subject to the usual assumptions[22] to be 188.8 ± 0.2 cm$^{-1}$ and $x_{11} = -0.15 \pm 0.04$ cm$^{-1}$.

The excitation profile of the $\nu_1(a_{1g})$ band of the $[RuBr_4(MeCN)_2]^-$ ion, that is, the plot of Raman band intensity of the $\nu_1(a_{1g})$ band as a function of excitation line wavelength,[21] is included in Fig. 1. The excitation profile of the $\nu_1(a_{1g})$ band clearly follows, albeit only approximately, the contour of the visible spectrum even including the central dip between the spin–orbit split components of the $e_u$(Br pπ) to $b_{2g}$(Ru dπ) transition. Thus there is no doubt that the $\nu_1(a_{1g})$ mode of the $[RuBr_4(MeCN)_2]^-$ ion is coupled strongly to this electronic transition.[24] The length of the $n\nu_1$ progression indicates that the RuBr bonds are significantly lengthened on excitation in agreement with expectation for resonance with a transition which is RuBr bonding ⟶ antibonding in nature.[25]

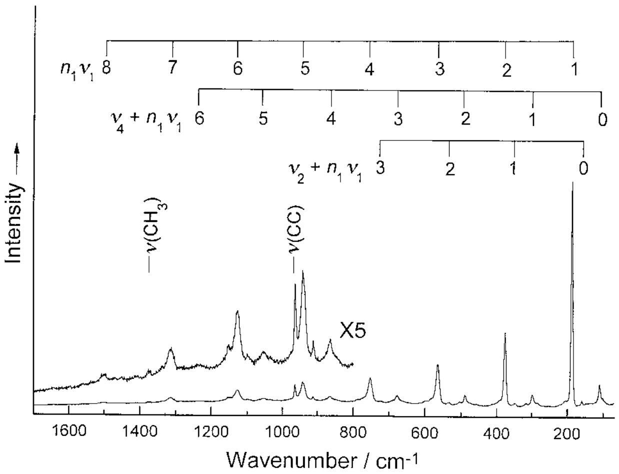

**Fig. 3** Resonance Raman spectrum of $[NBu_4][RuBr_4(MeCN)_2]$ as a KBr disc at *ca.* 80 K obtained with the excitation wavelength 488.0 nm (laser power 10 mW, integration time 2 s).

It is also worth noting that $[NBu_4][RuBr_4(MeCN)_2]$ is stable under the laser conditions described, whereas previous work[25] has indicated that salts of the $[RuBr_6]^{2-}$ ion (including the $NBu_4^+$ salt) are not. Bromide complexes of ruthenium are promising ones to study since the Br (pπ) ⟶ Ru (dπ) transitions are conveniently located in the mid visible region.

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## References

1 M. Hartmann, T. J. Einhauser and B. K. Keppler, *Chem. Commun.*, 1996, 1741.
2 W. Preetz and F. H. Johannsen, *J. Organomet. Chem.*, 1975, **86**, 397.
3 G. J. Leigh and D. M. P. Mingos, *J. Chem. Soc. A*, 1970, 587.
4 M. D. Rowe, A. J. McCaffery, R. Gale and D. N. Copsey, *Inorg. Chem.*, 1972, **11**, 3090.
5 C. M. Duff and G. A. Heath, *J. Chem. Soc., Dalton Trans.*, 1991, 2401.
6 A. J. McCaffery and M. D. Rowe, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 1767.
7 J. P. Al-Dulaimi, R. J. H. Clark and D. G. Humphrey, unpublished work.
8 J. P. Al-Dulaimi, R. J. H. Clark and D. G. Humphrey, *J. Chem. Soc., Dalton Trans.*, 1997, 2535.
9 V. T. Coombe, G. A. Heath, T. A. Stephenson and D. K. Vattis, *J. Chem. Soc., Dalton Trans.*, 1983, 2307.
10 P. Braunstein and J. Rose, *Inorg. Synth.*, 1989, **26**, 356.
11 D. H. Whiffen, *Spectroscopy*, Longmans, London, 1966, p. 141. The one-electron spin–orbit coupling constants ($\zeta$) of Cl and Br are 586 and 2460 cm$^{-1}$, respectively.
12 C. K. Jørgenson, *Mol. Phys.*, 1959, **2**, 309.
13 G. A. Heath and D. G. Humphrey, *J. Chem. Soc., Chem. Commun.*, 1991, 1668.
14 F. H. Johannsen and W. Preetz, *Z. Anorg. Allg. Chem.*, 1977, **436**, 143.
15 Y. M. Bosworth and R. J. H. Clark, *Chem. Phys. Lett.*, 1974, **28**, 611.

16 The Raman spectra of $[NEt_4][RuCl_4(MeCN)_2]$ was recorded as an undiluted salt at room temperature on a Renishaw Raman System 1000 using the 514.5 nm excitation line (0.1 mW) of an argon ion laser. There was no evidence for sample damage at this power, and the spectrum contained, in addition to a band attributable to the $\nu_1(a_{1g})$, $\nu_s$(RuCl) mode at 310 $cm^{-1}$, medium bands at 965 $cm^{-1}$ [assigned to $\nu$(CC)] and 1381 $cm^{-1}$ [assigned to $\delta(CH_3)$], and a strong band at 2305 $cm^{-1}$ [assigned to $\nu$(CN)]; these bands all have obvious analogues in the Raman spectrum of $[NBu_4][RuBr_4(MeCN)_2]$ (Table 2).

17 Y. M. Bosworth and R. J. H. Clark, *Inorg. Chem.*, 1975, **14**, 170.

18 K. Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.

19 J. J. F. Alves and D. W. Franco, *Polyhedron*, 1996, **15**, 3299.

20 R. J. H. Clark in *Advances in Infrared and Raman Spectroscopy*, ed. R. J. H. Clark and R. E. Hester, Heyden, London, 1975, vol. 1, pp. 143–172.

21 R. J. H. Clark and T. J. Dines, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 131.

22 J. R. Campbell and R. J. H. Clark, *Mol. Phys.*, 1978, **36**, 1133.

23 R. J. H. Clark and P. C. Turtle, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 2063.

24 The excitation profile and the electronic spectrum are expected, on theoretical grounds,[21] to match each other very closely, but not exactly; moreover, in the present case, the excitation profile relates to a KBr disc at 80 K whereas the electronic spectrum relates to a $CH_2Cl_2$ solution, a fact which might contribute to the slight difference.

25 R. J. H. Clark and T. J. Dines, *Mol. Phys.*, 1984, **52**, 859.

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