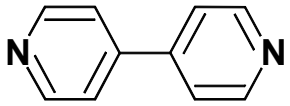
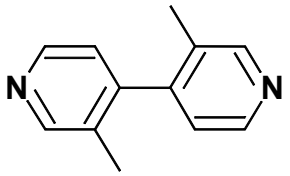
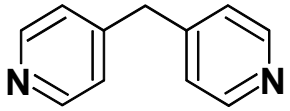
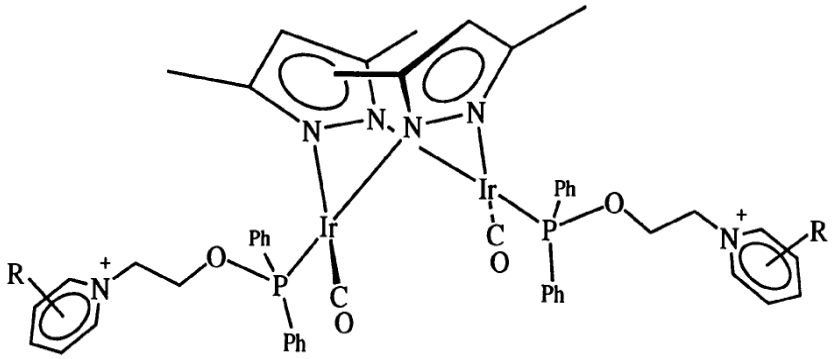
Problem Set 7
Ch 153a – Winter 2022
Due: 18 February, 2022

1) Intervalence charge transfer absorption bands have been observed in a large number of complexes of the type: $[(NH_3)_5RuL\text{-}LRu(NH_3)_5]^{5+}$; data for three of these are given in the following table.

L-L	*r*, Å	Abs_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$
	11.3	1030	920
	11.3	890	165
	10.5	810	30

For each complex, use the results from problem set 6 to determine the value of H_{AB} and λ, and predict the full-width at half-maximum of the intervalence band. Offer explanations for any trends that you observe in these parameters.

2) Fox and coworkers (*Science* **1990**, *247*, 1069-1071) reported the kinetics of electron transfer in a series of Ir dimers of the following type:



A plot of the driving force dependence of the rate contants and a data table are shown on the following page.

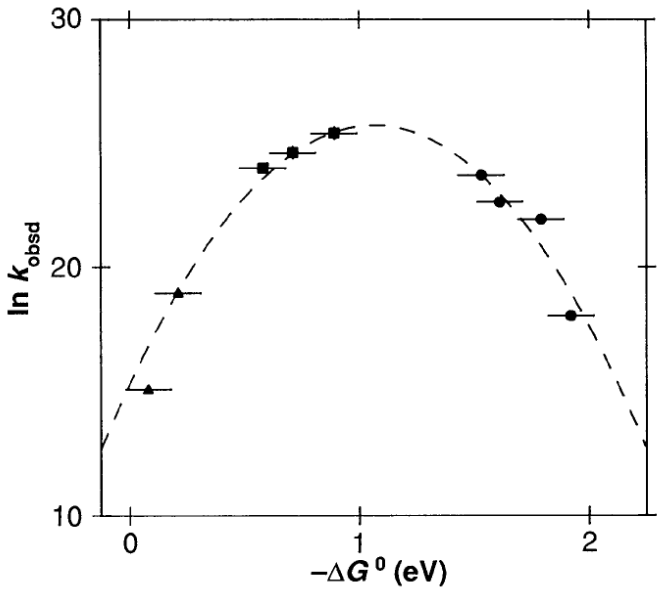


Table 2. Driving forces and rate constants for ET. Standard errors are 0.1 eV for $-\Delta G°$ and ±10% for k_{ET}, except where noted.

Donor	Acceptor	$-\Delta G°$ (eV)	k_{ET} (s^{-1})
$^3Ir_2$*	2,4,6-Me_3py^+	0.08	3.5×10^6
$^3Ir_2$*	4-$Mepy^+$	0.21	1.7×10^8
$^1Ir_2$*	2,4,6-Me_3py^+	0.58	2.7×10^{10}
$^1Ir_2$*	4-$Mepy^+$	0.71	5.0×10^{10}*
$^1Ir_2$*	py^+	0.89	1.1×10^{11}
$^1Ir_2$*	4-$Phpy^+$	0.97	$>1.1 \times 10^{11}$
4-$Phpy^{\bullet}$	Ir_2^+	1.53	2.0×10^{10}
4-$Mepy^{\bullet}$	Ir_2^+	1.61	6.7×10^9
$py^{\bullet}$	Ir_2^+	1.79	3.3×10^9
2,4,6-$Me_3py^{\bullet}$	Ir_2^+	1.92	6.7×10^7

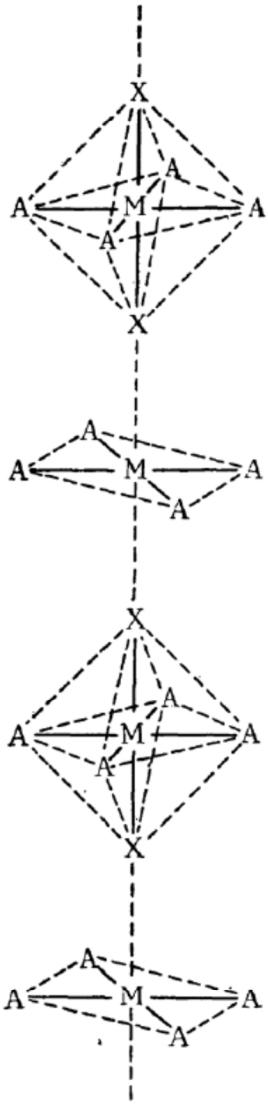
*±30%.

Semiclassical electron-transfer theory predicts that intramolecular rates can be described by the following equation:

$$k_{ET} = \sqrt{\frac{4\pi^3}{h^2 \lambda RT}} H_{AB}^2 \exp\left\{-\frac{(\Delta G° + \lambda)^2}{4\lambda RT}\right\}$$

On the basis of the electron transfer rate data, determine the value of H_{AB} for this series of complexes. Predict the positions, extinction coefficients, and widths of the Ir→(R–py)$^+$ charge transfer absorption bands for the four Ir compounds used in this study.

3) Wolffram's red salt, $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_4 \bullet 4H_2O$, consists of linear chains of halogen-bridged alternating Pt(II) and Pt(IV) subunits. Wolffram's red salt has the following properties: the Cl atom is displaced 0.44 Å from the midpoint between the two Pt atoms; an intense absorption is observed beginning at 580 nm, polarized parallel to the Pt-Pt axis; resonance Raman spectra with excitation into this band exhibit strong enhancement of a Pt-Cl stretching mode; a luminescence band maximizing at 1080 nm. Spectra are reproduced below and on the following page.



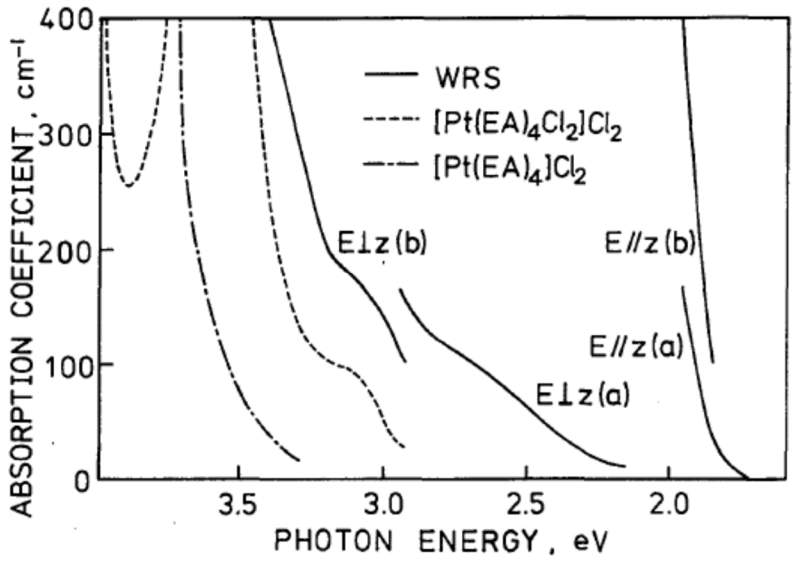


Fig. 11. Absorption spectra of Wolffram's red salt (—— (a) and (b)) and its constituent radicals $[Pt(EA)_4Cl_2]Cl_2$ (– – – –) and $[Pt(EA)_4]Cl_2$ (—·—), respectively, at RT. Curves (a) are the same spectra

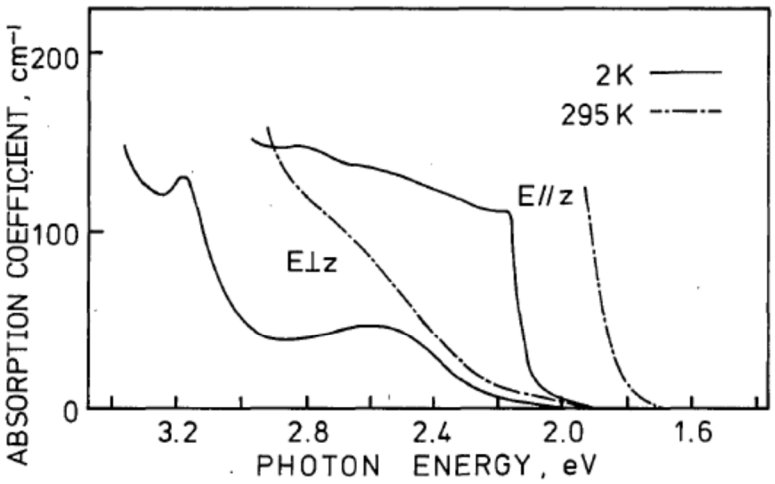
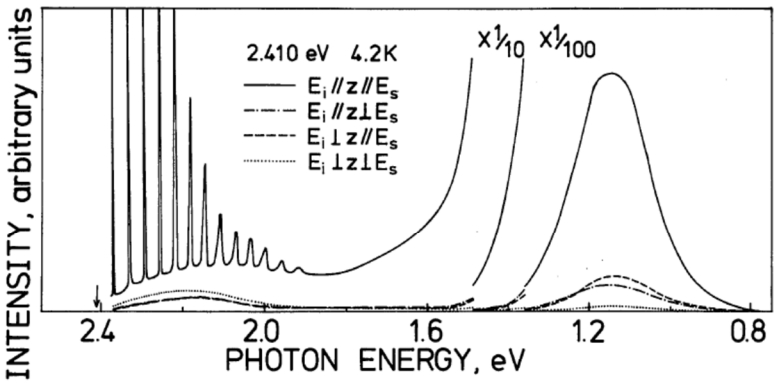


Fig. 2. Absorption spectra at RT and 2 K for $E//z$ ($E//(001)$) and $E \perp z$($E//(110)$).



Resonance Raman and luminescence spectra for 2.410 eV excitation (indicated by an arrow) at 4.2 K for $E_i//z//E_s$, $E_i//z\perp E_s$, $E_i\perp z//E_s$ and $E_i\perp z\perp E_s$.

Develop a molecular orbital diagram for Wolffram's red salt and propose an assignment for the 580 nm absorption. What structural distortion do you expect to accompany population of this excited state?

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