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The effect of deuteriation on the emission lifetime of inorganic compounds

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Contents

Abstract. 761
1. Introduction 762
2. Deuteriation methods 762
3. Theoretical considerations on the effect of deuteriation on excited state processes 764
   3.1 Competing processes in the deactivation of electronically excited states 765
   3.2 Coupling between electronically excited states 765
   3.3 Weak or strong limit! 766
   3.4 Origin of the deuterium induced perturbation of electronic excited state decay processes 767
4. Deuteriation studies: probing excited state decay processes 769
   4.1 Photophysical properties of deuteriated platinum group metal compounds 769
      4.1.1 Deuteriation and luminescence lifetimes 770
      4.1.2 Deuteriation and localised emissive excited states in heteroleptic ruthenium(II) complexes. 773
   4.2 Photophysical properties of deuteriated rare earth ions and complexes 776
      4.2.1 Solvent deuteriation 776
      4.2.2 Ligand deuteriation and shielding effects. 778
   4.3 Application of deuteriation to vibrational spectroscopies 780
5. Concluding remarks and outlook 782
Acknowledgements 783
References 783

Abstract

The application of deuteriation of both ligands and solvents on the photophysical properties of transition metal complexes in solution and glassy matrices is reviewed. The

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reduction in amplitude and frequency of vibrational modes due to deuterium's increased mass, relative to hydrogen, has a significant effect on non-radiative deactivation processes, which can occur through both intra- and inter-molecular vibrational coupling. The effect of deuteration on excited state lifetimes has allowed for its application in probing the nature of excited state decay processes. The effects of isotopic exchange on vibrational spectroscopies such as resonance Raman and low temperature high-resolution emission spectroscopies are also addressed briefly. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Deuteriation; Ruthenium; Lanthanides; Emission lifetimes; Excited states; Photophysics

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1. Introduction

The significance of the deuterium isotope effect on the photophysical properties of organic systems was recognised as early as 1960 [1,2]. Since then many polyaromatic hydrocarbons have been investigated and a theoretical understanding has been developed [3–5]. The application of deuteriation in organic photophysics has been concerned primarily with probing electronically excited state decay pathways and as such has proven to be an invaluable tool in the study of the nature of these processes. Far fewer investigations of this type have been reported in inorganic chemistry. The earliest applications of deuteriation to inorganic photophysics can be found in the work of Kropp and Windsor [6], who investigated the effects of deuteriation on the fluorescence of rare earth ions, and of Watts and co-workers on the emission lifetimes of the lowest ^{3}dd (metal centred) excited state of $[Rh(NH_3)_{6-n}X_n]^{(3-n)+}$ ($X = Cl$, Br, I, $n = 0,1$) [7a] and the ^{3}MLCT (Metal to Ligand Charge Transfer) excited state of $[Ru(bpy)_3]^{2+}$ [8].

This review is concerned primarily with the effect of deuteriation, via vibrational coupling, on the excited state decay processes in platinum and lanthanide group metal ions and complexes. A detailed discussion of the mathematical basis of the theory of non-radiative electronic transitions and the origins of the effect of deuteriation is beyond the scope of this review and the interested reader is referred to the work of Siebrands, Robinson and Frosch, Jortner and others [3–5]. Instead a less mathematical and more qualitative approach will be presented to describe the consequences of deuteriation on electronic transitions. Of particular interest in this review is the use of deuteriation in probing the emissive excited states and indirectly in probing other low lying excited states, which attain a significant Boltzmann population. In addition brief overviews concerning deuteriation techniques and the use of deuteriation as a probe in vibrational spectroscopies such as resonance Raman, Stark effect, low temperature high-resolution emission spectroscopies and line narrowing techniques have been included.

2. Deuteriation methods

Hydrogen isotope exchange reactions involving O–H, N–H, and C–H (D, T) bonds are of interest in many areas of research, from biological applications to photophysics. Deuteration has been applied to the elucidation of ^{1}H-NMR spectra of large polynuclear complexes [9] where the number of inequivalent protons results in spectra which are otherwise difficult to assign reliably. The number of specific examples of deuteriation of organic compounds is too great for an extensive review of the area to be presented here. However, examples of methods most relevant to the synthesis of ligands frequently employed in lanthanide and platinum group photophysical studies will be discussed briefly. Junk et al. have recently reviewed exchange reactions involving C–H bonds, placing particular emphasis on mild and regioselective procedures [10].

The methods available for deuteriation of ligands and transition metal complexes can be broadly divided into three main synthetic strategies:

- exchange of labile acidic hydrogen atoms,
- use of deuteriated precursors,
- metal catalysed hydrogen–deuterium exchange.

One of the most common methods of deuteriation is that of ^{1}H–^{2}D exchange of labile or acidic hydrogens, such as N–H [11], O–H [12,13], terminal acetylenes [14], α-methylenic protons [15–17], porphyrins [18,19] and heteroaromatic N-oxides such as 2,2′-bipyridyl-*N*,*N*-dioxide [20]. This H–D exchange method can be effected simply by dissolution in D_2O (or in a binary protic solvent system using for example MeOD or d_6-DMSO) with heat, pressure and/or acid/base [14]. Both partial [21–23] and complete [21,23,24] deuteriation of transition metal complexes has been achieved in this manner. The use of supercritical deuteroxide solutions for the deuteriation of weak organic acids ($pK_a < 50$), such as weakly activated methylenic protons, has been investigated by Evilla et al. [25]. This method allows for the deuteriation of a range of aromatic and weakly activated aliphatic moieties with reaction times of normally between 20 and 40 min. Several research groups have successfully employed boron [26a], tin [26b] and aluminium [26c] catalysts in both H–D exchange and halide deuterium exchange. Recently, microwave radiation has been employed in effectively promoting deuteriation of polyaromatic and heterocyclic aromatic compounds under a wide range of conditions [27].

Incorporation of deuteriated precursors into ligand synthesis has been used successfully by several research groups, in particular in the preparation of ligands for use in studying the photophysics of rare earth ions [17,19b,28–31]. However, a disadvantage of this route is that often the use of deuteriated solvents is required in order to prevent the re-protonation of acidic hydrogens of the target compound. Despite this limitation, this route has proven to be particularly useful in the synthesis of deuteriated ligands containing aliphatic moieties, such as polydentate macrocylic ligands [19b,28–30] and in the partial deuteriation of polyaromatic hydrocarbons via Diels–Alder reactions [31]. Incorporation of deuteriated precursors has also been used in the preparation of partially deuteriated dppz (d_6-dipyridophenazine) where oxidation of d_8-1,10-phenanthroline to the 5,6-diphenone was followed by condensation with *o*-phenylenediamine to form the target ligand [32].

Many research groups have employed H–D exchange utilising transition metal catalysts for the deuteriation of polyaromatic heterocyclic hydrocarbons. In recent years, catalysts such as Lindler's catalyst (deuteriation of alkenes) [33], Adam's catalyst ($PtO_2{\cdot}H_2O$) [34], $RhCl_3$ [35], $RuCl_3$ and $IrCl_3$ [36] (deuteriation of mono-substituted aromatics and α,β-unsaturated acids) have been used successfully towards deuterium exchange. The use of Pt/C and Pd/C for the stereoselective reduction of alkenes has been extensively investigated by Chiko et al. [37]. Although this method involves the reduction of an alkene, evidence of H–D exchange was also found. Reductive deuteriation of aryl-carbonyls using D_2 saturated acetic acid-d_1 Pd/C catalysts between 25 and 55°C has been observed with good yields (~ 70%) and with selectivity for the carbonyl carbon [38]. Fischer et al. [39] have reported the use of a Pt/asbestos catalyst for the deuteriation of a range of nitrogen based heterocyclic polyaromatic hydrocarbons using pressure, heat and D_2O as the deuterium source. This method shows wide range applicability for pyridine type aromatic systems. More recently, Vos and co-workers have reported the use of a more 'user-friendly' catalyst of 10% w/w Pd/C and D_2O under pressure and high temperature (~ 200°C) as an effective and general procedure for the deuteriation of a whole range of heteroaromatic compounds (e.g. pyridyls, pyrazyls, triazoles etc.) [40,41]. This latter method, which produces yields in excess of 80% [40–42] without the need for derivatisation, has the advantage over the method of Fischer et al. in that the catalyst is commercially available and requires no pre-treatment.

The degree of deuteriation is obtained from spectroscopic analysis, which is normally carried out using techniques such as infrared [43], ^{1}H-NMR [37,44] and mass spectrometry [13a,38].

3. Theoretical considerations on the effect of deuteriation on excited state processes

In 1960, Hutchinson [1], Wright [2], and co-workers reported the involvement of C–H vibrational modes in the radiationless deactivation of the phosphorescent triplet excited states of naphthalene and benzene. At 77 K in a durene matrix, deuteriation of naphthalene leads to an eight-fold increase in the triplet lifetime [1]. At that temperature matrix deuteriation had no effect on the decay lifetimes. At temperatures above 100 K a significant difference was observed in the temperature dependence of the triplet excited state lifetime [45]. These studies demonstrate that C–H vibrational modes of both the compound under examination and the matrix may participate in radiationless deactivation processes. These observations have stimulated the development of a theoretical understanding of the effect of deuteriation [3b].

The theoretical understanding of the nature of non-radiative deactivation processes initiated by Robinson and Frosch [3b] has since been further developed by Gelbart et al. [4], Jortner and co-workers [5], and Siebrand [3c]. Several groups [46] have extended the theoretical models developed for aromatic hydrocarbons to investigate non-radiative transitions in inorganic systems. In this section a general overview of the results obtained in these theoretical studies will be given. However, a detailed mathematical basis for these results is beyond the scope of this review and the interested reader is referred to the original work for more detailed analysis [3–5,46].

3.1. Competing processes in the deactivation of electronically excited states

To understand origins of the effect of deuteriation on excited state transitions, it is pertinent first to discuss the nature of the interaction between electronic states and the mechanisms which result in their deactivation. The lifetime of an excited state may be expressed by Eq. (1):

$$1/\tau_{\mathrm{obs}} = k_{\mathrm{r}} + \sum k_{\mathrm{nr}} \qquad (1)$$

where k_{r} is the natural radiative lifetime and Σk_{nr} is the sum of the rates of all non-radiative relaxation processes. The component k_{r} has been shown to follow an exponential dependence on the energy gap between the emitting state and the ground state [5a,47]. The component Σk_{nr} incorporates all other temperature dependent and independent terms, which contribute to the overall decay rate, such as thermal population of higher energy excited state(s), unimolecular photochemical deactivation, bimolecular (e.g. $^3O_2$) quenching, vibrionically coupled radiationless deactivation etc. The relative contribution of each component of the term k_{nr} is dependent on several factors, the principle of which are the relative energies of the various interacting excited states and the relative vibrionic and electronic coupling between the states (vide infra) [48].

3.2. Coupling between electronically excited states

Jortner and co-workers have proposed two limiting cases for the coupling of electronically excited states [5b,5c]. In the strong coupling limit a large horizontal displacement of the excited state potential wells is proposed (see Fig. 1) [5b]. The

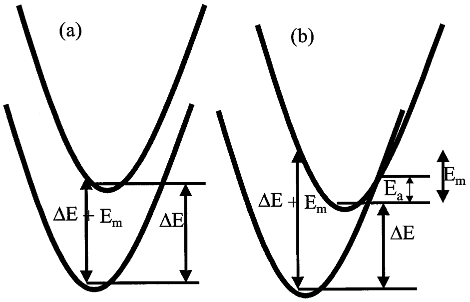


Fig. 1. (a) Weak coupling limit and (b) strong coupling limit between electronic states. The Franck–Condon absorption ($\Delta E + E_{\mathrm{m}} = h\upsilon_{\mathrm{abs}}$) and emission energies ($\Delta E - E_{\mathrm{m}} = h\upsilon_{\mathrm{em}}$), allow for the approximate calculation of the Stokes' shift $\approx (\Delta E + E_{\mathrm{m}}) - (\Delta E - E_{\mathrm{m}}) = 2E_{\mathrm{m}}$.

strong coupling limit can be used to describe systems (e.g. the ^{3}MC state of M^{II} platinum group complexes) where large distortions in the geometry of M–L bonds are observed (e.g. Ru–N, Rh–Cl). In addition to large geometric distortions between the ground and excited state, the potential energy curves of the donor and acceptor states have a cross-over point close to the minimum of the excited state potential well (see Fig. 1b) [49a]. Due to the greater contribution of low energy vibrational modes to the Franck–Condon overlap term $F(E)$ for the strong coupling case, all vibrational modes are in principle available to accept electronic energy [49]. In this case the lack of a large isotope effect is expected, as the transition probability is dependent on the mean vibrational frequency, which is expected to show only minor perturbation on isotopic substitution [50].

Coupling between excited states can be described by a weak coupling limit if the horizontal displacement of the potential wells is small and the potential energy curves of the states do not cross close to the energy minimum of the excited state potential well (see Fig. 1a). Radiationless deactivation between weakly coupled excited states is expected to involve conversion of electronic energy to vibrational energy. As a result of the relatively large amount of energy (compared to the typical energy difference between vibrationally excited states) that is converted by deactivation by such a route, overlap considerations favour high frequency vibrations and the application of the low temperature limit (i.e. only the lowest excited vibrionic state is populated significantly).

3.3. Weak or strong limit!

The question as to which limit is applicable in specific cases has been considered by Jortner and co-workers [5b]. They suggested that the energy of the Stokes shift can be used crudely in estimating the value E_m (see Fig. 1), which in turn can be related to the geometric distortion between the excited and ground state and hence discriminate between the weak and strong coupling limits [5b]. The weak coupling limit is the limit normally described by radiationless deactivation theory and is dominant when the Stokes' shift is less than the mean vibrational frequency of the molecule ($S < 1$) [51]. In this limit the rate of radiationless decay is normally largely dependent on the frequency of the highest energy vibrational modes of the molecule e.g. O–H, N–H and C–H stretching modes. If the Stokes' shift exceeds twice the mean frequency of the molecular vibrations ($S > 2$) then the strong coupling limit is relevant, and vice versa [51]. The use of the Stokes' shift as a diagnostic tool, although generally applicable in the case of polyaromatic systems, is problematic in the case of transition metal complexes where spin orbit coupling factors become significant. In particular when phosphorescent excited states are considered, direct absorption into the emitting state is spin-forbidden and hence population of the excited state must occur via a higher lying state of identical spin multiplicity to the ground state, increasing the observed Stokes' shift.

A further complication to the assignment of weak and strong coupling limits is their temperature dependence. Gelbart et al. [4] have considered both strong and weak coupling of electronic states and their implications towards photoisomerism, in particular stilbene type *cis–trans* photo-isomerisation [52]. The energy of the lowest triplet excited state of stilbene can be dissipated either via torsional or vibrational processes, with the former resulting in isomerisation. They concluded that non-radiative transition rate (k_{nr}) is proportional to the energy gap between the ground and excited electronic states (ΔE) and any changes in equilibrium configuration (Δ_j) [50]. For large displacements between ground and excited states, which may result in intramolecular rearrangements, the strong coupling limit is applicable (e.g. photoisomerism of stilbene results in radiationless deactivation of the lowest triplet (twisted) state). However, in glassy matrices at low temperature (77 K) where *cis–trans* isomerism is 'frozen out' or where such isomerisation is sterically hindered, more of the electronic energy is forced to dissipate through vibrational modes rather than torsional modes. The system then becomes better described by the weak-coupling limit as purely vibrational modes have an increased role in excited state deactivation.

3.4. Origin of the deuterium induced perturbation of electronic excited state decay processes

It has been suggested that in the case of the weak coupling limit, the vibrational contribution to the overall rate of non-radiative deactivation (Σk_{nr}) depends in part on the magnitude of the vibrational overlap integrals between the initial and final states of a transition [3b,3c,5b,48]. In particular, stretching modes have been suggested to be important channels for radiationless deactivation and as a result Σk_{nr} includes the term k_{X-H} (X = C, N or O), the rate of radiationless deactivation due to X–H vibrational coupling [5b]. This term can in turn be expressed in terms of Eq. (2) [22c,48a]:

$$k_{X-H} = (2\pi/\eta)\rho J F(E) \tag{2}$$

where ρ is the weighted sum of the energy gap between the vibrionic states, J is the electronic coupling between the two electronic states, and $F(E)$ is the Franck–Condon sum of the products of the overlap integrals [50]. Deuteriation reduces both the amplitude and frequency of X–H vibrational modes and hence C–D vibrations are of lower frequency and amplitude than the equivalent C–H vibrations. As a result, the vibrational overlap between two states will be diminished for the same energy gap (Fig. 2), hence the Franck–Condon factor component $F(E)$ and k_{X-H} are reduced [3,53a,54]. This results in an increase of the observed lifetime of the electronically excited state (since non-radiative deactivation is less effective). In addition, when X–H vibrational modes are available to act as promoting modes then the electronic coupling term (J) is also reduced by deuteriation [46f].

If deuteriation effects were solely due to Franck Condon factors $F(E)$ (and to a lesser extent electronic coupling J), then in principle each X–H vibrational mode would have equal probability of accepting electronic energy and hence isotopomers would exhibit equal deuterium effects. This was first investigated in detail for naphthalene by Lin et al. [55], who have suggested that the principle promoting modes in aromatic hydrocarbons are a few low energy C–C skeletal vibrations

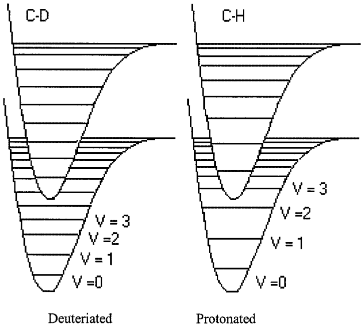


Fig. 2. Changes in vibrational levels and overlap which occur upon deuteriation.

whilst the principle accepting modes are a large number of C–H high frequency stretching modes. They reported no positional dependence of deuteriation and that each position regardless of electron density contributes equally [55].

Later studies of the positional dependence of deuteriation have been performed by several groups for both organic and inorganic compounds (vide infra) [31,56]. Henry et al. [31] have reported that location of the excited state electron density distribution is critical to the effect of deuteriation on emission lifetimes [31,56]. For example, for anthracene, deuteriation of the alpha position has an increased effect over deuteriation of the beta position. This effect has also been observed for *trans*-stilbene [57,48b].

Although the role of high energy vibrational modes, in particular X–H (X = N, C, O) modes, as acceptors of electronic energy (energy sinks) is largely due to the larger $F(E)$ values for these modes compared with lower energy skeletal modes, the role of such vibrational modes in promoting non-radiative transitions is less clear. Promoting modes can be loosely described as vibrational modes (usually symmetric), which stimulate transitions between excited states and undergo a single quantum (vibrational) change during the transition. Robbins et al. have examined the effect of the number of near neighbour hydrogens on the emission properties of octahedral chromium(III) complexes in glass matrices [46f]. The ^{3}dd emission originates from the ^2E_g (excited state) to $^4A_{ug}$ (ground state) transition, both of which are T_{2g} based, and hence shows only minimal perturbation by variations in ligand field strength. Hence in a series of complexes $\{[Cr(NH_3)_x(Y)_{6-x}]^{(3-x)+}$ (where Y = NCS; $x = 0, 2$), $[Cr(LL)_3]^{3+}$ (where LL = acetoacetate, formoacetate and malonate)$\}$ the ground–excited state energy gap is generally invariant, and the rate of radiationless decay is dependent only on the number of high-frequency acceptor modes and low frequency promoter modes. The results of these studies have suggested the involvement of C–H vibrational modes not only as acceptor modes but also as promoter modes. In the case of the latter set of complexes ($[Cr(LL)_3]^{3+}$) where the delocalisation of the excited state by π-conjugation occurs, the contribution of α-C–H vibrational modes as promotor modes is apparent. The rate of radiationless decay is dramatically reduced by their substitution by methyl groups. The existence of such 'active H-atom' vibrational modes, i.e. C–H bending modes, capable of promoting electronic relaxation was already suggested by Henry [31] and Siebrand [3c]. This explanation of the observed effect of removal of C–H oscillators may according to Robbins et al. also explain the effect of phenyl or methyl substitution of bipyridyl and phenanthroline complexes of d^6 ruthenium(II) and osmium(II) in reducing k_{nr} as being due to loss of promoting C–H modes [46f,48b].

Deuteriation has been shown in many cases, in particular in organic systems, to have a significant effect on vibrationally induced excited state non-radiative decay processes. However, particularly in the case of inorganic systems, the effect of deuteriation may not be as apparent. It can be said, however, that provided the coupling between electronic states can be described by the weak coupling limit [5], and provided that X–H vibrational modes make a significant contribution to the overall non-radiative rate constant (Σk_{nr}), an effect of deuteriation will be observed. In addition, an important observation is that the location of the excited state on a particular moiety of a compound (i.e. the electron density in the region of the accepting X–H oscillator), determines the extent of the effect of isotopic substitution. This point is of particular relevance to the application of deuteriation in the study of the excited state electronic structure of transition metal complexes. It is to be expected that deuteriation studies will lead to an improved understanding of excited state properties of inorganic compounds.

4. Deuteriation studies: probing excited state decay processes

Although deuteriation is widely applied to the study of ground state properties of both organic and inorganic complexes, its application to the study of photophysical properties, in particular as a probe into excited state processes, is much less extensive. The majority of the studies that have been reported in the literature involve metal complexes based on lanthanides and platinum group metals. The discussion in this review will therefore centre on these two groups and in particular their ions and complexes. Where appropriate other examples of the application of deuteriation will be considered.

4.1. Photophysical properties of deuteriated platinum group metal compounds

Within the platinum group metals the majority of the more recent investigations have been carried out on ruthenium polypyridyl complexes. This is not surprising since these compounds have well defined excited state properties and an extensive synthetic chemistry allows for systematic variation of the ligands around the metal centre [58]. Deuteriation has also been applied to the study of platinum, rhodium, chromium and molybdenum complexes. The application of deuteriation in inorganic photophysics can be broadly divided into two areas. In the first deuteriation has been applied to probing excited state decay processes. In these studies the effect of deuteriation on emission lifetimes (and occasionally unimolecular photochemical activity) has been studied. The second area in which deuteriation has been used is as a tool in spectroscopic techniques such as resonance Raman [22a,22c,19b,30,59] and high resolution emission spectroscopy [60], due to its significant isotopic effect on the energies of vibrational transitions. These latter studies are aimed at obtaining detailed information on the nature of electronically excited states through a study of their vibrational properties. In the present discussion we will concentrate on the former investigations, while some typical examples of the application of deuteriation to vibrational techniques will be discussed in Section 4.3.

4.1.1. Deuteriation and luminescence lifetimes

Thomas et al. have examined the effect of deuteriation on the lifetime of the lowest energy ^{3}dd excited state, for a series of related Rh(III) complexes of the type $[Rh(NH_3)_{6-n}X_n]^{(3-n)+}$ (X = Cl, Br, I; $n = 0,1$) [7a]. The increase in emission lifetime (at 77 K and 110 K in H_2O/MeOH 1:4 v/v) observed for these complexes upon solvent and ligand deuteriation is between 12 and 62 fold (for $X = NH_3$, $\tau_D/\tau_H = 62$; Cl, $\tau_D/\tau_H = 52$; Br, $\tau_D/\tau_H = 36$; I, $\tau_D/\tau_H = 12$). The decrease in effect with increasing mass of X is most likely due to the increased importance of the spin orbit coupling effect of the heavy halide atom, which facilitates deactivation by increasing the contribution of the radiative rate constant (k_r, see Eq. (1)) [61]. Ford and co-workers [62] have also studied the effect of deuteriation on the ^{3}dd emission of $[Rh(NH_3)_{6-n}X_n]^{(3-n)+}$ (X = Cl, Br; $n = 0,1$) in acidic aqueous solutions (to prevent H–D exchange of amine protons) at 298 K. For both Cl and Br complexes, ligand (NH_3–ND_3) deuteriation resulted in a doubling of emission lifetime in all solvents examined whilst solvent deuteriation resulted at most in a 20% increase. When the effect of ligand deuteriation on the photochemistry of the complexes was examined, the value of k_p, the rate constant for photochemical deactivation, increased in all cases by 20–25%. It was proposed that this increase in the rate k_p is due to a significant reduction in the k_{N-H} term (upon deuteriation) contribution to the overall non-radiative excited state decay rate Σk_{nr} and hence a relative increase in the importance of other terms. The effect of both ligand and solvent deuteriation on the ^{3}dd emission (at 77 K in H_2O/MeOH 1:4 v/v) of the complex *trans*-$[Rh(py)_4Br_2]Br$ (where py = pyridine) has also been examined [7]. Solvent deuteriation results in a 1.16–1.92 fold increase, whereas ligand deuteriation results in a more substantial 2.7–4.5 fold increase in emission lifetime. In a similar study, Islam et al. [63] have used deuteriation of the amine groups in the complex [*trans*-$Rh(en)_2Cl_2$]Cl (where en = ethylene diamine), to compare the efficiency of excited state deactivation due to N–D/N–H vibrational modes and the symmetric Cl–Rh–Cl stretching vibrational modes and have found the latter to be the most important. The two primary accepting modes were determined using spectral fitting and temperature dependent lifetime studies. Huang Rhys factors (S) of 0.1 and 21 were determined for N–H/D and Cl–Rh–Cl stretching vibrational modes respectively. The weak coupling nature of the former was expected to result in an observable deuteriation effect, which was found to be the case. Deuteriation of N–H leads to a 3.4 to 11 μs increase at 298 K and 17 to 274 μs increase in emission lifetime at 80 K. Krausz et al. [64] have shown that such dramatic effects of deuteriation on the emission lifetime of rhodium complexes are not restricted to systems exhibiting ^{3}dd emission. The emission of rhodium tris diimine complexes (e.g. $[Rh(bpy)_3]^{3+}$) has been classified as ^{3}IL in origin. Upon ligand deuteriation of $[Rh(bpy)_3]^{3+}$ an increase in emission lifetime of 280 to 570 μs (at 77 K) has been observed [64]. Watts et al. have examined the effect of deuteriation on $[Ir(bpy)_2Cl_2]^+$ [7b]. This complex has demonstrated a dual emissive behaviour arising from two close lying weakly interacting excited states (i.e. metal centred ^{3}dd emission and a higher energy ^{3}dπ* charge transfer state). At 77 K the two excited states are not equilibriated and exhibit different emission lifetimes (^{3}dd (5.9 μs) and ^{3}dπ* (4.8 μs)) and upon deuteriation the ^{3}dd emission lifetime increases to 12.2 μs. Above 231 K the excited states are thermally equilibrated and show equal emission lifetimes. Above 231 K the lifetimes of both emissions increase equally upon deuteriation (570 to 1190 ns). The origin of this difference in the effect of deuteriation has been explained on the basis of reduced involvement of C–H modes in deactivating the ^{3}dπ* excited state due to the change in vibrational force constants due to increased electron density on the aromatic ligands, reducing interaction between ground and excited vibrionic states. In contrast, for the metal centred transition, less change in electron density on the aromatic ligands, and hence force vibrational force constants, occurs.

Riesen et al. have examined the role of C–H oscillators as acceptor modes in the non-radiative decay of the ^{3}dd excited state of ruthenocene [65] by per-deuteriation and per-methylation of the cyclopentadienyl rings. The emission lifetimes of ruthenocene (127 μs) is increased to 627 μs upon per-methylation (decamethylruthenocene) and 990 μs upon per-deuteriation (d_{10}-ruthenocene) at 1.5 K. The large increase in emission lifetime strongly supports the idea in which C–H modes act as energy acceptors.

Milder et al. [66] have studied the effect of solvent and ligand deuteriation on the complex $[Pt_2(POP)_2]^{4-}$ (POP = μ-$P_2O_5H_2$). The complex shows both phosphorescence ($^3A_{2u}(E_u)$–$^1A_{1g}$) and fluorescence ($^1A_{2u}$–$^1A_{1g}$) at 293 K. The very low quantum yield of fluorescence has been due to the rapid ISC to a slightly higher energy state ($^3B_{2u}$) with which it has ‘strong coupling’ and the ‘weak coupling’ phosphorescent $^3A_{2u}$ state. The coupling in both cases refers to the displacement with respect to the fluorescent $^1A_{2u}$ state and not the ground state. Ligand deuteriation did not result in significant changes in the fluorescence lifetime of the complex, either in propionitrile/2-methyltetrahydrofuran glass or in polymethylmethacrylate at 77 K. However, solvent deuteriation in the case of ethanol/methanol matrices resulted in dramatic increases in fluorescence lifetimes: C_2H_5OH/CH_3OH 750 ps, C_2H_5OD/CH_3OD 1900 ps, C_2D_5OD/CD_3OD 2170 ps. The origin of this increase in fluorescence lifetime was determined to be due primarily to the reduction in the rate of ISC to the weak coupling phosphorescent $^3A_{2u}$ excited state from the fluorescent $^1A_{2u}$, a process that is suggested to be coupled to O–H and C–H solvent vibrational modes.

Although the effect of deuteriation on several transition metal systems has been examined in the past, more recently significant attention has been given to ruthenium(II) diimine complexes. The first observation of an effect of deuteriation on the emission lifetime of $[Ru(bpy)_3]^{2+}$ was made by Watts et al. [7]. They found that deuteriation of 2,2′-bipyridine (bpy) results in a doubling of its emission lifetime (0.9 s to 2.2 s at 77 K), whilst deuteriation of the complex $[Ru(bpy)_3]^{2+}$ results in a more modest 20% increase in (5.1 to 6.1 μs at 77 K in EtOH/MeOH and 0.58 to 0.69 μs at 298 K in H_2O). In contrast, solvent deuteriation (H_2O to D_2O) leads to a doubling of the emission lifetime of $[Ru(bpy)_3]^{2+}$ (0.58 to 1.02 μs at 298 K). It was suggested, based on the theories of radiationless transitions developed for organic compounds [3–5], that this difference between ligand C–H and solvent O–H vibrational modes' ability to deactivate the lowest ^{3}MLCT states is due to the charge-transfer-to-solvent character (CTTS) of the ^{3}MLCT state. They suggested that a significant proportion of the excited state's electron density is distributed over the solvent cage, facilitating transfer of electronic energy to solvent vibrational modes. A similar difference in the effect of solvent and ligand X–H vibrational modes on the emitting states of rare earth ions has been observed (vide infra). In addition, O–H vibrational modes tend not to be as well defined as C–H vibrations and hence an energy match between the excited and ground state of the complex and the vibrational transition of the solvent is more efficient. More recently Krausz et al. [64] (Table 1) have examined the effect of partial and complete deuteriation of $[Ru(bpy)_3]^{2+}$ on emission lifetime in a range of matrices showing a linear dependence of emission lifetime on the number of hydrogens exchanged, in agreement with the findings of Robbins et al. (vide supra) [46f].

Kincaid and co-workers [22] have examined the positional dependence of the deuteriation effect in $[Ru(bpy)_3]^{2+}$. The studies showed that deuteriation of the 3,3′ or 4,4′ positions of the bpy ligand had no observable effect on the emission lifetimes (610 and 605 ns respectively) compared with non-deuteriated $[Ru(bpy)_3]^{2+}$ (590 ns). Deuteriation of the 5,5′ or 6,6′ positions in contrast increased the emission lifetime to 635 and 645 ns respectively. Similar trends were observed when two or three of the available positions were deuteriated. These studies are in agreement with similar studies carried out on organic compounds (vide supra) and again suggest that the ability of X–H vibrational modes to deactivate an excited state is dependent on the electron density distribution in the excited state.

Studies of the effect of deuteriation on the photochemical properties of $[Ru(bpy)_3]^{2+}$ have shown that at elevated temperatures competing processes for excited state deactivation become more important and the effects of ligand and solvent deuteriation are equally reduced [7,67]. It was suggested that a set of excited

Table 1
The effect of extent of deuteriation and matrix on the emission lifetime of $[Ru(bpy)_3]^{2+}$

	D_0	D_8	D_{16}	D_{24}
H_2O, 298 K	610 ns	640 ns	690 ns	760 ns
D_2O, 298 K	950 ns	1080 ns	1180 ns	1340 ns
5 K, single crystal	64 μs	68 μs	75 μs	80 μs
77 K, PVA	5.2 μs	5.7 μs	6.1 μs	6.7 μs

states (^{3}MC or metal centred) lying higher than the lowest excited states (^{3}MLCT) are thermally populated from the same. Importantly, deactivation via these states (^{3}MC) was found to be independent of both ligand and solvent deuteriation [67], as would be expected for a strong coupling system. These results are in agreement with the conclusions reached in Section 3 in that in order for a deuteriation effect to be observed, X–H vibrational coupling must make a significant contribution to the overall non-radiative decay rate constant of the excited state.

4.1.2. Deuteriation and localised emissive excited states in heteroleptic ruthenium(II) complexes

The studies on ruthenium polypyridyl complexes discussed above are concerned with the excited state properties of homoleptic complexes. The effect of partial and complete deuteriation on the emission lifetimes of heteroleptic ruthenium(II) and osmium(II) diimine complexes has also been examined. Krausz et al. have observed an increase in the emission lifetime of $[Ru(bpy)_2(5,5\text{-dicarboxybipyridine})]^{2+}$ (6.3–6.9 μs at 77 K in EtOH/MeOH 4:1 v/v) [64] upon deuteriation of the bpy ligand. This increase is close to the increase in emission lifetime from $[Ru(h_8\text{-bpy})_2(bpy)]^{2+}$ to $[Ru(d_8\text{-bpy})_2(bpy)]^{2+}$ (5.2–6.1 μs at 77 K in PVA) [64]. Kober et al. have reported the effect of bpy deuteriation on a range of heteroleptic osmium(II) complexes [68a] ($[Os(bpy)_2(LL)]^{2+}$, LL = dppy, dppm, diars, bpy). They observed increases of between 40 and 100% in the emission lifetime, showing that the relative effect of ligand deuteriation for osmium(II) complexes is greater than that observed for of $[Ru(bpy)_3]^{2+}$. Bergkamp et al. have found similar increases in emission lifetime upon per-deuteriation of $[Os(bpy)_3]^{2+}$ at 10 K (1.05 to 2.5 μs) [68b].

In mixed ligand compounds the issue as to which ligand the emitting ^{3}MLCT state is localised on is of interest. This location of excited states is of particular interest to the field of supramolecular chemistry, where energy vectoring is of significant interest and where in the design of suitable molecular assemblies the nature and location of the lowest excited state is often a controlling factor [58a]. In heteroleptic complexes, such as $[Ru(bpy)_2(LL)]^{n+}$, the excited state may lie on either the bipyridine ligand or the ligand (LL) or even on a component of a ligand [30]. Methods of determining its location are required for the correct assignment of spectroscopic bands and LUMO energies. Resonance Raman spectroscopy [30], electrochemistry [58a] and acid/base studies [69] have proven useful in determining excited state electronic distribution, however a more recent approach has investigated the application of deuteriation of ligands for this purpose. Partial deuteriation in combination with the measurement of the excited state lifetime has been proposed as a method for the location of the emitting states of hetereoleptic ruthenium polypyridyl complexes [30,40–42]. It has been suggested that deuteriation of one of the ligands in a mixed ligand complex will only affect the emission lifetime if the emitting state is based on that ligand. To illustrate this, Vos and co-workers [40,41] have carried out partial deuteriation of two mixed ligand complexes, $[Ru(bpy)_2(HL^1)]^{2+}$ (**1**) and $[Ru(bpy)_2(L^2)]^{2+}$ (**2**) (see Fig. 3). For the non-deuteriated complexes the emission lifetimes of 225 (**1**) and 740 ns (**2**) were obtained. Deuteriation of the 2,2′-bipyridine ligands leads to lifetimes of 480 (**1**) and

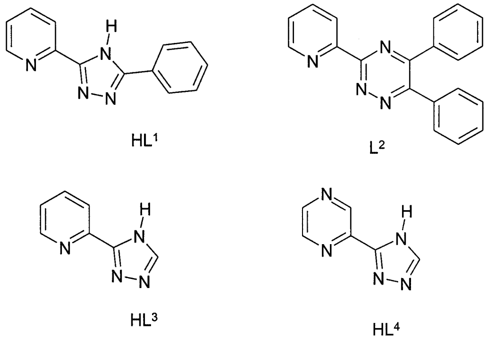


Fig. 3. Triazole and triazine based ligands used in the study of the effect of partial deuteriation on mixed ligand ruthenium polypyridyl complexes.

780 ns (**2**). So deuteriation of **1** leads to almost a doubling of the emission lifetime while for complex **2** deuteriation has little effect (Table 2). They concluded from this that the emitting states were located on the bpy ligand for complex **1** and electron-poor triazine ring L^2 ligand for complex **2** [40,41]. These observations were in agreement with resonance Raman studies on these compounds. In a similar study, partial deuteriation of the complexes, $[Ru(bpy)_2(L^3)]^+$ (**3**), $[Ru(bpy)_2(L^4)]^+$ (**4**) and $[Ru(bpy)_2(HL^4)]^{2+}$ (**5**) (Fig. 3) [42] was carried out and lifetime measurements in conjunction with excited state RR were carried out to determine the nature of the emitting state. For complex **3** deuteriation of the bpy ligand leads to an increase in the emission lifetime from 145 to 250 ns (Fig. 4) whilst deuteriation of the L^3 had no effect. For complex **4** deuteriation of the bpy ligand leads to a small increase in emission lifetime (230 to 290 ns) whilst deuteriation of L^4 had little or no effect on the emission lifetime. RR suggests that in both **3** and **4** the emitting state is bpy based. The increase observed for bpy deuteriation in **4** was, however, less than expected. Detailed studies carried out on this compound suggest that this reduced sensitivity is explained by the presence of two emitting states, one bpy and one pyrazine based. Complex **5** showed no increase in emission lifetime upon deuteriation of the 2,2′-bipyridine. Deuteriation of HL^4 however did result in a doubling of the emission lifetime (230 to 470 ns) indicating that in the protonated state the lowest excited state is HL^4 based, again in agreement with resonance Raman studies [42].

Table 2
Effect of deuteriation on the emission lifetime of complexes **1**–**5**; measured in N_2 degassed acetonitrile

	τ (ns)		τ (ns)
$[Ru(bpy)_2(HL^1)]^+$ (**1**)	225	$[Ru(d_8\text{-bpy})_2(HL^1)]^+$	480
$[Ru(bpy)_2(L^2)]^{2+}$ (**2**)	740	$[Ru(d_8\text{-bpy})_2(L^2)]^{2+}$	780
$[Ru(bpy)_2(L^3)]^+$ (**3**)	145	$[Ru(d_8\text{-bpy})_2(L^3)]^+$	250
$[Ru(bpy)_2(L^4)]^+$ (**4**)	230	$[Ru(d_8\text{-bpy})_2(L^4)]^+$ (**4**)	290
$[Ru(bpy)_2(HL^4)]^{2+}$ (**5**)	230	$[Ru(bpy)_2(d_4\text{-}HL^4)]^{2+}$ (**5**)	470

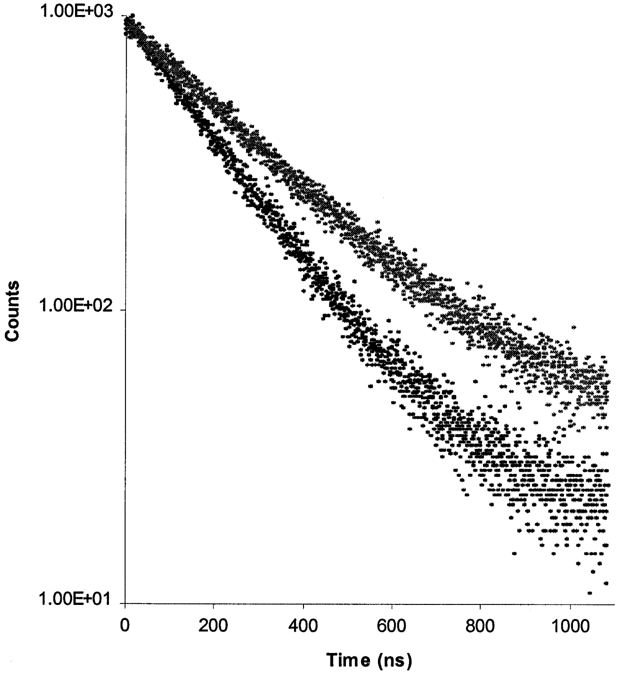


Fig. 4. Time correlated single photon counting traces of the complexes $[Ru(bpy)_2(L^3)]^+$ (lower trace) and $[Ru(d_8\text{-}bpy)_2(L^3)]^+$ (upper trace).

The issue of the temperature at which measurements are made has been raised by Krausz et al. [64]. At low temperatures where only the lowest excited state has a significant Boltzmann population, the effect of deuteriation observed is the effect on that state alone. At higher temperatures when several low-lying electronically excited states of similar orbital parentage are populated, then the effect of deuteriation observed is an averaged effect on the populated states. At yet higher temperatures, thermal population of states which exhibit strong coupling with the ground state and undergo fast decay directly to the ground state may result in a reduction or even elimination of any observable effect of deuteriation. This is particularly important when assignment of excited state localisation is being attempted by selective deuteriation techniques, where excited states of similar character (e.g. ^{3}MLCT) but different orbital parentage are close in energy. The effect of deuteriation on the emission lifetime of platinum group transition metal complexes shows a strong dependence on the deactivating ability of X–H vibrational modes. In addition, the effect of selective deuteriation experiments can potentially provide information on the nature of emissive states and hence can be applied to investigating the localisation of excited states on specific ligands. However, in contrast to many organic systems, X–H vibrational modes are seldom the primary route towards radiationless deactivation. For example, in the case of $[Ru(bpy)_3]^{2+}$, it has been found that skeletal C–C–C vibrational modes, deactivation via the lowest ^{3}MC excited state and quenching (e.g. $^3O_2$ quenching) constitute a dominant contribution towards radiationless deactivation, with C–H vibrational modes only being of secondary importance [22]. As would be expected based on Eq. (1), this limits the observable effects of deuteriation and as a result the application of deuteriation as a probe in these studies may not be universally applicable, particularly in systems which can be described best by the strong coupling limit of Jortner et al. [5c].

4.2. Photophysical properties of deuteriated rare earth ions and complexes

Rare-earth ions have been used as probes in biological systems, as substitutes for spectroscopically inert Ca^{2+}, Mg^{2+} and Zn^{2+} ions and as materials for laser applications [53,70]. However, the low quantum yields and short emission lifetimes, which are typical of these ions, have prevented full exploitation of their photophysical properties. Deuteriation techniques have been used both to increase the lifetime of the emitting states and to investigate the interaction between the excited metal ions and the surrounding medium. In these studies the deuteriation of both solvents and ligands has been employed.

The M^{3+} (M = rare-earth ion) ions show narrow fluorescence bands over a broad range of wavelengths from the near-infrared (Tb^{3+}, Eu^{3+}) or the ultraviolet region (Gd^{3+}). The shape and energies of these f–f transitions show little solvatochromic behaviour. They are formally Laporte forbidden and their absorptivities and quantum yields are therefore low, particularly in solution [6]. Overcoming these shortcomings has been achieved by enhancement of absorptivities by use of aromatic sensitisers, and by the reduction in the contribution of non-radiative deactivation to the overall decay rate of the emitting excited states [6b].

4.2.1. Solvent deuteriation

Kropp et al. have investigated the influence of deuteriation of ligands and solvents on the photophysical properties of the Cl^- and NO_3^- salts of Eu^{3+}, $Tb^{3+}$and Gd^{3+}, in H_2O/D_2O [6]. These studies have shown that the relative emission intensity (I_D/I_H), between deuteriated and non-deuteriated solvents is dependent on the nature of the metal ion, with values of 19.7 for Eu^{3+}, 8.2 for Tb3$^+$ and 1 for Gd^{3+}. This variation was accounted for by the energy gap between the emitting and ground states (Eu^{3+} 12 300 cm^{-1}, Tb^{3+} 14 200 cm^{-1}, Gd^{3+} 32 100 cm^{-1}) [24]. As the energy gap increases, the contribution of O–H vibrational modes to the overall rate of radiationless deactivation diminishes because of a reduced Franck–Condon overlap and hence a reduced deuteriation effect is observed [71]. Similar results for deuteriated and non-deuteriated hydrated rare earth chloride crystals were obtained by Freeman et al. [72]. Deuteriation of methanol (0.37 to 1.49 ms) and acetone (0.38 to 1.18 ms) has also been found to increase the lifetime of Eu^{3+} ions, demonstrating that C–H as well as O–H vibrational modes are capable of deactivation the metal based excited state in these systems [6b].

For Sm^{3+} and Dy^{3+} the emission energies (7300 cm^{-1} and 7800 cm^{-1}) are considerably lower than for the previously mentioned lanthanide ions. As a result, the excited state lifetimes of these ions are short and emission signals have been difficult to observe in H_2O. Both lifetimes and emission intensities show a considerable increase ($I_D/I_H = 12$) in D_2O, however it is difficult to quantify these increases reliably due to the difficulties in accurately measuring these values in H_2O [6b].

Solvent deuteriation has since been developed as a probe into the solvation of M^{3+} ions, in particular into the estimation of the number of solvent molecules in the innermost solvation sphere of the ion. Several groups have investigated the relationship between emission lifetime (τ_D/τ_H) and intensities (I_D/I_H) and the percentage of deuteriated solvents [6,53,70,73,74]. It has been shown that deuteriation can be applied to estimate the apparent hydration state (q) in the first coordination sphere of Eu^{3+} ions using 'Horrocks' equation:

$$q = 1.05(1/\tau_{H_2O} - 1/\tau_{D_2O}) \tag{3}$$

This equation has since been adapted to other solvent systems, in particular methanol [28a,75], and to other rare earth ions [28c,70,75]:

$$q = 2.1(1/\tau_{CH_3OH} - 1/\tau_{CH_3OD}) \tag{4}$$

This approach has been used extensively [29,76–79] and is accurate to ± 0.5 O–H bonds. In the case of M^{3+} ions complexed with polydentate ligands, the error can be higher than 0.5. Polydentate encapsulating ligands are often capable of excluding solvent molecules from the inner coordination sphere of the M^{3+} ion [76], however the exclusion is not complete and hence solvent–M^{3+} ion distances can vary dramatically depending on the environment. In addition, whereas deuteriation of solvent (H_2O) can in increase the lifetime of $EuCl_3$ from 0.26 to 2.53 μs, this increase can be reduced due to proximal C–H vibration modes of the ligands employed [24].

Recently Faulkner and co-workers [29,71] have examined the effectiveness of O–H, N–H and C–H oscillators in deactivating luminescent excited states of Eu^{3+}, Tb^{3+}, and Yb^{3+}. Based on the results of these studies they have proposed that Eq. (3) be rewritten to the more general form:

$$q = A'(k_{H_2O} - k_{D_2O})_{corr} \tag{5}$$

where q is again the hydration state and A' the ion specific factor: A' for Eu^{3+} is 1.2 ms, Tb^{3+} 5 ms, and Yb^{3+} 1 μs. Faulkner et al. [71a] have also noted that in addition to the use of the revised A' values a further error should be corrected for in the use of Horrocks equation. Closely diffusing solvent molecules can potentially make a significant contribution to the overall non-radiative decay rate, and hence must be accounted for before the true effect of coordinated solvent molecules can be accurately assessed [71].

Deuteriation has also been employed to study the mechanism for energy transfer to solvent [4,24,80]. Three possible mechanisms for the transfer of electronic energy to O–H modes have been suggested [53b]. Either energy transfer takes place to a single O–H bond, leading to a single transition from a low lying vibrational level to a higher one, to several vibrational modes of one molecule or to vibrational modes of several molecules. The quantum yield of emission from an f–f transition is given by the following equation:

$$\Phi = k_r \Big/ \left(k_r + k_H[H]^n + k_D[D]^m + \sum k_i[Q_i] \right) \tag{6}$$

where n and m are the number of hydrogen/deuterium atoms involved in the quenching process. The ratio of intensity of a mixed (H_2O/D_2O) system to a purely deuteriated solvent system (I_x/I) is given by:

$$I_x/I = \Phi_x/\Phi = 1 + \left\{ k_H \Big/ \left(k_D[D]^m + k_r + \sum k_i[Q_i] \right) \right\} [H]^n \tag{7}$$

Assuming that $(k_r + \Sigma k_i[Q_i]) \geq k_D[D]^m$ then:

$$\Phi_x/\Phi = 1 + C[H]^n \tag{8}$$

where

$$C = \left\{ k_H \Big/ \left(k_r + k_D[D]^m + \sum k_i[Q_i] \right) \right\}$$

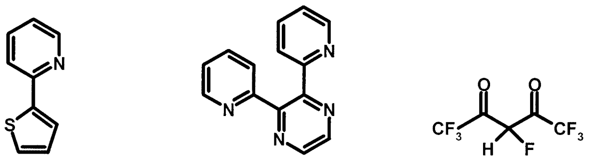
Hence a plot of I_x/I against % H_2O should be linear if $n = 1$, which is what is found for Eu^{3+} and Tb^{3+} [24,53b,81], suggesting that energy transfer is to a single O–H bond. Calculations [24] show that $\Delta v \geq 5$ for Tb^{3+}, $\Delta v \geq 4$ for Eu^{3+}, $\Delta v \geq 2$ for Sm^{3+} and Dy^{3+}, where Δv is the number of O–H vibrational quanta required to deactivate the ions emissive excited state.

4.2.2. Ligand deuteriation and shielding effects

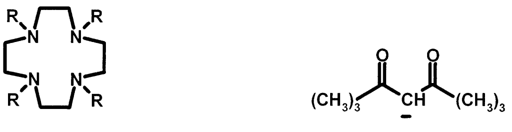
The presence of ligands containing aromatic moieties has been shown to enhance the emission intensities and lifetimes of rare earth ions. The increase in emission intensity is due to the increased absorption and rapid energy transfer to the emitting excited states due to the ligands. The increase in the emission lifetime observed is not, however, due to delayed energy transfer for the sensitising ligand but rather due to a shielding of the excited state from the surrounding solvent and thus a reduction in solvent induced quenching. This has been demonstrated by the reduced effect of solvent deuteriation on the emission lifetime compared with the free ions. It was observed that ligand deuteriation was effective in increasing the fluorescence lifetime of Eu^{3+} and Tb^{3+}, although to a lesser extent than solvent deuteriation [6b]. The results obtained suggest that C–H and N–H oscillators may open an intra-molecular vibronic deactivation pathway of the Eu^{3+} ^5D_o emissive state [28b,76]. In the presence of strong chelating ligands such as EDTA, the increase in fluorescence lifetime, upon solvent deuteriation, has been found to be diminished (0.58–1.04 ms) compared with uncoordinated $EuCl_3$ (0.26–2.53 ms) [28a], indicating shielding of the metal centred excited state from the solvent molecules. Similar results were obtained for SO_4^{2-} and acetate complexes [28a].

The relative abilities of the various vibrational modes involved is dependent on the coupling, e.g. energy match between the vibrational modes of the excited and ground states and the distance of the X–H bond from the emissive state. The effect of distance between the potentially deactivating X–H oscillator and the metal centre has been examined [28a,76]. Partial and complete deuteriation of 1,4,7,10-tetraazacyclododecane ligands (Fig. 5) containing carboxylate pendant arms has demonstrated that C–H and N–H bonds close to the ligating atoms of the ligands are most efficient at quenching the M^{3+} emission [28a,81]. Dickens et al. have also found that for the Eu(III) complexes based on the ligands of the type 1,4,7,10-tetraazacylcododecane, deuteriation of moieties of the ligand more distant to the metal centre results in a much reduced effect on the emission lifetime (5 s^{-1} per C–H oscillator) compared with deuteriation of moieties close to the metal ion (26 s^{-1} per C–H oscillator) [76,82]. (The values of 5 and 26 s^{-1} refer to the contribution to the term k_{nr} in Eq. (1)).

In light of the work of Kropp et al. [6] and Dickens et al. [76], Schwendemann et al. [17] have reported a study of the effect of deuteriation on the emission decay of anhydrous single crystals of Eu(III) complexes containing the 2,2,6,6,-tetramethyl-3,5-heptanedionato ligand (thd) (Fig. 5) and its partially and fully deuteriated analogues. In addition, to eliminate the possibility of energy transfer effects in the single crystal a 0.5%Eu:Gd$(thd)_3$ single crystal was prepared for comparison. Measurement of the emission decay rate constants at temperatures below 210 K, where contributions due to thermal population to non-emissive deactivating states is minimised, shows that the single α-methylene C–H oscillator contributes 157 s^{-1} to the overall rate constant whilst the *tert*-butyl C–H oscillators in total contribute 175 s^{-1}. This is in agreement with the distance dependence of the oscillator to the location of the emissive state. It should, however, be noted that due to contributions from a low lying MLCT state, the results from this system can only be comparable in a qualitative manner to results obtained for other systems. These results are in agreement with those reported by Ermaloeav et al. [83], who have recently reviewed the use of deuteriation in luminescence kinetic



2-thiopyridine (2-thpy) **2,3-dipyridopyrazine (dppz)** **Heptafluoroacetoacetate**



Substituted 1,4,7,10-tetraazacyclodecane **22,66-tetramethyl-3,5-heptanedionate (thd)**

Fig. 5. Ligands described in the text.

studies of the formation and stability of lanthanide complexes in solution and have discussed the general theory behind the mechanisms involved in energy transfer to vibrational bands. They suggest that the energy transfer mechanism described by Forster's theory [84] can be extended to encompass the inductive-resonance transfer theory of non-radiative transitions in lanthanide ions, the difference being that in the latter the energy acceptor is a purely vibrational oscillator. Hence energy transfer from the luminophore to the solvent or ligand occurs via a Förster mechanism, i.e. $k_{12} = Cr^{-6}$ (where k_{12} is the rate of energy transfer between emissive and ground states, r is the distance between the states and C is a constant for the system). From this it is immediately apparent that the strongest interactions inducing the non-radiative transition involve vibrational modes of groups closest to the emissive La^{3+} ion, i.e. the innermost coordination sphere of the ion.

Recently Yanagida et al. [85] have reported the 'remarkable luminescence' of a Nd(III) complex incorporated into a polymeric matrix, by complete elimination of the majority C–H and O–H vibrational oscillators from both the complex Nd(-HFA-D)$_3$(D$_2$O)$_2$ where HFA is hexafluoroacetylacetone (the D_2O molecules are replaced by preferential coordination of $(CD_3)_2SO$ in preparation of the polymer matrix), and polymer matrix (poly(hexaflouroisopropyl)methacrylate, P-FiPMA) using not only deuteriation but also fluorination (which in itself can be viewed as 'ultra heavy hydrogen'). The effectiveness of the enhancement in quantum yield of emission of this system can be easily seen compared with systems of higher concentrations of C–H and O–H oscillators. For Nd(HFA-H$_1$)$_3$ in polymethylmethacrylate (PMMA) the quantum yield of emission $\Phi < 0.01$; for Nd(HFA-D)$_3$ in PMMA $\Phi = 0.1$; for Nd(HFA-D)$_3$ in PMMA/DMSO-d_6 $\Phi = 0.5$; for Nd(HFA-D)$_3$ in P-FiPMA/DMSO-d_6 $\Phi = 0.7$. Such dramatic enhancements clearly demonstrate that the removal of high energy oscillators is effective in photophysical studies of rare earth ions but can be extended to more applied systems such as in the development of solid state devices such as plastic fibre lasers, plastic photoamplifiers, and light emitting materials.

4.3. Application of deuteriation to vibrational spectroscopies

The use of isotope exchange and in particular deuteriation in assigning vibrational modes is of significant interest. An extensive discussion of the results of studies involving the use of deuteriation in vibrational spectroscopies is beyond the scope of this review and is dealt with elsewhere [60]. However, some notable examples of the use of deuteriation in assigning vibrational bands are presented to illustrate the effectiveness of deuteriation in both interpreting vibrational spectra and applying the results to understanding photophysical processes and electronic excited state structure.

The application of H–D exchange to vibrational spectroscopy has been well demonstrated in the study of the complexes $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$ by Hempleman et al. [86]. In the Raman spectra (at 20 K) of these complexes the band at 404 cm^{-1}, which had been assigned to Mo–Mo stretching modes by metal isotope substitution, is essentially unchanged by deuteriation whilst Mo–O and

OCO bands are noticeably shifted to lower energy. Clark et al. have extended the use of isotopic labelling as a tool for the unambiguous assignment of vibrational bands of Raman and resonance Raman spectra to the complex $Rh_2(O_2CCH_3)_4$-$(PPh_3)_2$ [87]. Deuteriation has also been used to probe the excited state (T_1) structure of copper(II) porphyrins using time resolved resonance Raman (TR^3) spectroscopy [19].

Coates et al. [30b] have used the partial deuteriation of dppz (dipyridophenazine) to d_6-dppz to aid assignment of the transient resonance Raman spectra of $[Ru(dpp)_2(dppz)]^{2+}$ (where dpp is 4,7-diphenyl-1,10-phenanthroline) and $[Ru(dpp)_2(d_6\text{-dppz})]^{2+}$ in H_2O, DNA and CH_3CN. These studies have shown that although many of the bands observed are attributable to vibrations which involve the entire dppz ligand skeleton, isotopic substitution suggests the involvement of vibrational modes more confined to a particular moiety of the dppz ligand.

In addition to providing information on the origin of vibrational modes by isotopic shift effects, the use of deuteriation has been extended by Kincaid et al. [22] to providing additional data to allow for refinement of ground state force field calculations obtained from normal coordinate analysis (NCA). They have carried out resonance Raman and TR^3 studies in fluid solution on a series of isotopomers of $[Ru(bpy)_3]^{2+}$ using selective deuteriation and ^{15}N labelling. The data obtained have allowed for the derivation of a corresponding force field for the anion radical fragment of the ^{3}MLCT excited state. This has allowed identification of the presence of vibrations in the excited state Raman spectra of $[Ru(bpy)_3]^{2+}$, which are similar to those observed for the $bpy^{-\bullet}$ radical anion. Based on the results of these empirical and theoretical studies, Kincaid et al. [22] have suggested that for $*[Ru(bpy)_3]^{2+}$ a localised excited state with the formula $[Ru^{III}(bpy)_2(bpy^-)]^{2+}$ exists, in agreement with the conclusions of Krausz et al. [60b,60c].

The use of vibrational spectroscopy, in particular resonance Raman and TR^3, in probing excited states, although useful, may be ambiguous as has been demonstrated by Humbs et al. [59] in the study of the complexes $[Pt^{II}(h_8\text{-bpy})_{2-n}(d_8\text{-bpy})_n]^{2+}$ (where $n = 0, 1, 2$). Raman spectra of these complexes were obtained as their neat perchlorate powders and interestingly the Raman scattering intensities due to the per-deuterio ligand in the mixed ligand complex were found to be significantly higher than for the per-protio ligand. This is not an unusual occurrence and has also been found by Humbs et al. to occur in the analogous $[Rh^{III}(h_8\text{-bpy})_{3-n}(d_8\text{-bpy})_n]^{3+}$ (where $n = 1, 2$) complexes. The results of these Raman studies were then used to aid assignment of vibrational features of the highly resolved low temperature emission spectrum (vide infra) of the Pt(II) complexes $\{[Pt^{II}(h_8\text{-bpy})_{2-n}(d_8\text{-bpy})_n]^{2+}$ (where $n = 0, 1, 2$), albeit where only vibrational modes due to the per-protio ligands were observed in all but the per-deuteriated complex, indicating that emission from the per-protio ligand based excited state alone is occurring. Danzer et al. have examined the resonance Raman and TR^3 spectra of ruthenium complexes containing bpy, pypz (2-(pyrid-2′-yl)-pyrazine), bpz (2,2′-bipyrazine) and their partially deuteriated analogues in order to assign Raman bands and assign the location of the excited state [30a]. The results of these studies allowed confirmation of the localisation of the excited state on the pyrazine moiety in hetereoleptic complexes. Similar studies on the pyridinyl- and pyrazinyl-1,2,4-triazole complexes (Fig. 3) described in Section 3.1 have been carried out. In these studies partial and complete deuteriation have allowed determination of the emitting state for these compounds [40–42].

Low temperature (< 5 K) high resolution emission studies on a series of platinum group complexes have been carried out by Yersin et al. [60a] and Krausz et al. [16,88]. Both matrix and ligand deuteriation have been employed in these studies. The results of these studies have recently been reviewed in detail by Yersin et al. [60a] and Krausz et al. [60b,60c] and only experimental effects of deuteriation will be dealt with here.

Obtaining highly resolved emission and excitation spectra of transition metal complexes is often hampered by the lack of adequate matrices. However, several matrices have been found which are suitable such as $[Pt(bpy)_2](ClO_4)_2$, $[Zn(bpy)_3](ClO_4)_2$, $[Rh(bpy)_3](ClO_4)_2$, $[Ru(bpy)_3](ClO_4)_2$, $[Os(bpy)_3](ClO_4)_2$ etc. [60]. These are suitable due to the presence of inequivalent sites, the so-called X traps, which allow the transition metal complexes in neat crystal matrices to have their emitting states several tens of cm^{-1} lower than those of the majority of complexes and/or below the exciton band. At very low temperatures these 'sites' can be populated selectively and hence highly resolved spectra obtained [60a]. A second strategy for isolating transition metal complexes is based on the effect of deuteriation on electronic transition energies. By doping per-deuteriated matrices with the partially or completely per-protonated metal complexes, a similar effect to the X-trap effect can be observed [60a], i.e. the electronic origins of the non and partially deuteriated complexes are several tens of cm^{-1} lower than those of the completely deuteriated matrix.

Deuteriation has been applied to similar studies of chromium(III) amine complexes by Flint et al. [89] and later Kirk et al. [90], of ruthenocene by Riesen et al. [65], of vanadium(II) hexaaquo complex by McDonald et al. [91], of $Pd(2\text{-thpy})_2$ [92] and of $[Rh(h_8\text{-bpy})_{3-x}(d_8\text{-bpy})_x]^{3+}$ ($x = 0–3$) by Yersin et al. [59a]. In general the application of deuteriation to these studies have been to allow for assignment of vibrational bands rather than as a direct probe into electronically excited state decay processes. In a similar manner deuteriation has also been applied in investigations involving Stark effect spectroscopy [93], fluorescence and excitation line narrowing and transient spectral hole burning [59a,93–95].

5. Concluding remarks and outlook

The effect of deuteriation on vibrational energies, in the case of the Pt group metals, has been of primary interest and its application to vibrational spectroscopies is already very well developed [60]. Deuteriation has also been used as a probe of the excited state electronic structure of inorganic complexes, in particular Ru^{II} diimine and Rh^{III} amine complexes (Section 4.1). The potential of deuteriation in both elucidating molecular structure and in probing excited state electronic structure is of particular relevance to the field of supramolecular chemistry where large complex molecular assemblies are frequently employed and where characterisation of complex molecular systems is inherently difficult.

In contrast, the application of deuteriation to the study of free rare-earth ions and their complexes has been almost exclusively directed towards improving quantum yields of emission for potential laser applications and probing their coordination environment in inorganic systems and bioinorganic systems (Section 4.2).

The effect of deuteriation of inorganic complexes on non-radiative deactivation processes has been found to mirror that found for organic systems. However, whereas X–H vibrational modes can dominate the overall rate of non-radiative deactivation in organic systems, for inorganic complexes and ions other vibrational modes such as skeletal vibrations and solvent modes can dominate. Despite this, the application of deuteriation as a probe of the nature of electronically excited states has been demonstrated and shows considerable potential. It is also of note that while ostensibly excited state decay processes of organic systems seem of only minor relevance to the study of the rare earth and platinum group metals, it is in fact possible to extend such organic photophysical theories to inorganic systems [46].

It is ironic however that although the earliest applications of deuteriation have been in the probing of electronically excited states, it has not been exploited to its full potential in this regard. The main reason for this in the past is likely to be due to the difficulties encountered in preparing deuteriated complexes, however with the ever-increasing number of relatively facile routes becoming available this situation is changing for the better.

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$$k_{\rm nr} = (2\pi/\hbar)\Sigma_r\,\Sigma_s\,p(mr)|v_{mr,\,ns}|^2\delta(E_{mr}-E_{ns}) \qquad \text{(a)}$$

Where $p(mr)$ is the Boltzmann factor for the state of energy E_{mr}, $v_{mr,ns}$ is the matrix element for the total Hamiltonian for the zero order Born–Oppenheimer state, E_{mr} and E_{ns} are the energy of the donor and acceptor states respectively. By applying the low temperature limit the term r is only $r=0$ and hence $\delta(E_{mr}-E_{ns})$, the weighted sum of the energy gap, becomes $\delta(E_{m0}-E_{ns})$ and thence Eq. (a) may be written as Eq. (b)

$$k_{\rm nr} = (2\pi/\hbar)\Sigma_s\,p(m0)|v_{m0,\,ns}|^2\delta(E_{m0}-E_{ns}) \qquad \text{(b)}$$

and hence:

$$k_{\rm nr} = (2\pi/\hbar)\rho v_{mn}^2 \qquad \text{(c)}$$

where $v_{mn}^2 \approx |v_{m0,ns}|^2$ and $\rho \approx \Sigma_s\,\delta(E_{m0}-E_{ns})$. v_{mn}^2 is a simple function of electronic factors and vibrational overlaps ($v_{(mr,ns)} = \Sigma_k\,J^k_{(m,\,n)}F^k_{(mr,ns)}$). By separating v_{mn}^2 into its electronic (J or $J^k_{(m,n)}$) and vibrational components ($F(E)$ or $F^k_{(mr,ns)}$), Eq. (2) is obtained:

$$k_{\text{X–H}} = (2\pi/\hbar)\rho JF(E) \qquad (2)$$

The integral in Eq. (d) is only significant when ζ_{mn} is large in the region of the vibrating nuclei and hence increasing electron density (ζ_{mn}) in the region where vibrations act as promoting modes should therefore lead to larger values of $k_{\rm nr}$.

$$J \propto \int \zeta_{mn}(r)(\mathrm{d}V/\mathrm{d}Q_k)\mathrm{d}r \qquad \text{(d)}$$

where ζ_{mn} is the electronic transition density from $\psi_m - \psi_n$, $\mathrm{d}Q_k$ are the nuclear coordinates of the promoting modes and V is the one-electron electron–nuclear interaction. (Promoting modes undergo change of one quantum in the radiative transition; accepting modes appear in the FC overlap integral in Eq. (2)).

[49] Two consequences of the low value of E_a (Fig. 1) are (a) the thermal energy required to overcome the potential barrier is generally available at low temperatures and (b) as the probability of the vibrionic state is greatest at the edge of the potential well then the excited state distortion will result in large overlaps of the lowest vibrionic states of the excited state with the isoenergetic ground vibrionic states.

[50] The mean vibrational frequency of a molecule is given by the weighted average of all vibrational frequencies (i.e. $\Sigma_j \Delta_j^2 \omega_j / \Sigma_j \Delta_j^2$ where Δ_j is the excited state fractional displacement with respect to the ground state and ω_m is the frequency of the deactivating vibrational mode). Due to the large contribution of C–C (and in the case of transition metal complexes metal ligand vibrations e.g. Ru–N, Ru–Cl etc.) to the overall value of the mean molecular vibrational frequency then deuteriation of a large molecule would be expected to show only very minor perturbations to this value.

[51] The Huang Rhys factor (S) corresponds to the electron vibrational coupling constant, which is related to the displacement of the excited state potential well along the molecular coordinates corresponding to the vibrational mode in question. $S = 1/2\Sigma_j \Delta_j^2$ or half the sum of the square of the fractional displacement of the ground and excited states for the deactivating mode(s).

[52] The energy of the lowest triplet excited state of stilbene can be dissipated via either torsional or vibrational processes, with the former resulting in isomerisation. The non-radiative rate constant in such systems contains contributions from both torsional (which may result in photochemical deactivation) and vibrational modes.

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