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DFT calculations of the structures and vibrational spectra of the $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes

Bruce D. Alexander [a], Trevor J. Dines [b,*], Rayne W. Longhurst [b]

[a] School of Science, University of Greenwich at Medway, Central Avenue, Chatham Maritime, Kent ME4 4TB, UK
[b] Division of Electronic Engineering and Physics, University of Dundee, Dundee DD1 4HN, UK

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ABSTRACT

Structures of the $[M(bpy)_3]^{2+}$ complexes (M = Fe and Ru) have been calculated at the B3-LYP/DZVP level. IR and Raman spectra were calculated using the optimised geometries, employing a scaled quantum chemical force field, and compared with an earlier normal coordinate analysis of $[Ru(bpy)_3]^{2+}$ which was based upon experimental data alone, and the use of a simplified model. The results of the calculations provide a highly satisfactory fit to the experimental data and the normal coordinate analyses, in terms of potential energy distributions, allow a detailed understanding of the vibrational spectra of both complexes. Evidence is presented for Jahn-Teller distortion in the ^1E MLCT excited state.

1. Introduction

In the last twenty years there has developed considerable interest in the *ab initio* calculation of molecular vibrations, as an aid to the interpretation of IR and Raman spectra. Until a few years ago such studies were limited to molecules of small molecular mass. The availability of more powerful computational resources has now made it possible to carry out calculations on much larger molecules, in particular transition metal complexes. The ability to compute force constants, dipole derivatives and polarizability derivatives is crucial to the interpretation of the vibrational spectra of larger molecules. Whereas a complete normal coordinate analysis based upon experimental data alone is usually possible for molecules of up to about 25 atoms, this is often not feasible for larger molecules, due to the extremely large number of force constants in relation to the number of observable IR and Raman bands. For this reason, normal coordinate analyses of metal complexes often involve simplified models, for example involving the metal ion and a single ligand, and often reliant upon the availability of additional vibrational data from isotopomers. In larger molecules it is often the case that some of the $3N-6$ vibrations overlap, or may be negligibly weak in both the IR and Raman spectra. The interpretation of resonance Raman (RR) spectra of larger molecules can be particularly difficult due to the selective nature of resonance enhancement. These problems are especially manifest in the vibrational spectra of the tris-bipyridyl complexes $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$, in which there is a great deal of current interest.

Ab initio calculations at the Hartree–Fock (HF-SCF) level are relatively straightforward for metal complexes and provide a complete set of force constants, from which a potential energy distribution may be determined for every normal coordinate. However, HF-SCF calculations yield force constants that are consistently high for two main reasons. Firstly, such calculations tend to give excessively short bond lengths, even with large basis sets and secondly, the harmonic oscillator approximation is assumed. The neglect of anharmonicity leads to abnormally large force constants for vibrations that are known to be appreciably anharmonic, e.g. those involving the motion of hydrogen atoms. Typically, force constants computed at the HF-SCF level require scaling by factors of the order of 0.80–0.85, and are not generally improved by invoking larger basis sets. Scaling is necessary for two reasons; primarily because HF-SCF calculations yield vibrational wavenumbers which are too high due to the overestimation of force constants resulting from bond distances that are too short. Secondly, scaling is required in order to compare the computed harmonic wavenumbers with experimental anharmonic wavenumbers. Although more realistic results can be achieved from MP2 calculations, these are computationally demanding and essentially prohibitive for metal complexes. In the last ten years hybrid SCF-density functional methods have become popular since they provide vibrational wavenumbers which are comparable with those calculated at the MP2 level, but require significantly less computation time. These methods are ideal for modelling the structures and vibrational

* Corresponding author. Tel.: +44 1382 344728; fax: +44 1382 388316.
E-mail address: t.j.dines@dundee.ac.uk (T.J. Dines).

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spectra of metal complexes, although scaling of force constants is needed to take account of anharmonicity. It is possible to estimate anharmonicity constants from calculations of cubic and quartic force constants, but such calculations are extremely demanding.

In this report we present the results of some B3-LYP calculations and normal coordinate analyses of M(II) tris-(2,2′-bipyridyl) complexes, where M = Fe or Ru. These complexes display intense resonance Raman (RR) spectra with visible laser excitation and are of considerable theoretical and technological importance as the archetypes of this class of complexes. Ruthenium (II) complexes with 2,2′-bipyridyl (bpy) have been intensively studied [1–9] due to their interesting photochemical properties, which can be modified by introduction of different functionalities onto the bipyridyl ligands. One of the most important examples of the use of these complexes is as photo-sensitizers in the new generation of solar cells, i.e. Grätzel cells, where sensitizers such as Ru(2,2′-bipyridyl-4,4′-dicarboxylato)$_2$-*cis*-(NCS)$_2$ are typically chemisorbed onto nanocrystalline titanium dioxide by pendant carboxylic acid groups.

RR and time-resolved RR (TR^3) spectroscopy have been exploited in the quest to understand the nature of the lowest energy singlet and triplet excited states of ruthenium (II) tris-polypyridyl complexes [10–12]. TR^3 measurements of $[Ru(bpy)_3]^{2+}$ have provided the most conclusive evidence of a localised ^{3}E MLCT excited state [11–13]. Woodruff and co-workers [11,12] observed bands in the TR^3 spectrum of $[Ru(bpy)_3]^{2+}$ attributed to both the ground state neutral bpy and radical anion bpy$^{\bullet-}$ ligands, providing convincing evidence that the ^{3}E state should be formulated as $[Ru^{III}(bpy)_2(bpy^{\bullet-})]^{2+}$. In a recent time-dependent DFT study of the excited states of Ru(II) tris-2,2′-bipyridyl and tris-2,2′-bipyrazyl complexes, Alary et al. [14] have shown that the strong emission observed from these complexes may originate from two quasi-degenerate ^{3}MLCT states rather than a single one.

Iron(II) α-diimine complexes are of current interest in relation to their spin crossover properties and the photophysical behaviour of the $[Fe(bpy)_3]^{2+}$ complex shows fundamental differences from that of $[Ru(bpy)_3]^{2+}$ in that emission is from a quintet state with ligand field character rather than ^{3}MLCT states. In $[Fe(bpy)_3]^{2+}$ intersystem crossing, following excitation of the ^{1}MLCT state, results in population of the lowest energy $^5T_2$ state with almost 100% quantum yield, thus providing a means of light-induced spin crossover. The population of the $^5T_2$ state has recently been shown by Gawelda et al. [15] to occur within 1 ps following excitation. Using picosecond X-ray absorption spectroscopy these authors have determined the structure of $[Fe(bpy)_3]^{2+}$ in the $^5T_2$ state [16].

Normal coordinate analyses of both the $^1A_1$ ground state, and the ^{3}E MLCT excited state of $[Ru(bpy)_3]^{2+}$ were reported by Kincaid et al. [17,18], although their analysis was based upon a simplified model complex containing only one ligand, with C_{2v} symmetry, and restricted to in-plane vibrations. In a recent report we have established that DFT calculations on tris-α-diimine complexes provide a route to complete normal coordinate analysis of such complexes [19] and this work is now extended to the 2,2′-bipyridyl complexes.

2. Experimental

$[Fe(bpy)_3]SO_4$ and $[Ru(bpy)_3]Cl_2$ were prepared following literature methods [20]. IR spectra were recorded on a Perkin-Elmer GX2000 Fourier-Transform spectrometer with a resolution of 4 cm^{-1}. In the mid-IR region, and for RR measurements, samples were prepared as 1% (w/w) pressed KBr discs, but far-IR measurements were obtained from samples prepared as nujol mulls mounted on very thin PVC film. RR spectra were recorded using a Spex 1403 double monochromator fitted with a Hamamatsu R928 photomultiplier detector. Excitation was provided by Coherent Radiation Innova 90-6 or Spectra-Physics Series 2000 argon ion lasers. The typical spectral slit width was ca. 4 cm^{-1}. Band wavenumbers were calibrated using the emission spectrum of neon and all spectra were corrected for the spectral response of the instrument.

3. Computational details

SCF-DFT calculations were performed using the *Gaussian 98* program [21], employing the B3-LYP method. This incorporates Becke's three-parameter hybrid functional [22] and the Lee, Yang and Parr correlation functional [23]. All calculations were performed with the DZVP basis set [24], which is the largest basis set available for ruthenium. Geometry optimization was carried out for each complex with the symmetry constrained to be D_3. The vibrational spectrum of each species was calculated at the optimised geometry. For computation of the potential energy distributions associated with the vibrational modes, the Cartesian force constants obtained from the *Gaussian 98* output were converted to force constants expressed in terms of internal coordinates. Scaling factors were applied to the force constants before input to a normal coordinate analysis program derived from those of Schachtschneider [25]. Scaling is necessary to match the calculated harmonic vibrations with the observed vibrations, which are anharmonic. Scaling of force constants, expressed in internal coordinates, was applied according to the following formula:

$$f_{ij}^{\text{scaled}} = f_{ij}^{\text{calc}} \sqrt{s_i s_j}$$

where s_i and s_j are scale factors relating to internal coordinates i and j, following the Pulay SQM-FF method [26]. In these calculations the scale factors were 0.90 for CH stretching, 0.95 for in-plane and out-of-plane CH deformation, and 0.96 for all other coordinates. These were chosen to give the best fit to the experimental data.

4. Results and discussion

4.1. Structures

The optimised molecular geometry for both complexes is shown in Fig. 1, together with the atom numbering scheme. The atom numbering schemes used by various authors in describing structures and vibrational assignments of these complexes have been different from each other and the scheme we use here is not the same. Computed bond distances and interbond angles are listed in Table 1 with the experimentally determined structures of $[Fe(bpy)_3](ClO_4)_2$ [27] and $[Ru(bpy)_3](PF_6)_2$ [28]. For both complexes the calculated geometries are in good agreement with the XRD data, although it is important to note that in the solid state the complexes are slightly distorted from regular D_3 symmetry. Computed metal–ligand bond distances are ca. 3% higher than the experimental values, and the computed CC and CN bond distances are mostly somewhat higher. Exceptions are the C2N and C6C6′ distances which are very close to the experimental values. All of the calculated bond angles are within 2° of those obtained from the XRD measurements, and most are within 1°. Although an improvement in the calculated structures might have been obtained using a larger basis set, there are none currently available for ruthenium. In fact, it has been shown that comparable results could be obtained using a much more compact effective core basis set such as LanL2DZ [29,30], which we have successfully used in the interpretation of the vibrational spectra of some other tris-α-diimine complexes [19], and of metal complexes with the ligand 1-(2-pyridylazo)-2-naphtholate) [31].