Nonadiabaticity in the photoinduced electron transfer reactions of metal complexes

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Abstract. The rate of electron transfer (ET) in a variety of chemical and biological processes is influenced by factors like the free energy change (ΔG), the donor–acceptor electronic coupling and the medium. The effect of donor–acceptor electronic coupling on the rate of photoinduced intermolecular electron transfer is considered by taking Ru(II) and Cr(III) metal complexes in the excited state as electron acceptors and organic compounds as electron donors. The electronic coupling between the donor and acceptors depends strongly on donor-acceptor distance. The electron transfer distance is varied by introducing alkyl groups of different sizes either on the bipyridine ligand of the metal complex or on the quencher. The semiclassical theory of electron transfer expresses k_{ET} as the product of a nuclear and an electronic transmission coefficient (K_n and K_{el} respectively) and an effective nuclear-vibration frequency (v_n), $k_{ET} = v_n K_{el} K_n$. The electron transfer reaction becomes nonadiabatic if the donor–acceptor distance is long. The change of electron transfer mechanism from adiabatic to nonadiabatic due to the introduction of bulky groups is explained in terms of semiclassical theory and from the temperature-dependence study of photoinduced electron transfer reactions of metal complexes.

Keywords. Metal complexes; photoinduced electron transfer; nonadiabaticity.

1. Introduction

Excited state electron transfer (ET) reactions involving ruthenium(II) and chromium(III) complexes have been studied extensively owing to their possible use in solar energy conversion and in checking the validity of the theories of electron transfer (Jamieson *et al* 1981; Kalyanasundaram 1982; Kavarnos and Turro 1986; Fox and Chanon 1988). For quite some time photoinduced electron transfer reactions have been considered as adiabatic, but more and more evidence for the nonadiabaticity of such reactions has now come to light (Sandrini *et al* 1985; Jones and Chatterjee 1988). The nonadiabatic character of a particular chemical process is generally reflected by the small pre-exponential factor in the rate expression and hence, should in principle be discussed by comparing activation parameters (McLendon 1988). Further, an increase in the internuclear distance between two reactants may lead the reaction to be nonadiabatic. To test the nonadiabatic behaviour of photoredox reactions of metal complexes, the reductive quenching of a series of structurally related complexes of the type RuL_3^{2+} and CrL_3^{3+} (L = 4,4'-dialkyl,2,2'-bipyridyl or 1,10-phenanthroline) with aromatic amines, phenolate ions and organic sulphides has been investigated and the important conclusions are presented here.

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2. Theoretical aspects

The electron transfer reaction may be adiabatic, nonadiabatic or somewhere in between (Marcus and Siders 1982). A first-order quantum perturbation treatment of non-adiabatic electron transfer reactions yields

$$k(r) = 2\pi/\hbar |H_{AB}(r)|^2 (FC). \qquad (1)$$

In (1) $H_{AB}(r)$ is the matrix element between the reactant and product electronic states of the perturbation that gives rise to electron transfer. When frequency changes in individual vibrational modes are neglected, the Franck–Condon factor (FC) reduces to the expression below,

$$FC = (4n\lambda k_B T)^{-1/2} \exp[-(\Delta G + \lambda)]^2/(4\lambda k_B T)], \qquad (2)$$

where ΔG and λ are the free energy changes accompanying the electron transfer and reorganisation energy respectively. An adiabatic model corresponding to the nonadiabatic model of (2) yields

$$k_{ad} = v \exp[-(\Delta G + \lambda)^2/(4\lambda k_B T)]. \qquad (3)$$

In (3), v is a typical frequency for nuclear rearrangement, $v \sim 10^{13} \, s^{-1}$. If one assumes that at van der Waal's contact ($r = \sigma$), the reaction is adiabatic and that it becomes nonadiabatic for longer r's, one can then evaluate the preexponential factor in (1) approximately by matching (1) with (3) at $r = \sigma$. Equation (4) below is obtained when this joining is made at $r = \sigma$.

$$(2\pi/\hbar)|H_{AB}(r)|^2 (4\pi\lambda k_B T)^{-1/2} \sim 10^{13} \, s^{-1}. \qquad (4)$$

Here r is the sum of the radii of the reactants and it is equal to σ when the reaction is adiabatic. For a reaction for which λ is 70 kJ/mol, the $H_{AB}(\sigma)$ calculated from (4) is ~ 0.023 eV. If the reaction is nonadiabatic at $r = \sigma$, the actual value of $H_{AB}(\sigma)$ is less than this.

For an exponential dependence of the matrix element on r, $H_{AB}(r)$ is given by

$$|H_{AB}(r)|^2 = |H_{AB}(\sigma)|^2 \exp[-\beta(r - \sigma)], \qquad (5)$$

where $r - \sigma$ is an average, and for spherically symmetric reactants, the edge-to-edge distance between the reactants. The theoretically estimated or experimentally inferred values of β range from 2·6 to 1·1 Å^{-1}. The value of 2·6 refers to a theoretical calculation where the electron tunnels from one reactant to the other via vacuum.

The semiclassical theory expresses the electron transfer rate constant, k_{ET}, as the product of a nuclear and an electronic transmission coefficient (K_n and K_{el} respectively) and an effective nuclear-vibration frequency (v_n), (6) (Marcus and Sutin 1985; Isied et al 1988; MacQueen and Schanze 1991).

$$k_{ET} = v_n K_{el} K_n, \qquad (6)$$

when the redox sites are far apart, the electronic coupling between them will be weak and the reaction will be nonadiabatic. Under these conditions the product $K_{el} v_n$ is

given by (7)

$$K_{el}v_n = [2H_{AB}^2/h][(\pi^3/\lambda RT)^{-1/2}].$$ (7)

The assumption that H_{AB}^2 decreases exponentially with distance leads to

$$K_{el}v_n = 10^{13}\exp[-\beta(r-\sigma)].$$ (8)

The term K_n is related to ΔG and λ by (9),

$$K_n = \exp[-(\Delta G + \lambda)^2/4\lambda k_B T].$$ (9)

This semiclassical expression, (6) defines a quantitative relationship between k_{ET} and ΔG_{ET}, T and parameters which are related to the structure of the donor, acceptor and surrounding medium (e.g., H_{AB} and λ). This expression has been extremely successful in correlating rate data for a variety of weakly exothermic normal-region ET reactions. Recent theoretical arguments suggest that when the overall entropy change for ET is small ($\Delta S \simeq 0$), the nuclear and electronic terms can be estimated from the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ by (10) (Isied *et al* 1988),

$$\ln K_n \simeq -\Delta H^{\neq}/RT,$$ (10a)

$$\ln K_{el} \simeq \Delta S^{\neq}/RT.$$ (10b)

Implicit in the use of (10b) to calculate K_{el}, the electronic transmission coefficient from the $\Delta S^{\neq}$ is the assumption that the Franck–Condon activation entropy is negligible. If this is the case, then $\Delta S^{\neq}$ directly provides a measure of the degree of nonadiabaticity of the ET reaction. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be evaluated experimentally from the quenching rate data (k_q) using the Eyring equation below,

$$\ln(k_q/T) = \ln K_{12}k_B/T - \Delta H^{\neq}/RT + \Delta S^{\neq}/R,$$ (11)

where k_{12} is the formation constant of a precursor complex.

3. Results and discussion

The structures of ligands (L) and the abbreviations are shown in figures 1 and 2 for RuL_3^{2+} and CrL_3^{3+} respectively.

3.1 *Quenching of* $*RuL_3^{2+}$ *with aromatic amines and phenolate ions*

The spectroscopic and electrochemical data reveal that the introduction of methyl groups at the 4 and 4′ positions of 2,2′-bipyridine results in small changes in the above properties of RuL_3^{2+} (Kitamura *et al* 1987). However, further increase in the size of the alkyl substituent (isobutyl (III) and neopentyl (IV)) has little effect on the redox potentials or on the excited state properties of RuL_3^{2+}. Temperature effects on the emission lifetimes of II, III and IV are analogous to those of $Ru(bpy)_3^{2+}$ (Durham *et al* 1982; Kitamura *et al* 1982; Caspar and Meyer 1983). However the quenching rate constants and the activation parameters are highly influenced by the introduction
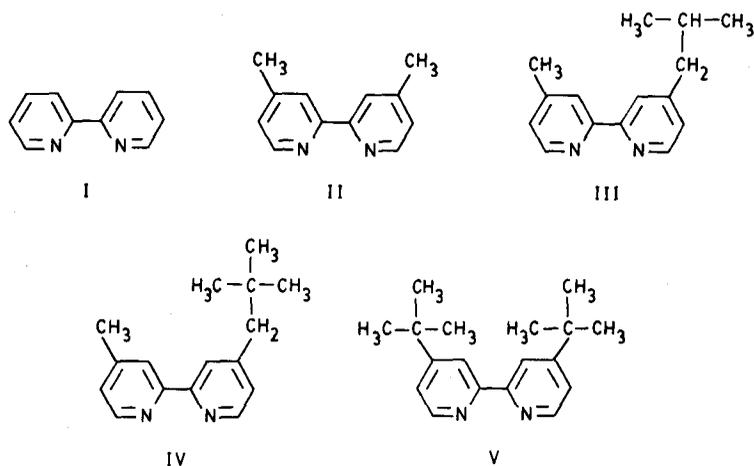
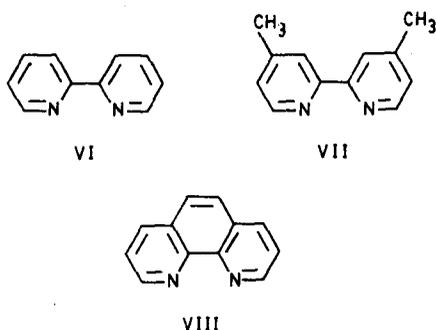**Figure 1.** Structures of L and abbreviations for RuL_3^{2+}

Figure 2. Structures of L and abbreviations for CrL_3^{3+}.

of alkyl groups on bipyridine (tables 1 and 2). When the data for II are compared with those for I, the rate retardation in the II-aromatic amine systems can be ascribed to the change in the excited state reduction potential of the complex. However, while the reduction potential is not affected any longer by the introduction of bulkier substituents on the ligands, the k_q of IV or V by N,N-dimethylaniline decreases by a factor of ~ 2 or ~ 20 as compared with that of II (Kitamura *et al* 1987; Rajagopal and Vijayalakshmi 1991). Sandrini *et al* (1985) also observed a decrease in k_q with increasing bulkiness of the ligands, which agrees very well with the present results. Similar decrease in k_q with increase in the bulkiness of ligand is observed in the luminescence quenching of RuL_3^{2+} with phenolate ions (table 3) (Rajagopal *et al* 1992). Oxidative quenching of $*RuL_3^{2+}$ by methylviologen and nitroaromatics has also been shown to depend on the alkyl chain length on the bipyridine ligands (Rau and Frank 1986; Rajagopal *et al* 1991). It seems to be a general trend that bulky substituents on ligands reduce the rate of luminescence quenching.

Change in the internuclear distance between two reactants may be a dominant factor when bulky ligands are involved. One way that bulky ligands could influence electron transfer rates is to prevent sufficient overlap between the donor and acceptor

Table 1. Quenching of $*RuL_3^{2+}$ by aromatic amines in acetonitrile.

Quencher ($E_{1/2}$(V) vs. SCE)	$k_q(M^{-1}s^{-1})$ at 298 K				
	I	II	III	IV	V
1. TMPD(0·12)*	$3·6 \times 10^{10}$	$2·2 \times 10^{10}$	$1·4 \times 10^{10}$	$9·6 \times 10^9$	$5·9 \times 10^9$
2. 4-Aminodiphenylamine(0.27)		$1·2 \times 10^{10}$	$9·8 \times 10^9$	$6·0 \times 10^9$	$3·0 \times 10^9$
3. TMP(0·43)	$2·0 \times 10^{10}$	$1·4 \times 10^{10}$	$9·0 \times 10^9$	$7·1 \times 10^9$	
4. Phenothiazine(0·53)	$7·6 \times 10^9$	$2·6 \times 10^9$	$1·9 \times 10^9$	$1·4 \times 10^9$	$1·1 \times 10^9$
5. N,N-dimethyl-*p*-toluidine	$1·2 \times 10^9$	$6·3 \times 10^7$	$6·2 \times 10^7$	$3·9 \times 10^7$	$4·0 \times 10^7$
6. N-methylphenothiazine(0·73)	$1·7 \times 10^9$	$1·3 \times 19^8$	$1·2 \times 10^8$	$8·0 \times 10^7$	
7. N,N-diethylaniline(0·76)	$2·5 \times 10^8$	$4·3 \times 10^6$	$3·6 \times 10^6$	$2·4 \times 10^6$	
8. N,N-dimethylaniline(0·81)	$9·9 \times 10^7$	$2·1 \times 10^6$	$1·5 \times 10^6$	$1·1 \times 10^6$	$1·0 \times 10^5$

*TMPD (1) and TMB(3) are N,N,N',N'-tetramethylphenylenediamine and N,N,N',N'-tetramethylbenzidine respectively
Oxidation potential of the quencher in acetonitrile is given in parentheses

Table 2. Activation parameters for the quenching of $*RuL_3^{2+}$ by aromatic amines in acetonitrile.

| Q	I			II			III			IV		
	$\Delta H_{23}^{\#}$	$\Delta S_{23}^{\#}$	$\Delta G_{23}^{\#}$	$\Delta H_{23}^{\#}$	$\Delta S_{23}^{\#}$	$\Delta G_{23}^{\#}$	$\Delta H_{23}^{\#}$	$\Delta S_{23}^{\#}$	$\Delta G_{23}^{\#}$	$\Delta H_{23}^{\#}$	$\Delta S_{23}^{\#}$	$\Delta G_{23}^{\#}$
1.	0·9	−9·4	3·7	2·2	−3·9	3·4	2·9	−2·5	3·6	3·5	−0·7	3·7
2.				2·5	−4·3	3·7	3·0	−3·0	3·8	4·4	1·2	4·1
3.	1·7	−8·1	4·1	2·3	−4·7	3·7	2·9	−3·2	3·9	3·8	−0·7	4·0
4.	1·3	−11·1	4·6	2·1	−6·7	4·6	1·8	−10·1	4·8	4·4	−2·0	5·0
5.	1·4	−14·6	5·8	3·8	−10·0	6·8	3·2	−12·5	6·9	4·3	−9·3	7·1
6.	1·8	−12·8	5·6	3·3	−10·2	6·4	3·6	−9·8	6·5	4·1	−8·6	6·6
7.	2·4	−14·2	6·6	4·1	−14·5	8·5	4·4	−13·5	8·5	5·4	−11·1	8·7
8.	2·8	−14·5	7·1	5·1	−12·8	8·9	4·9	−13·9	9·1	5·8	−11·3	9·2

For the numbering of the quencher, see table 1

orbitals. The linear relationships in figures 3 and 4 (for amines and phenolate ions respectively) suggest that one of the factors responsible for the rate retardation is the change in the electron transfer distance: $r_M + r_Q$. The electronic interaction between the donor and acceptor orbitals may thus become inefficient with increasing bulkiness of the ligand. If this is the case, the present observations of the sequence of $k_q I >$ II > III > IV > V should be interpreted in terms of $\Delta S_{23}^{\neq}$. Temperature-dependence studies of quenching of RuL_3^{2+} with amines lead to the following results (Kitamura *et al* 1987):

(i) The reductive quenching of $*Ru(bpy)_3^{2+}$ at highly exoergic regions is adiabatic, $K = 1$.

(ii) The bulky substituents on ligands do not necessarily bring about a large decrease in the transmission coefficient for the highly exoergic electron transfer reactions of III and IV. However, the comparison of the observed activation parameters with the

Table 3. Quenching rate constants k_q for $*RuL_3^{2+}$ in acetonitrile-water (80:20 v/v) at 298 K.

Quencher	$k_q(M^{-1}s^{-1})(\times 10^9)$		
	$Ru(bpy)_3^{2+}$	$Ru(dmbpy)_3^{2+}$	$Ru(mnbpy)_3^{2+}$
Phenol	5·8	1·4	0·6
m-Cresol	4·9	3·9	2·5
p-Cresol	7·8	4·5	2·4
p-Chlorophenol	4·2	0·7	0·5
m-Chlorophenol	1·9	1·3	0·2
p-Nitrophenol	13·0	19·0	19·0
o-Cresol	8·4	4·3	2·1
2,6-Dimethylphenol	13·0	10·0	5·6
α-Naphthol	18·0	16·0	9·6
β-Naphthol	14·0	7·4	4·9

$[OH^-] = 0.01 M$
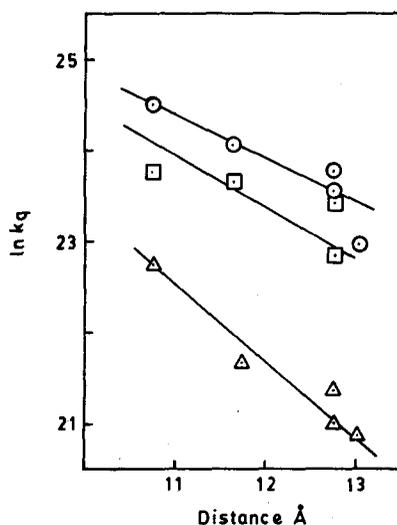
Figure 3. Relationships between the quenching rate constant and the close contact distance d in acetonitrile at 298 K for the quenchers TMPD ($\bigcirc$), TMB ($\square$), and phenothiazine ($\triangle$).

theoretical $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is of primary importance to reveal the nonadiabaticity problem of the particular electron transfer reactions. Theoretical evaluation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for III and IV is not attempted.

(iii) The increase in ΔG leads to the sharp decrease in $\Delta S^{\neq}$ for the bulkier ligands. The present $\Delta S^{\neq}$ data suggest that, although favourable overlap between the donor amine and acceptor metal t_{2g} orbital is achieved at relatively large separations of reactants (i.e., $d = 12.7 \text{Å}$) for highly exoergic reactions, the presence of bulky substituents in II, III and IV will cause less efficient orbital overlap with increasing ΔG.

It has been reported that ET reactions at normal region have rate maxima at close contact of the reactants while those at inverted region proceed at larger separations. Although the present systems are all in normal regions, the introduction of bulky
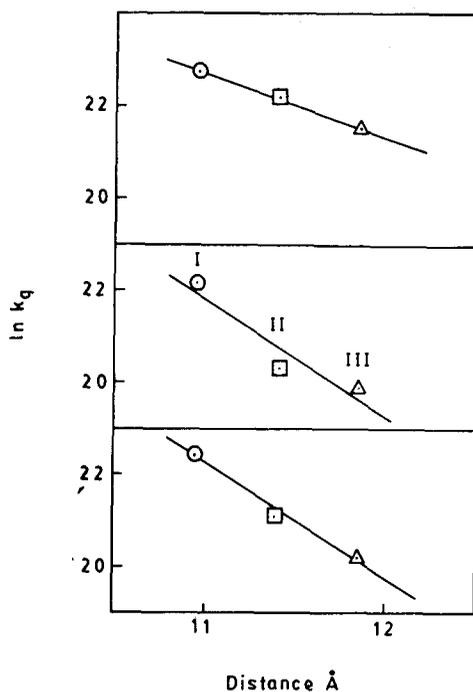
Figure 4. Distance dependence of k_q: p-cresol (○); p-chlorophenol (□); phenol (△). I, $Ru(bpy)_3^{2+}$; II, $Ru(dmbpy)_3^{2+}$; III, $Ru(mnbpy)_3^{2+}$.

alkyl substituents on bipyridine, which brings about a longer electron transfer distance (from $d = 10.9$ to 12.7 Å) is supposed to play a dominant role to reduce the orbital overlap with increasing ΔG, in particular, at endoergic regions. The large and sharp decrease in $\Delta S^{\neq}$ for II, III and IV will thus be ascribable to nonadiabaticity while the nonadiabaticity in the quenching of $*Ru(bpy)_3^{2+}$ at endoergic regions is marginal. The present results indicate that K (transmission coefficient) depends on ΔG.

3.2 *Quenching of* $*CrL_3^{3+}$ *with organic sulphides*

The k_q values estimated from the luminescence quenching technique for the three CrL_3^{3+} complexes 6–8 with alkyl aryl sulphides are given in table 4 and these values indicate the importance of change of alkyl group in RSPh on the electron transfer reaction of sulphides with $*CrL_3^{3+}$ (Allen Gnanaraj *et al* 1993). The change of alkyl group in RSPh alters the polar as well as steric effects. The effect of change of alkyl group in RSPh on the reactivity of sulphides with the excited states of Cr(III) complexes may be understood from the analysis of the k_q data in terms of Taft's equations below

$$\log k_q = \log k_0 + \rho^* \sigma^*, \tag{12}$$

$$\log k_q = \log k_0 + \delta E_s, \tag{13}$$

where σ^* and E_s are the Taft's polar and steric substituent constants and ρ^* and δ are the corresponding susceptibility constants (Shorter 1982). However the correlations

Table 4. Quenching rate constants, k_q for $*CrL_3^{3+}$ with alkyl phenyl sulphides in acetonitrile at 298 K.

Quencher	Cr(bpy)$_3^{3+}$		Cr(dmbpy)$_3^{3+}$		Cr(phen)$_3^{3+}$	
	k_q	ΔG	k_q	ΔG	k_q	ΔG
Methyl phenyl sulphide	$7{\cdot}1 \times 10^7$	$-0{\cdot}96$	$2{\cdot}9 \times 10^6$	17·36	$7{\cdot}4 \times 10^6$	0·96
Ethyl phenyl sulphide	$2{\cdot}6 \times 10^7$	10·58	$7{\cdot}3 \times 10^5$	28·91	$2{\cdot}3 \times 10^6$	12·54
i-Propyl phenyl sulphide	$1{\cdot}3 \times 10^7$	8·7	$2{\cdot}8 \times 10^5$	27·01	$1{\cdot}9 \times 10^6$	10·61
t-Butyl phenyl sulphide	$4{\cdot}8 \times 10^6$	10·58	$8{\cdot}3 \times 10^4$	28·91	$6{\cdot}7 \times 10^5$	12·54
Diphenyl sulphide	$6{\cdot}0 \times 10^6$	10·58	$6{\cdot}6 \times 10^5$	28·91	$1{\cdot}4 \times 10^6$	12·54

k_q values are in $M^{-1}s^{-1}$; ΔG values are in kJ/mol.

of $\log k_q$ values of alkyl aryl sulphides with σ^* and E_s values are poor. This analysis leads us to conclude that the steric effect is not significant in these reactions.

Another approach for the steric influence on the rate of electron transfer reactions is in terms of change of electron transfer distance. The differences in the quenching constants, k_q, with bulky quenchers are best related to the transmission coefficient, K, which is mainly determined by the degree of electronic coupling. For the analysis of the distance dependence of electron transfer in a reaction series, G should almost remain constant in the series. In the present instance, G is not significantly varied for the series of alkyl phenyl sulphides. Thus the lower k_q values for sulphides containing bulky alkyl groups can be related to the transmission coefficient, K, the size of which reflects the degree of electronic coupling between the electron transfer reactant and product states. Under circumstances in which there is relatively poor overlap of donor and acceptor wave functions, $K \ll 1$, the electron transfer step is nonadiabatic and the value of the preexponential term is

$$k_{el} = Kv_n \exp(-\Delta G^{\neq}/RT), \tag{14}$$

which is related to the electron transfer distance by (8)

$$K(r)v_n = 10^{13} \exp[-\beta(r - \sigma)], \tag{8}$$

where $K(r)$ is the transmission coefficient at distance r (r is the sum of the radii of the reactants) and σ is defined so that the reaction is adiabatic (i.e., $K = 1$) at $r = \sigma$. Thus one may expect that the principal source of steric retardation involves the exponential fall off in transmission coefficient with distance and that $r = \sigma$ for electron transfer with PhSMe. If the bulky *t*-butyl group contributes to the distance of separation (r) an increment of 2·0 Å compared to ethyl (ΔG remains almost constant for ethyl, isopropyl, *t*-butyl and phenyl, cf. table 4) the result is a reduction in k_q for *t*-BuSPh of ≈ 7, which is of the proper order of magnitude observed with PhSEt and PhS(*t*-Bu) quenching. A value of $\beta = 1 Å^{-1}$ is assumed for this reaction (McLendon

1988). More details on the nonadiabaticity of the reaction of sulphides with bulky groups may be obtained from the temperature-dependence study of quenching of $*CrL_3^{3+}$ with sulphides which is in progress.

4. Conclusion

The arguments presented above lead us to conclude that introduction of bulky groups either on the ligand of ML_3^{2+} or in the quencher brings in nonadiabaticity through the increase in the separation distance between the reactants particularly in endoergic regions.

Acknowledgements

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