Diagnosis of the Redox Levels of TCNQF₄ Compounds Using Vibrational Spectroscopy**

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The vibrational spectroscopy of TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻ has been investigated by means of density functional theory. Band assignments in infrared and Raman spectra have been clarified and a series of diagnostics developed for redox level characterisation of TCNQF₄ compounds. In the C=C stretching region (1460–1600 cm⁻¹), TCNQF₄⁰ and TCNQF₄¹⁻ show two bands, with the more energetic being at 1600 cm⁻¹ in TCNQF₄⁰ and at approximately 1535 cm⁻¹ in TCNQF₄¹⁻; in TCNQF₄²⁻ both modes absorb below 1500 cm⁻¹, often merging to give a single band. In the C–F and endocyclic C–C stretch-

ing region (1290 and 1360 cm⁻¹), TCNQF₄⁰ and TCNQF₄¹⁻ show strong bands, whereas TCNQF₄²⁻ absorbs weakly or not at all. (Additional bands, e.g. from co-crystallised solvent molecules, may complicate this region.) In the nitrile stretching region (2000–2250 cm⁻¹), modes are highly sensitive to nitrile coordination by metal cations. All three redox levels can produce bands above 2200 cm⁻¹, however bands below 2150 cm⁻¹ are usually due to TCNQF₄²⁻. This sensitivity to coordination is likely to affect the spectra of many organic molecular ions.

Introduction

The properties of complexes of TCNQ (7,7,8,8-tetracyanoquinodimethane) and many of its derivatives have attracted enormous attention owing to their range of useful physical characteristics.^[1] Of interest here is the 2,3,5,6-tetrafluorinated species, TCNQF₄ (Figure 1). Materials derived from TCNQF₄ have attractive electronic,^[2] conductivity,^[3] magnetism^[4] and field-

emission properties^[5] as well as applications as electronic switches and memory storage devices.^[3b]

The facile charge-transfer properties of TCNQF₄ have led to a wealth of monoanion derivatives that have been studied for several decades.^[6] More recently, interest has also developed in the TCNQF₄ dianion.^[6] However, it has emerged that the designation of the redox level of the TCNQF₄ moiety is often ambiguous, with mixtures of neutral, mono- and dianionic TCNQF₄ species.^[7] (Throughout this work, we refer to the neutral TCNQF₄ molecule as TCNQF₄⁰, the radical monoanion is denoted as TCNQF₄¹⁻ and the dianion as TCNQF₄²⁻. "TCNQF₄" is used for the molecule in general.)

Assignment of the TCNQF₄ redox level is primarily from single-crystal X-ray analysis.^[8] However, where crystals are not forthcoming, vibrational spectroscopy is typically used as the main tool for the characterisation of TCNQF₄ redox levels.^[6] Reduction produces characteristic changes in band intensities and positions in both infrared (IR) and Raman spectra. These changes can be used to identify which species are present in a material and, to some extent, how the ions are arranged with respect to each other. However, this analysis has been complicated by confusion over band assignments.

Early interest in TCNQF₄ focussed on the synthesis and characterisation of charge-transfer complexes formed by mixing TCNQF₄⁰ with species capable of producing molecular cations.^[9] Spectroscopic studies were used to detect whether and to what extent charge transfer (to produce TCNQF₄¹⁻) occurred. To facilitate this analysis, Meneghetti and Pecile produced high-quality IR and Raman spectra of TCNQF₄⁰ and TCNQF₄¹⁻ (as the Rb salt).^[10] By using a variety of spectroscopic techniques, coupled with frequency calculations performed using an optimised force field, they assigned all bands of

Figure 1. The structure of TCNQF₄⁰ with the atom and axis labels used in this study. The electronic structures of the anion and dianion cannot be simply described. (Note: the numbering scheme used here is not related to IUPAC molecular nomenclature.)

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[**] TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane

Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/cplu.201402013>.

TCNQF₄⁰ according to their symmetries and identified the internal coordinates that contribute to each normal mode.^[10] The highest energy bands (at ~2200 cm⁻¹) were identified as C≡N stretches. Bands at 1665 and 1598 cm⁻¹ (Raman and IR, respectively) were found to be predominantly due to endocyclic C=C stretching modes, whereas stretching of the exocyclic C=C bonds were observed to be the dominant contributors to the 1456 cm⁻¹ Raman and 1551 cm⁻¹ IR bands. The corresponding bands in TCNQF₄¹⁻ were found at 1655, 1536, 1455 and 1500 cm⁻¹, respectively. As the C≡N stretching modes were found to be sensitive to intermolecular interactions, ν(C≡C) in IR spectra were recommended for the identification of TCNQF₄ redox levels.^[10] In a later study, Dixon, Calabrese and Miller used *ab initio* calculations to predict the vibrational frequencies of TCNQF₄⁰ and TCNQF₄²⁻.^[11] Although their scaled frequencies for TCNQF₄⁰ were consistent with the earlier work, different symmetries were reported for some modes.

Recent investigations of TCNQF₄ complexes have predominantly used ν(C≡N) in IR spectra to identify the redox level.^[3a,4b,c,5-7,8b,12] They have tended not to consider the IR modes at 1530–1550 cm⁻¹, however, some studies have mentioned the bands at approximately 1500 cm⁻¹, recording them as C=C stretches.^[4c,6,12b] On one occasion these were further described as endocyclic modes.^[3a] Some studies also mention the IR bands at approximately 1200 cm⁻¹, which are described as C–F bending modes,^[5-7,12a,b,e] and the Raman modes at approximately 1450 cm⁻¹. The latter have generally been described as C–CN wing modes,^[3a,6-7,12a,b,e] however, on one occasion they were identified as endocyclic C=C stretches.^[5] In contrast, Meneghetti and Pecile believed the C–CN wing modes were responsible for the 1200 cm⁻¹ IR bands, and assigned the ap-

proximately 1450 cm⁻¹ Raman modes as being predominantly due to stretching of the exocyclic C=C bonds. They did not find any out-of-plane motion in modes above 750 cm⁻¹.

With advances in computing power over the last 30 years and the development of fast and accurate density functional (DFT) methods, it is now possible to make far more reliable predictions of IR and Raman spectra. Although DFT studies of TCNQ vibrational spectra have been reported,^[13] mixing of δ(C–H) and ν(C–C) in TCNQ mean that it is spectroscopically very different from TCNQF₄ and the results are not transferable. Given the level of confusion in the chemical literature, there is a need for a reassessment of the TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻ spectra to provide a definitive correlation between vibrational frequency, mode symmetry and molecular motion. Herein we use DFT with a large basis set to calculate accurate harmonic vibrational frequencies for TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻, providing both the corresponding symmetry representation and a graphical depiction of each mode. Using these data, we assign the features of the IR and Raman spectra of the three TCNQF₄ species and provide an expanded set of diagnostics for identifying the redox level in compounds where this is unknown.

Results and Discussion

Calculated gas-phase harmonic vibrational frequencies for the 20 highest energy modes of TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻ are reported in Table 1. Data for all modes can be found in Table S4 in the Supporting Information. In each case an indication of the predicted intensity of the corresponding bands in the IR and Raman spectra is also given. Throughout this work

Table 1. Calculated harmonic vibrational frequencies of TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻ (above 750 cm⁻¹). In each case the corresponding infrared (IR) and Raman (Ra) band intensities are given. For the TCNQF₄⁰ modes, the identifying label (ID) used by Meneghetti,^[10] the mode symmetry and a brief description of the predominant motion of each mode is also shown. We emphasise that these descriptors cannot be directly applied to TCNQF₄¹⁻ and TCNQF₄²⁻ for reasons described in the text.

No.	TCNQF ₄ ⁰ ID	Sym.	Mode	$\tilde{\nu}$ [cm ⁻¹]	IR ^[a]	Ra ^[a]	TCNQF ₄ ¹⁻ $\tilde{\nu}$ [cm ⁻¹]	IR ^[a]	Ra ^[a]	TCNQF ₄ ²⁻ $\tilde{\nu}$ [cm ⁻¹]	IR ^[a]	Ra ^[a]
1	ν_1	A_g	C≡N stretch	2231	–	s	2198	–	s	2173	–	m
2	ν_{18}	B_{1u}	C≡N stretch	2234	w	–	2194	s	–	2163	s	w
3	ν_{32}	B_{2u}	C≡N stretch	2214	w	–	2162	s	–	2128	s	m
4	ν_{41}	B_{3g}	C≡N stretch	2214	–	s	2162	–	m	2127	m	m
5	ν_2	A_g	ring C=C stretch	1679	–	s	1645	–	s	1633	–	s
6	ν_{33}	B_{2u}	ring C=C stretch	1608	s	–	1535	s	–	1475	m	–
7	ν_{19}	B_{1u}	exocyclic C=C stretch	1553	m	–	1483	m	–	1470	s	–
8	ν_3	A_g	exocyclic C=C stretch	1485	–	s	1445	–	s	1429	–	m
9	ν_{42}	B_{3g}	C–F and ring C–C stretch	1452	–	w	1505	–	w	1543	–	–
10	ν_{34}	B_{2u}	C–F and ring C–C stretch	1390	m	–	1339	m	–	1297	w	–
11	ν_{20}	B_{1u}	C–F and ring C–C stretch	1358	s	–	1343	m	–	1302	w	–
12	ν_4	A_g	C–F and ring C–C stretch	1305	–	w	1282	–	w	1234	–	w
13	ν_{43}	B_{3g}	C–CN stretch	1192	–	w	1195	–	w	1224	w	–
14	ν_{35}	B_{2u}	C–CN stretch	1194	w	–	1196	m	–	1220	m	–
15	ν_{44}	B_{3g}	ring stretch	1150	–	–	1132	–	–	1107	–	–
16	ν_{21}	B_{1u}	ring stretch	1142	w	–	1145	m	–	1131	m	–
17	ν_{36}	B_{2u}	ring stretch	988	s	–	980	m	–	968	m	–
18	ν_5	A_g	ring stretch	886	–	–	886	–	–	880	–	–
19	ν_{22}	B_{1u}	ring mode	804	m	–	790	w	–	778	m	–
20	ν_{45}	B_{3g}	ring substituent bend	775	–	–	772	–	–	768	–	–

[a] s=strong, m=medium, w=weak, –=silent/too weak to be observed in spectra.

we have used a simplified numbering scheme (column 1) to identify individual vibrational modes, rather than the more formally correct identifications used by Meneghetti and Pecile^[10] (cf. column 2). This simplified scheme allows modes of the same type to be clustered together, with the assigned number giving an indication of the relative energy of the mode. A graphical depiction of the nature of TCNQF₄⁰ modes 1 to 20 can be found in Figure 2. Depictions of all modes of TCNQF₄⁰, TCNQF₄¹⁻ and TCNQF₄²⁻ can be found in Figures S1, S2 and S3, respectively. Most modes retain the same fundamental character across all three species, however some do show mixing, particularly for TCNQF₄²⁻. While both TCNQF₄⁰ and TCNQF₄¹⁻ belong to the *D*_{2h} point group, a slight loss of planarity in TCNQF₄²⁻ reduces the symmetry to *D*₂. This deviation is sufficiently small that the vibrational modes can be projected onto a two-dimensional plane with no significant loss of information (see Figure S3).

Identification of TCNQF₄⁰ modes

Comparison of the TCNQF₄⁰ mode descriptions in Table 1 with the identifications of earlier studies (see the Introduction) confirms the accuracy of the assignments of Meneghetti and Pecile.^[10] Although their potential-energy distribution data do not give a full picture of the nature of the vibrational modes, in all cases they are consistent with Figure 2. In summary (from high energy to low):

- The characteristic C≡N stretching modes absorb at approximately 2225 cm⁻¹. This assignment has never been in question.
- There is general consensus that the next highest energy bands result from C=C stretching modes, although there have been some difficulties in their precise identification. Figure 2 shows that the ring C=C stretches are higher in energy, absorbing at approximately 1670 cm⁻¹ and approximately

1600 cm⁻¹ for *A*_g and *B*_{2u} modes, respectively. Bands corresponding to exocyclic C=C stretches appear at 1553 (IR) and 1485 cm⁻¹ (Raman). It is important to note that the 1485 cm⁻¹ Raman mode has been misidentified as a C–CN wing mode in many previous publications.^[3a,6–7,12a,b,e]

- Next comes a series of stretching modes that typically involve both C–F and endocyclic C–C bonds. Previously, only Meneghetti and Pecile^[10] have discussed these bands. Generally, we agree with their assignments, however, we do query the association of the *B*_{3g} mode (mode 9) with a band

Figure 2. The 20 highest energy vibrational modes of TCNQF₄⁰. Blue diamonds show the equilibrium positions of the atoms (see Figure 1). Red circles show the extent of the movement of the atoms due to the vibration.

at 1498 cm^{-1} . Our calculated frequency is 1452 cm^{-1} . It would be surprising if this prediction was nearly 50 cm^{-1} too low, particularly as any deviations of our calculations from experiment tend to be on the high side. We suspect that this mode might be better assigned to the shoulder at 1447 cm^{-1} or the weak band at 1430 cm^{-1} in their spectral data.

- A pair of modes (one IR active and the other Raman active) absorb at approximately 1200 cm^{-1} . Figure 2 reveals that these are the two C–CN wing stretching modes, not C–F bending modes as indicated in previous studies.
- The readily detectable region of the spectra concludes with a series of complex modes, mainly involving the six-membered ring. The first four of these primarily consist of ring deformations with varying degrees of substituent contribution, whereas mode 20 involves a concerted bending of all substituents in the same direction around the ring.

While the modes of TCNQF_4^0 are quite distinct in terms of both mode type and vibrational frequency, the situation becomes more complicated as the molecule is reduced. As illustrated in Figure 3, most modes show a red-shift (a shift to

Figure 3. The changes in the vibrational frequencies of TCNQF_4^n ($n=0, 1^-, 2^-$) modes 5 to 14 with increasing negative charge. Mode symmetries are distinguished by colour (blue = A_g , green = B_{1u} , red = B_{2u} , purple = B_{3g}) and mode types by symbols (squares = C=C stretches; diamonds = combined C–F and ring C–C stretches; triangles = C–CN stretches).

lower energy) associated with increasing negative charge on the molecule. In contrast, mode 9 is shifted towards higher energies (blue-shift). This results in a change in the ordering of the modes between the three redox levels. While mode 9 is lower in energy than the C=C stretches (modes 5 to 8) for TCNQF_4^0 , it splits the exo- and endocyclic C=C modes for TCNQF_4^{1-} and rises to become the sixth highest mode for TCNQF_4^{2-} . The C–CN stretching modes (13 and 14) are also blue-shifted as TCNQF_4^0 is reduced to TCNQF_4^{2-} .

Mixing of modes

The red-shifting of (most of) modes 5 to 12 is accompanied by a mixing of vibrations of the same symmetry. This is shown for modes with A symmetry in Figure 4 and for modes of B symmetry in Figure 5. As seen in Figure 4, mode 5 largely retains

Figure 4. The mixing of vibrational modes of A symmetry with increasing negative charge.

its endocyclic $\nu(\text{C}=\text{C})$ character in TCNQF_4^{1-} and TCNQF_4^{2-} , however, increasing movement is seen in atom C1 (see Figure 1), indicating some mixing with the lower energy exocyclic C=C stretch (mode 8). For mode 8, the changes in the nature of the vibration with TCNQF_4 reduction are far more dramatic. Although clearly an exocyclic C=C stretch in TCNQF_4^0 , this mode acquires significant C–F and ring C–C stretching character from mode 12 in TCNQF_4^{1-} and TCNQF_4^{2-} to become essentially a ring breathing motion with stretching components from all substituents. Mode 12 mirrors the behaviour of mode 5, showing only a slight increase in exocyclic C=C stretching character as the molecule is reduced.

In the same way, each of the B_i modes of TCNQF_4^0 (shown in Figure 5) have very different characters. Mode 7 clearly corresponds to an anti-symmetric exocyclic C=C stretch, while mode 11 involves the C–F and ring C–C bonds but has no contribution from the exocyclic C=C linkages. In TCNQF_4^{1-} and TCNQF_4^{2-} , however, these modes are strongly mixed. For the B_2 modes (modes 6 and 10), the structural changes seen in Figure 5 are far less dramatic than for the B_i vibrations. The TCNQF_4^0 and TCNQF_4^{1-} modes are essentially unchanged, however for TCNQF_4^{2-} careful examination reveals a slight increase in the horizontal movement of C1 in mode 6 and in the vertical movement of C2 in mode 10. Given these small structural changes, it might be expected that the frequencies would not vary significantly with the redox level. It is therefore surprising to observe that these fall by 133 and 93 cm^{-1} for modes 6 and 10, respectively, as TCNQF_4^0 is reduced to its dianion. This dra-

Figure 5. The mixing of vibrational modes of *B* symmetry with increasing negative charge.

matic red-shift can also not be attributed solely to changes in bond lengths between redox levels. Although modes 5 and 6 involve the same bonds, the analogous red-shift of mode 5 is only 46 cm^{-1} .

Raman spectra

The mixing of modes of *A* symmetry has important implications for the Raman spectra of TCNQF_4^0 , TCNQF_4^{1-} and TCNQF_4^{2-} . As seen in Figure 6 (theoretical spectra) and Figure S4 (experimental), the most significant difference between the Raman spectra is the relative intensity of modes 5 and 8. In TCNQF_4^0 and TCNQF_4^{1-} , mode 8 is the dominant band in the spectrum, whereas in TCNQF_4^{2-} its intensity is dramatically reduced and there is a corresponding increase in the height of the mode 5 band. As noted in previous studies,^[6] the frequencies of the $\text{C}\equiv\text{N}$ stretching modes (modes 1 and 4) are red-shifted from approximately 2225 cm^{-1} in TCNQF_4^0 , to approximately 2180 cm^{-1} in TCNQF_4^{1-} and approximately 2150 cm^{-1} in TCNQF_4^{2-} . Mode 12 is also red-shifted as the molecule is reduced, absorbing at 1305, 1282 and 1234 cm^{-1} in TCNQF_4^0 ,

Figure 6. Calculated gas-phase Raman spectra for A TCNQF_4^0 , B TCNQF_4^{1-} and C TCNQF_4^{2-} .

TCNQF_4^{1-} and TCNQF_4^{2-} , respectively. It should be noted, however, that mode 12 has a very low Raman intensity in TCNQF_4^0 such that it is generally not observed in experimental spectra (see Figure S4A). In addition, mode 13 (the B_{3g} C–CN stretching mode) is more strongly absorbing in TCNQF_4^0 than in TCNQF_4^{1-} and TCNQF_4^{2-} and hence can be detected in spectra of the former but not the latter (see Figure S4). This has led to some confusion in the literature, with mode 13 of TCNQF_4^0 and modes 12 of TCNQF_4^{1-} and TCNQF_4^{2-} being mistakenly identified as the same vibration.^[6]

Theoretical IR spectra

In the same way as mixing of the A symmetry modes affects the Raman spectra of TCNQF_4 species, mixing of the B_1 and B_2 modes alters the IR-active vibrational modes. For TCNQF_4^0 , four clear bands are seen between 1250 and 1750 cm^{-1} in Figure 7A, corresponding to modes 6, 7, 10 and 11. For TCNQF_4^{1-} , however, the red-shifting of mode 10 means that it absorbs at the same frequency as mode 11, producing a single band at approximately 1340 cm^{-1} (Figure 7B). Likewise, red-shifting of mode 6 as TCNQF_4^{1-} is reduced to TCNQF_4^{2-} causes its band to align with that of mode 7. Hence, in the calculated spectrum

Figure 7. Calculated gas-phase IR spectra for A TCNQF_4^0 , B TCNQF_4^{1-} and C TCNQF_4^{2-} .

of TCNQF_4^{2-} (Figure 7C) there are only two bands between 1250 and 1750 cm^{-1} . In addition, the intensity of the combined mode 10 and 11 band is greatly reduced in TCNQF_4^{2-} , producing a spectrum that has only three strong bands: the combined mode 6 and 7 band and the two $\text{C}\equiv\text{N}$ stretching modes. These $\text{C}\equiv\text{N}$ modes also provide a useful tool for identifying the TCNQF_4 redox level. TCNQF_4^0 can readily be identified by the very weak IR activity of these bands. In the calculated gas-phase spectra, a clear red-shift of approximately 30 cm^{-1} between TCNQF_4^{1-} and TCNQF_4^{2-} is also seen for these modes (2194 and 2162 cm^{-1} versus 2163 and 2128 cm^{-1} , respectively). A note must also be made about modes 4 and 13, which have been indicated in Figure 7C even though they absorb at identical frequencies to modes 3 and 14, respectively. In TCNQF_4^0 and TCNQF_4^{1-} these modes have B_{3g} symmetry and are therefore not IR active. In TCNQF_4^{2-} , however, the $\text{C}(\text{CN})_2$ wings rotate away from the plane of the six-membered ring, reducing the point group of the molecule to D_2 . The B_{3g} modes are therefore reduced to B_3 symmetry and their transitions become IR active.

Effects of the crystalline environment

 TCNQF_4^{1-} IR spectra

Experimental IR spectra for complexes of TCNQF_4^{1-} (LiTCNQF_4 , Figure 8A, and $(\text{Pr}_4\text{N})\text{TCNQF}_4$, Figure 8C)^[7] show several additional bands not found in the theoretical gas-phase spectrum (Figure 7B). In many cases the associated frequencies correspond to bands in the TCNQF_4^{1-} Raman spectrum (Figure 6B). Although analysis of the spectroscopic principles behind the appearance of these bands is beyond the scope of this work (this will be addressed elsewhere), we find that remarkably good simulations of the experimental IR spectra can be obtained by simply placing a positive charge (Li^+) in out-of-plane positions close to the surface of the molecule (Figure 8, parts B and D). We emphasise that these simulations are not intended to exactly reproduce the experimental spectra of Figure 8, parts A and C. Indeed, it would be very surprising if a simple model with a single cation could replicate the complex electronic environment found in real crystals. Nevertheless, the agreement between the simulated and experimental spectra is sufficiently good to confirm that these additional bands do indeed arise from the formally IR-silent symmetric vibrational modes.

As a Li^+ probe is scanned across the surface of TCNQF_4^{1-} , two fundamentally different spectra are produced: Figure 8B, which reproduces the features of the experimental spectrum of LiTCNQF_4 (Figure 8A),^[7] and Figure 8D, which mimics the $(\text{Pr}_4\text{N})\text{TCNQF}_4$ spectrum^[7] (Figure 8C). (We note that the $(\text{Pr}_4\text{N})\text{TCNQF}_4$ spectrum is complicated by Pr_4N^+ bands.) The most significant difference between the two spectra is seen in the behaviour of modes 8 and 10. In the spectrum of Figure 8B these are separated by nearly 100 cm^{-1} and both are of medium intensity. In the Figure 8D spectrum, however, mode 10 is blue-shifted by 40 cm^{-1} , while mode 8 is red-shifted by over 50 cm^{-1} and its intensity is increased by over 20-

Figure 8.

A Experimental IR spectrum for LiTCNQF_4 .^[7] B Calculated IR spectrum for TCNQF_4^{1-} with Li^+ at the location of the red dot and 4 Å above the molecular plane, that is, at $(x, y, z) = (1 \text{ Å}, 2 \text{ Å}, 4 \text{ Å})$ relative to the centre of the molecule. C Experimental IR spectrum for $(\text{Pr}_4\text{N})\text{TCNQF}_4$.^[7] D Calculated IR spectrum for TCNQF_4^{1-} with Li^+ at position (2, 2, 4).

fold. Interestingly, in scanning across the surface we do not see a smooth transition between the two spectra. Except when the probe is placed on the *X* axis or in the plane of the molecule, the spectrum produced clearly belongs to either the type in Figure 8B or the type in Figure 8D (see Figure S5).

TCNQF₄²⁻ IR spectra

While all of the TCNQF_4^{1-} IR spectra published thus far have shown bands corresponding to formally IR-silent modes, the spectra of TCNQF_4^{2-} are more variable. As shown in Figure 9A, the IR spectrum^[7] of $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ shows only the bands found in the theoretical gas-phase spectrum of Figure 7C. In contrast, the spectrum of CoTCNQF_4 (Figure 9B)^[12a] shows bands at 1620 cm^{-1} (consistent with mode 5) and 1369 cm^{-1} (consistent with the perturbed frequency of mode 8 seen in Figure 8D). Although the spectrum of $\text{Li}_2\text{TCNQF}_4$ (Figure 9C)^[7] also shows a strong mode 5 band at 1622 cm^{-1} , there is only a very weak band between 1320 and 1450 cm^{-1} (1354 cm^{-1}), which may correspond to mode 8. It is likely that the appearance of these bands in the TCNQF_4^{2-} spectra is dependent on the charge distribution within the crystalline environment of the molecule.

C≡N stretching frequencies

The nitrile stretching frequencies in IR spectra (2000 to 2250 cm^{-1}) have been the predominant tool used to identify TCNQF_4 redox levels.^[3a,4b,c,5-7,8b,12] However, as noted by Meneghetti,^[10] these frequencies are sensitive to the crystalline environment (see, for example, Figure 9). Computational modelling has proved useful for probing this sensitivity. Figure 10 shows some of the variations in this spectral region produced by varying positions of single or multiple cation probes around the TCNQF_4 architecture. For comparison, gas-phase spectra of TCNQF_4^{1-} and TCNQF_4^{2-} are shown in Figure 10, parts A and E, respectively.

As seen in X-ray crystal structures (for example AgTCNQF_4 ^[4c]), monatomic cations often coordinate TCNQF_4^{1-} and TCNQF_4^{2-} by means of the nitrile groups. To simulate this, we used four symmetrically placed Li^+ probes, one coordinated to each of the nitrogen atoms. While the two bands of TCNQF_4^{1-} show only a slight blue-shift in comparison with the free anion ($\sim 15 \text{ cm}^{-1}$ to 2176 and 2213 cm^{-1} , Figure 10B), for TCNQF_4^{2-} blue-shifting of the higher energy B_1 mode is much more significant than for the lower energy B_2 and B_3 modes (Figure 10F). The lower energy modes remain close to

Figure 9. Assigned experimental IR spectra for: A $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$,^[7] B CoTCNQF_4 ,^[12a] C $\text{Li}_2\text{TCNQF}_4$.^[7]

2130 cm^{-1} , hence the presence of bands around 2130 cm^{-1} has been considered characteristic of TCNQF_4^{2-} complexes. In contrast, the higher energy bands are blue-shifted to approximately 2200 cm^{-1} , similar to the values seen for TCNQF_4^{1-} . Blue-shifting of these modes can be even more extreme when divalent cations are present. For instance, in a computational study of dimeric $(\text{ZnTCNQF}_4)_2$, the highest energy nitrile modes of TCNQF_4^{2-} were found to absorb at 2229 cm^{-1} .^[14] Hence, the presence of nitrile bands above 2200 cm^{-1} cannot be used to diagnose the TCNQF_4 redox level.

Caution should also be employed when considering the lower energy nitrile modes. As shown in Figure 10, parts C and

Figure 10. Variations in the nitrile stretching regions of IR spectra with Li^+ probe position(s) (red dot(s) on the molecular diagrams). No probe is present in A and E; in B, C, F and G the probe(s) are in the plane of the molecule. Coordinates of probe positions are given in Table S3.

G, variations in the charge distribution around the TCNQF_4 molecule can lead to spectra for TCNQF_4^{1-} that are similar to the TCNQF_4^{2-} spectrum in Figure 10F and, likewise, spectra for TCNQF_4^{2-} that have two high-energy bands, as seen for TCNQF_4^{1-} in Figure 10B. Although we do not advocate disregarding the information provided by these bands altogether, we do recommend that it should be used in conjunction with data found in other regions of the spectrum.

In calculating the spectra in Figure 10, parts B,C,F and G the cation–anion complexes were allowed to fully optimise. This led to linear coordination of the nitrile groups in parts B and F and in-plane positions for the cations in Figure 10, parts C and G. As noted earlier, however, the charge distributions in crystals are often complex and out-of-plane effects can be very significant. Their impact can be seen in Figure 9, part C and Figure 10, parts D and H, where three rather than two nitrile bands are found. Surprisingly, however, it is a different set of three modes that give rise to the three bands in Figure 10, parts D and H. In the TCNQF_4^{1-} spectrum (Figure 10D) the bands correspond to two “symmetric” nitrile stretch modes (modes 1' and 2'; note: symmetry is broken due to the presence of the probe, partially decoupling the modes, see Figure S6) and one “asymmetric” mode (4'). The other “asymmetric” nitrile stretch (3') has low IR intensity. In contrast, in the TCNQF_4^{2-} spectrum (Figure 10H) all four modes are IR active, however, the two “symmetric” modes absorb at the same frequency. Hence the three bands correspond to modes 1' and 2' combined, mode 3' and mode 4'. It is important to note that all four $\nu(\text{C}\equiv\text{N})$ modes can be IR active and absorb at different frequencies, hence up to four bands could be observed in the nitrile stretching region of the TCNQF_4^{1-} and TCNQF_4^{2-} IR spectra.

It is important to note that this sensitivity of vibrational modes to metal-cation coordination is likely to affect many organic molecular ions. Anion coordination may similarly perturb the spectra of organic cations. Hence, this is an important factor that must be considered in the analysis of vibrational spectra for redox level characterisation whenever organic ions are involved.

Diagnostics of TCNQF_4 Redox Level

In conclusion, we present an expanded set of diagnostics for identifying the redox level of TCNQF_4 species based on their Raman and IR spectra. These diagnostics represent a significant improvement on our earlier work on this problem.^[6] Details of the changes in band frequency and intensity with TCNQF_4 reduction are shown in Tables 2 and 3, respectively (values taken from experimental spectra^[7,12a,b,d]). The important regions of the IR spectra for distinguishing the presence of TCNQF_4^0 , TCNQF_4^{1-} and TCNQF_4^{2-} are shown in Figure 11, along with representative spectra for species in which the redox level is known. Three important spectral regions are identified:

Mode	TCNQF_4^0	TCNQF_4^{1-}	TCNQF_4^{2-}
1	2230 (m)	2190–2240 (m)	2150–2240 (w)
4	2216 (w)	2150–2200 (w)	2070–2150 (m)
5	1665 (m)	~1640 (m)	~1645 (s)
8	1460 (s)	~1445 (s)	~1428 (w)

[a] s=strong intensity, m=medium, w=weak.

Mode	TCNQF_4^0	TCNQF_4^{1-}	TCNQF_4^{2-}
1–4	2228 (vw)	2150–2240 (s)	2070–2240 (s) ^[b]
6	1600 (s)	~1535 (s–m)	~1475 (s)
7	1551 (w)	~1500 (m)	~1475 (s)
11	1341 (s)	~1350 (s–m)	~1300 (vw)

[a] s=strong intensity, m=medium, w=weak, vw=very weak. [b] In general, at least one mode below 2150 cm^{-1} is expected.

Figure 11. Calculated and experimental^[7,12a,b,e] IR spectra of TCNQF_4^0 , TCNQF_4^{1-} and TCNQF_4^{2-} showing the critical regions for distinguishing the TCNQF_4 redox level.

- 1290–1360 cm^{-1} (blue box in Figure 11): TCNQF_4^0 and TCNQF_4^{1-} show strong absorbance in this region (bands from 8, 10 and 11 are much stronger than those between 1000 and 1250 cm^{-1}). TCNQF_4^{2-} absorbs weakly (weaker than the ~1230 cm^{-1} band), however, bands from counter ions or co-crystallised solvent molecules may complicate the spectrum.

- 1460–1600 cm^{-1} (red box in Figure 11): In TCNQF_4^0 , mode 6 appears at 1599 cm^{-1} . In TCNQF_4^{1-} it is significantly red-shifted to $\sim 1535 \text{ cm}^{-1}$ but remains clearly distinct from mode 7 (at $\sim 1500 \text{ cm}^{-1}$). In TCNQF_4^{2-} , mode 6 is further red-shifted; some red-shifting is also seen for mode 7 so that both lie closer to 1490 cm^{-1} . This region is less likely to be affected by extraneous bands and should be used as the primary diagnostic of the redox level.
- 2040–2150 cm^{-1} ($\nu(\text{C}\equiv\text{N})$ region; green box): modes 1–4 are generally found above 2150 cm^{-1} in TCNQF_4^0 and TCNQF_4^{1-} . In TCNQF_4^{2-} , significant absorbance is usually seen below 2150 cm^{-1} . We note that complex charge distributions within a crystal structure may make diagnosis using these modes alone unreliable.

Experimental Section

Geometry optimisations and harmonic vibrational frequency calculations were performed for gas-phase TCNQF_4^0 , TCNQF_4^{1-} and TCNQF_4^{2-} using the B3LYP density functional^[15] in conjunction with the 6-31G(2df,p) basis set.^[16] This model chemistry is known to give good accuracy for the calculation of vibrational frequencies. For instance, it is employed in G4 theory for the accurate calculation of zero-point energies.^[17] In each calculation the full symmetry of the molecule was used: D_{2h} for TCNQF_4^0 and TCNQF_4^{1-} ; D_2 for TCNQF_4^{2-} . Cartesian coordinates for the optimised geometries can be found in Table S1.

B3LYP/6-31G(2df,p) vibrational frequencies are normally scaled by a factor of 0.9854^[18] to account for known deficiencies in the method^[19] (incomplete basis set, anharmonicity, etc.). This factor gives good agreement between theory and experiment for most frequencies below 2000 cm^{-1} , however the nitrile stretching frequencies (at $\sim 2200 \text{ cm}^{-1}$) are consistently over-predicted. Benchmarking calculations (Table S2a) indicate that nitrile stretches are particularly challenging for quantum chemical calculations. We therefore determined a new scaling factor of 0.9556 (See Table S2b), which was applied to all calculated frequencies over 2000 cm^{-1} in this work.

The effects of the local electronic environment on the IR spectra of TCNQF_4 species were simulated using an Li^+ probe. Single-point harmonic frequency calculations were performed using the optimised B3LYP/6-31G(2df,p) geometries for TCNQF_4^{1-} and TCNQF_4^{2-} with the probe placed at various positions across the surface of the molecule. Where these points were close to geometric minima, full-geometry optimisations were performed before harmonic frequencies were calculated. Cartesian coordinates for all $\text{TCNQF}_4\text{--Li}^+$ complexes can be found in Table S3.

All calculations were performed using the Gaussian09 suite of programs^[20] on the Trifid HPC cluster at the Victorian Partnership for Advanced Computing (VPAC).

Acknowledgements

The calculations in this work were performed on the Victorian Partnership of Advanced Computing high-performance computing facilities and funded by Deakin University.

Keywords: density functional calculations • IR spectroscopy • Raman spectroscopy • redox chemistry • 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane

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Received: February 10, 2014

Published online on April 6, 2014