

Supplementary Material

Optical transitions of symmetrical mixed-valence systems in the Class II/III transition regime

Bruce S. Brunshawig, Carol Creutz and Norman Sutin

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Derivation of transition moment expression, eqn. (39c).

The adiabatic transition moment can be expressed in terms of the coefficients of the wave function. For a multilevel system

$$\Psi_i = \sum_k c_{k,i} \mathbf{f}_k \quad (\text{A1})$$

where Ψ_i and \mathbf{f}_k are the adiabatic and diabatic wave functions, respectively. By definition in the diabatic representation all the transition dipole moments are zero. This leads to the following expression for the adiabatic transition dipole moments

$$\mathbf{m}_{i,j} = \sum_k c_{k,i}^* c_{k,j} \mathbf{m}_k^0 \quad (\text{A2})$$

where \mathbf{m}_k^0 are the diabatic dipole moments of state k (e.g. \mathbf{m}_a of the manuscript). For the three- or four-state symmetric system we can assume that for the bridge state ($D^+B^-A = AB^-A$) the dipole moment is the average of the dipole moments of the reactant and product states

$$\mathbf{m}_3^0 = \frac{1}{2} (\mathbf{m}_1^0 + \mathbf{m}_2^0) \quad (\text{A3})$$

where \mathbf{m}_1^0 and \mathbf{m}_2^0 are the \mathbf{m}_a and \mathbf{m}_b used in the manuscript. The orthogonality of the wave functions gives

$$\sum_k c_{k,i}^* c_{k,j} = 0 \quad (\text{A4})$$

Using eqn. (A4), (A3) and (A2) we obtain

$$\begin{aligned} \mathbf{m}_{i,j} &= \frac{1}{2} [c_{2,i}^* c_{2,j} - c_{1,i}^* c_{1,j}] (\mathbf{m}_2^0 - \mathbf{m}_1^0) \\ &= \frac{1}{2} [c_{b,i}^* c_{b,j} - c_{a,i}^* c_{a,j}] (\mathbf{m}_b - \mathbf{m}_a) \end{aligned} \quad (\text{A5})$$

Table 1. Band maxima and full-widths at half height for the different two-state treatments.

Treatment	Expression	ν_{\max}	$\Delta\nu_{1/2}$
Semiclassical $\frac{e}{n}$ vs. n	$\frac{e_{\text{sc}}(n)}{n} = \frac{4p^3 m_{12} ^2}{3 \times 10^3 \ln(10) c \sqrt{p I R T}} \exp \left[-\frac{(1 - hm)^2}{4 I R T} \right]$	λ	$2 [4 \ln(2) I R T]^{1/2}$
ϵ_{sc} vs. ν	$e_{\text{sc}}(n) = \frac{4p^3 m_{12} ^2 n}{3 \times 10^3 \ln(10) c \sqrt{p I R T}} \exp \left[-\frac{(1 - hm)^2}{4 I R T} \right]$	$\lambda(1 + 2RT/I)^a$	$2 [4 \ln(2) I R T]^{1/2} \times (1 - RT/I)^a$
Classical ϵ_{cl} vs. ν	$e_{\text{c}}(n) = \frac{4p^3 m_{12} ^2 n_{\max}}{3 \times 10^3 \ln(10) c \sqrt{p I R T}} \exp \left[-\frac{(1 - hm)^2}{4 I R T} \right]$	λ	$2 [4 \ln(2) I R T]^{1/2}$

^aAssuming that the “correct” plot is ϵ/ν vs. ν .

Table 3. Intervalence Band Maxima and Widths for Mixed-Valence Ru(II)/(III) Complexes in Acetonitrile^a

L	Series	ν_{\max} , cm ⁻¹	$\Delta\nu_{1/2}$, cm ⁻¹	G^b	$-\Delta G_{\text{com}}^b$, cm ⁻¹	Class
	$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+c}$					
Me ₂ dicyd ²⁻		7100	2430	0.40	2740	II ^g
dicyd ²⁻		6890	2760	0.31	2310	
Cl ₂ dicyd ²⁻		6910	3390	0.15	1710	
Cl ₄ dicyd ²⁻		7320	3890	0.05	1200	
	$[\{\textit{trans,trans}\text{-Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})]^{3+c}$					
Me ₂ dicyd ²⁻		7480	1920	0.54	3200	III ^g
dicyd ²⁻		7230	2090	0.49	2900	
Cl ₂ dicyd ²⁻		6690	2700	0.31	2110	
Cl ₄ dicyd ²⁻		6580	3350	0.14	1360	
	$[\{\textit{mer,mer}\text{-Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-L})]^{3+c}$					
Me ₂ dicyd ²⁻		7970	1760	0.59	3400	III ^g
dicyd ²⁻		7550	1700	0.59	3320	
Cl ₂ dicyd ²⁻		6910	2440	0.39	2650	

L	Series	v_{\max} , cm ⁻¹	$\Delta v_{1/2}$, cm ⁻¹	G^b	$-\Delta G_{\text{com}}^b$, cm ⁻¹	Class
	$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{5+ d}$					
pz		6250	1400	0.63	3468	
4,4'-bpy		9700	5200	-0.10	620	II
		8700	5500	-0.23	AN	
	$\text{trans}-((\text{NH}_3)_4\text{LRu})_2(\mu\text{-pz})^{5+ e}$					
3,5-(CH ₃) ₂ py		5872	1970	0.47	2863	
py		5935	1850	0.50	2742	
3-Fpy		5918	1940	0.48	2460	
3-Clpy		5910	1940	0.47	2590	
2,6(CH ₃) ₂ pz		5888	3307	0.11	2258	
	$\text{cis}-((\text{NH}_3)_4\text{LRu})_2(\mu\text{-pz})^{5+ e}$					
py		6068	1770	0.53	2445	
3-Fpy		6057	1790	0.52	2405	
	$[\{\text{mer,mer-Ru}(\text{NH}_3)_3(\text{bpy})\}_2(\mu\text{-L})]^{3+ e}$					
pz		8772	4010	0.11	1843	
	c^f					
phen		7580	5000	-0.20	44	II
(NO ₂ phen)		7875	4500	-0.06	44	II
(CH ₃) ₂ phen		7519	4700	-0.13	44	II
(CH ₃) ₄ phen		7692	4700	-0.11	206	

^adicyd²⁻ = 1,4-dicyanamidobenzene dianion, bpy = 2,2'-bipyridine, pz = pyrazine.

^b $G = 1 - (\Delta v_{\text{FW}})/(2310v_{\max})^{1/2}$; ΔG_{com} is the free energy change for the comproportionation.

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