Characterisation of fac-tris [2-phenylpyridinato-\(C^2\), N]iridium(III) by inelastic neutron scattering spectroscopy and periodic density functional theory

Stewart F Parker
ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom

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Abstract
fac-Tris[2-phenylpyridinato-\(C^2\), N]iridium(III) (tris-(2-phenylpyridine) iridium, \([\text{Ir}(\text{ppy})_3]\)), is a metal complex with applications that range from its use in organic light emitting diodes, to its acting as an efficient photocatalyst for a variety of organic reactions. In this paper the INS spectrum of this material is recorded for the first time and it is analysed by periodic density functional theory calculations of both its trigonal and tetragonal polymorphs. The differences between the calculated INS spectra of the trigonal and tetragonal forms and the isolated molecule demonstrate that the intermolecular interactions play a significant role. This is surprising for what is, nominally, a van der Waals solid.

1. Introduction
fac-Tris[2-phenylpyridinato-\(C^2\), N]iridium(III) (tris-(2-phenylpyridine) iridium, \([\text{Ir}(\text{ppy})_3]\)), see figure 1, is an emissive heavy metal complex [1] that is the most frequently used precursor molecule for the synthesis of electro-phosphorescent materials. These are used in organic light emitting diodes (OLEDs) [2]. It provides green-colour emission with a phosphorescence quantum yield close to unity [3]. The complex has also been used as an efficient photocatalyst for a variety of organic processes ranging from benzylation, \(\alpha\)-amino arylation, intramolecular cyclization, polymerization, addition to styrenes, decarboxylative arylation, \(\beta\)-arylation of carbonyls, to decarboxylative trifluoromethylation [4, 5].

The structure of the complex has been investigated in both the gas [6] and solid state [6–8] and shows that the ligand is covalently bound via the pyridine nitrogen atom and by cyclometallation of the ortho-carbon atom of the phenyl ring. The photophysics of the complex has been comprehensively characterised in a variety of media [9], however, the vibrational spectroscopy of the complex [10] has been much less explored.

Inelastic neutron scattering (INS) spectroscopy is a complementary form of vibrational spectroscopy that is particularly sensitive to modes involving motion of hydrogen [11]. For a complete vibrational characterisation, INS spectra are essential, particularly to understand the low energy metal-to-ligand modes that are important in energy dissipation. In previous work [12], we showed how for a sequence of platinum bipyridyl thiolato complexes, with a combination of INS and Raman spectroscopy, supported by periodic density functional theory (DFT) calculations it was possible to assign all of these important modes. In the present work, we use INS, infrared and Raman spectroscopies to observe the modes and use periodic DFT of the complete unit cell to provide assignments.

2. Experimental
\([\text{Ir}(\text{ppy})_3]\) (99%) was obtained from Sigma-Aldrich and used as received. INS spectra were recorded using the high resolution broadband spectrometer TOSCA [13] at ISIS [14]. The sample was wrapped in aluminium foil and placed inside an indium-wire sealed aluminium can. This was cooled to \(< 20 \text{ K}\) in a closed cycle refrigerator and the spectrum measured for \(\sim 10\) hours. This experiment is made challenging by the large absorption cross

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section of iridium: 425 barn. This means that irrespective of the actual sample thickness, only the topmost 100 μm, or so, of the sample is measured. Beyond this distance, the low energy neutrons that TOSCA requires for the energy analysis do not escape and are absorbed. It also means that only the back scattering detectors yield a useful spectrum. At the rear of the sample, where neutrons can escape into the forward scattering analysers, the incident flux distribution has been modified by the absorption, such that the normalisation to the incident monitor spectrum is not valid. The FT-Raman spectrum was recorded at room temperature with a Bruker MultiRam spectrometer using 500 mW laser power, 1064 nm excitation, 4650 scans with 4 cm⁻¹ resolution. Infrared spectra were recorded using a Bruker Vertex70 FTIR spectrometer, over the range 50 to 4000 cm⁻¹ at 2 cm⁻¹ resolution with a DLaTGS detector using 64 scans and the Bruker Diamond ATR. The use of the ultra-wide range beam splitter enabled the entire spectral range to be recorded without the need to change beam splitters. The spectra have been corrected for the wavelength-dependent variation in path length using the Bruker software.

The plane wave pseudopotential based program CASTEP was used for the calculation of the vibrational transition energies and their intensities [15, 16]. The generalised gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) functional was used in conjunction with optimised norm-conserving pseudopotentials. The initial structures were those of Breu et al [7] and Takayasu et al [8]. The calculations were converged to better than 0.0095 eV Å⁻¹. After geometry optimisation, the vibrational spectra were calculated in the harmonic approximation using density-functional perturbation-theory [17]. This procedure generates the vibrational eigenvalues and eigenvectors, which allows visualisation of the modes within Materials Studio [18] and is also the information needed to calculate the INS spectrum using the program ACLIMAX [19]. Unless otherwise stated, the calculated spectra include overtones and combinations up to the 10th order. It is emphasised that the transition energies have not been scaled.

3. Results and discussion

The vibrational spectra of Ir(ppy)₃ are shown in figure 2. The complementarity of the spectra is immediately apparent. The infrared and Raman spectra provide good detail in the region >600 cm⁻¹ where the internal modes of the 2-phenylpyridinato ligands are found. This is particularly noticeable in the C–H stretch region, 3000–3200 cm⁻¹. The INS data in this region are dominated by combinations of the C–H stretch and the lattice modes. These are apparent because (i) they are allowed transitions in INS spectroscopy and (ii) the instrument’s characteristics are such that these modes are amplified. This is explained in more detail elsewhere [20, 21]. Below 600 cm⁻¹ is where the ligand-metal modes occur and these are best seen in the INS spectrum.

Ir(III) is a d⁶ ion, thus is potentially either high spin, with four unpaired electrons, or low spin with no unpaired electrons. Calculations were carried out for both configurations. The high spin version did not converge, while convergence was straightforward for the low spin version. Low spin complexes are the norm for second and third row transition elements [22].

Ir(ppy)₃ exhibits two polymorphs: a trigonal one in space group P3 [7] with six molecules in the unit cell (Z = 6) and a tetragonal form in P421c [8] with Z = 8. The former is the polymorph that is commonly found. However, the structure of the complex is very similar in both modifications. Table 1 shows a comparison of selected bond lengths and angles in the structure of Ir(ppy)₃ (in both polymorphs) as calculated by CASTEP, in the gas phase by electron diffraction [6] and the single crystal x-ray diffraction determinations [7, 8]. It can be
seen that the calculation well-reproduces the observed structure, apart from the expected differences in C–H bond length, due to their under-estimation by x-ray diffraction.

Figures 3 and 4 compare the experimental INS and infrared spectra with those calculated for \( \text{Ir(ppy)}_3 \) in the trigonal form, \( Z = 6 \), and that for the tetragonal form, \( Z = 8 \). It can be seen that the two forms are readily distinguishable by vibrational spectroscopy. In the INS spectra, figure 3, there are differences at \( \sim 150, 275 \) and \( 415 \) cm\(^{-1} \) (shown by dashed lines). These correspond to ring torsions that result in relatively large motions at the periphery of the molecule and hence are exploring the intermolecular space, so it is perhaps not surprising that they are particularly sensitive to the polymorph. In the infrared spectra, figure 4, the out-of-plane C–H bending modes at 700–750 cm\(^{-1} \) are diagnostic of the polymorph. It is likely that the Raman spectra may also be used, unfortunately calculating the Raman spectra for such large systems would be prohibitively expensive. By inspection, it is apparent that the form used here is the trigonal polymorph, a result confirmed by powder x-ray diffraction. The tetragonal form is made by sublimation of the trigonal form\(^8\), however, the INS spectrum of a sample purified by sublimation (Aldrich) was identical to the standard material. It is possible that the tetragonal reverts to the trigonal one or that forming the tetragonal form is more difficult than the literature suggests.

The differences between the polymorphs shows that the intermolecular interactions are significant. The calculation of the trigonal form was repeated for the same unit cell but with five of the \( \text{Ir(ppy)}_3 \) molecules removed. This procedure approximates an isolated (gas phase) molecule and allows an assessment of the importance of the intermolecular interactions. The results are shown in figure 5 and it can be seen that the calculation of the complete unit cell is in much better agreement with the experimental data. This is not only the case in the external mode region, where it would be expected, but also for the internal modes. This is particularly

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**Table 1. Comparison of selected observed and calculated bond lengths and angles of \( \text{Ir(ppy)}_3 \).**

|                | Gas phase [6] | Trigonal form [7] | Calculated | Tetragonal form [8] | Calculated |
|----------------|--------------|-------------------|------------|---------------------|------------|
|                | Observed     | Calculated        | Observed   | Calculated          |            |
| **Distance/Å** |              |                   |            |                     |            |
| Ir–N           | 2.158        | 2.071             | 2.104      | 2.137               | 2.114      |
| Ir–C           | 2.033        | 2.061             | 2.003      | 2.018               | 2.007      |
| Phenyl–pyridyl | 1.458        | 1.437             | 1.457      | 1.470               | 1.460      |
| Phenyl C–C (average) | 1.396 | 1.386             | 1.405      | 1.394               | 1.406      |
| Pyridyl C–C (average) | 1.398 | 1.388             | 1.395      | 1.386               | 1.394      |
| C–N (average)  | 1.362        | 1.372             | 1.367      | 1.352               | 1.368      |
| Phenyl C–H (average) | 1.128 | 0.949             | 1.090      | 0.952               | 1.089      |
| Pyridyl C–H (average) | 1.128 | 0.930             | 1.088      | 0.918               | 1.088      |
| **Angle/°**    |              |                   |            |                     |            |
| C–Ir–N (same ligand) | 79.6 | 80.1              | 79.6       | 79.8                |            |
| C–Ir–N (different ligand) | 93  | 91.9              | 91.9       | 92.4                |            |
| C–Ir–C         | 94.9         |                   | 91.7       | 91.2                |            |
| N–Ir–N         | 98           | 94.1              | 94.1       | 93.5                |            |
| Phenyl–pyridyl (dihedral) | 5  | 5.9               | 5.4        | 5.4                 |            |

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**Figure 2.** Vibrational spectra of \( \text{Ir(ppy)}_3 \). (a) INS at 10 K, (b) infrared at room temperature and (c) FT-Raman at room temperature. In (b) and (c) the 2900–3300 cm\(^{-1} \) region is \( \times 2 \) ordinate expanded as compared to the 0–1700 cm\(^{-1} \) region.
Figure 3. Comparison of INS spectra of Ir(ppy)$_3$: (a) calculated for the $P\overline{3}$ structure, (b) experimental and (c) calculated for the $P\overline{2}1c$ structure. The dashed vertical lines are at 150, 275 and 415 cm$^{-1}$ where significant differences occur between the polymorphs.

Figure 4. Comparison of infrared spectra of Ir(ppy)$_3$: (a) calculated for the $P\overline{3}$ structure, (b) experimental and (c) calculated for the $P\overline{2}1c$ structure.

Figure 5. Comparison of experimental (middle) and calculated as an isolated molecule ($Z = 1$, bottom) and the complete $P\overline{3}$ structure ($Z = 6$, top) INS spectra of Ir(ppy)$_3$. 

evident in the 700–900 cm⁻¹ region. These are out-of-plane C–H bending modes, thus they involve motions that are associated with atoms at the periphery of the complex, so are the most sensitive to the intermolecular environment. This emphasises the need to include the complete unit cell for the assignment of the modes, in contrast to previous work that assumed an isolated molecule [10].

The DFT-calculated INS spectra provide a means to access specific modes. By setting the cross sections of all the atoms to zero except those of interest, the resulting ‘pseudo-spectra’ only contain modes where the atom(s) of interest have significant motion. Figure 6 shows the results of this exercise where only the nitrogen (figure 6(b)) and the iridium (figure 6(c)) atoms have a non-zero cross section. This procedure allows the metal–ligand modes to be highlighted. It can be seen that there is no significant motion of the iridium ions above 350 cm⁻¹ and that the modes at 178, 233, 273 and 305 cm⁻¹ involve both atoms. Visualisation of the modes shows that the 178 cm⁻¹ mode is a L–Ir–L (L = ligand) bend and the others are Ir–L stretch modes. The mode at 375 cm⁻¹ is the C–C stretch that links the pyridyl and phenyl moieties of the ligand. Inspection of the mode visualisations confirms the previous assignments [10].

4. Conclusions

The differences between the calculated INS spectra of the trigonal and tetragonal polymorphs and isolated molecule demonstrate that the intermolecular interactions play a significant role. This is somewhat surprising for what is, nominally, a van der Waals solid.

What is not generally realised is just how far vibrational analysis has evolved in the last few decades. From a discipline that was dominated by empirical force fields based on ball-and-spring models (the Wilson GF method [23]) that meant that molecules larger than a few dozen atoms were completely intractable, through Hartree–Fock and then DFT isolated molecule calculations and currently to periodic-DFT calculations involving hundreds of atoms (the tetragonal unit cell of Ir(ppy)₃ contains 488 atoms). This advance has been driven by two factors: the availability of user-friendly computer codes but much more by the increase in computational power described by Moore’s Law. Neutron science, and particularly INS spectroscopy, would not be in such robust good health without such computing power.

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ORCID iDs

Stewart F Parker https://orcid.org/0000-0002-3228-2570
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