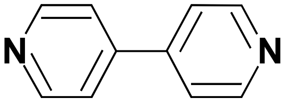
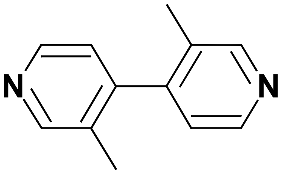
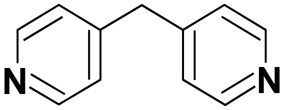
Problem Set 9

Ch 153a - Winter 2021

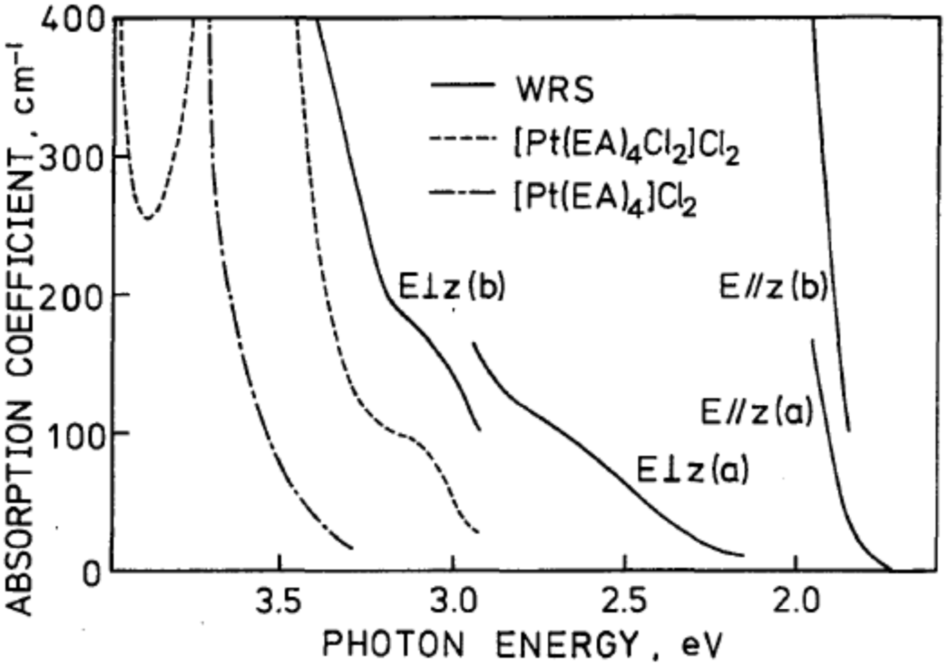
Due: Monday, 8 March, 2021 (note the extra time)

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.

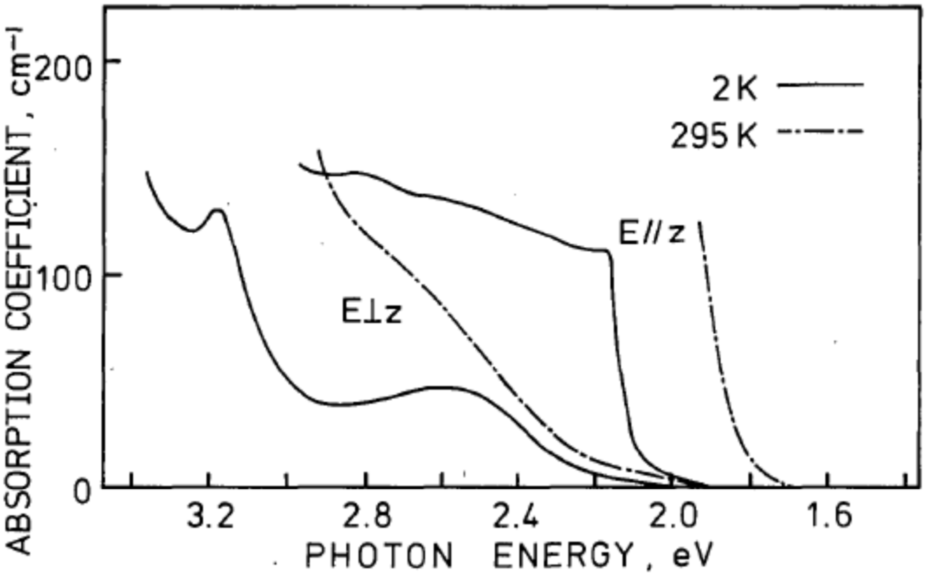
L-L	*r*, Å	Abs_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$
	11.3	1030	920
	11.3	890	165
	10.5	810	30

For each complex, use the results from problem set 7 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.

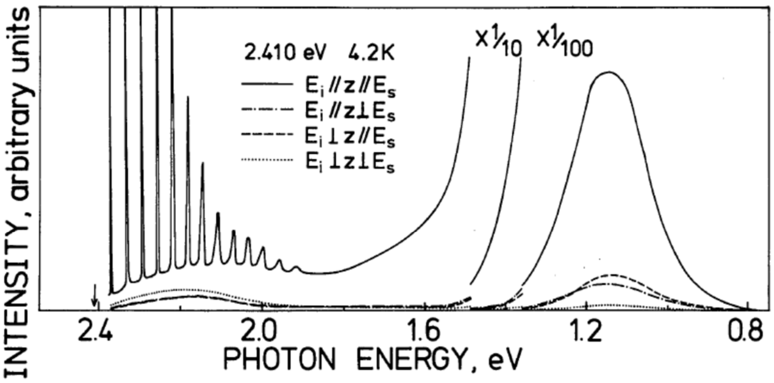
2) Wolffram's red salt, $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4]Cl_2]Cl_4 \cdot 4H_2O$, consists of linear chains of halogen bridged alternating Pt(II) and Pt(IV) subunits. Wolffram's red salt has the following properties: the Cl atom is displaced 0.44 Å from the midpoint between the two Pt atoms; an intense absorption band is observed at ~480 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 the following pages.



Absorption spectra of Wolffram's red salt (—— (a) and (b)) and its constituents $[Pt(EA)_4Cl_2]Cl_2$ (----) and $[Pt(EA)_4]Cl_2$ (—·—), respectively, at RT.



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

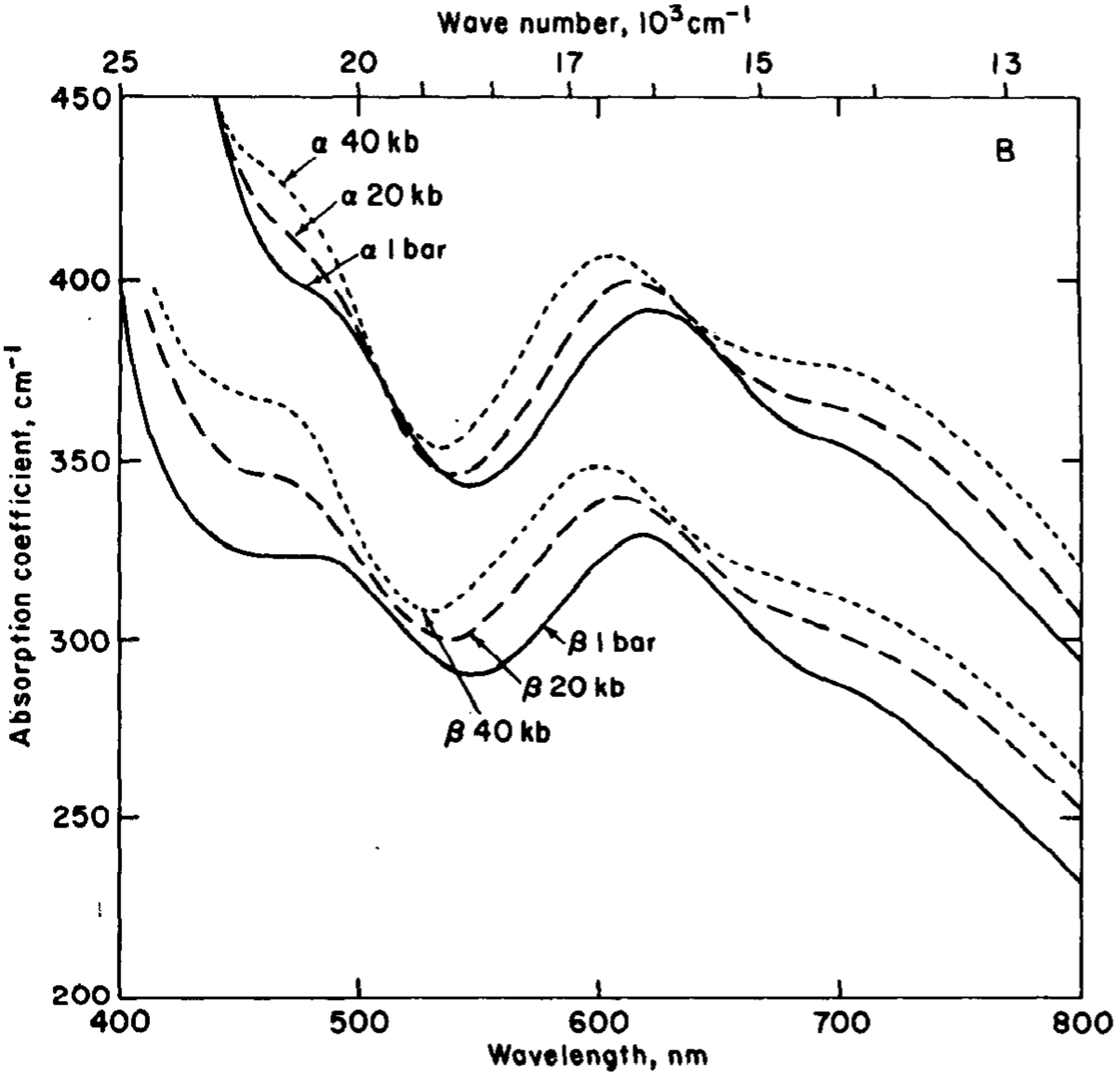


Resonance Raman and luminescence spectra for 2.410 eV excitation (indicated by an arrow) at 4.2 K for $E_i//z//E_s$, $E_i//z\perp E_s$, $E_i\perp z//E_s$ **and** $E_i\perp z\perp E_s$.

Develop a molecular orbital diagram for Wolffram's red salt and propose an assignment for the 480 nm absorption band. What structural distortion do you expect to accompany population of this excited state?

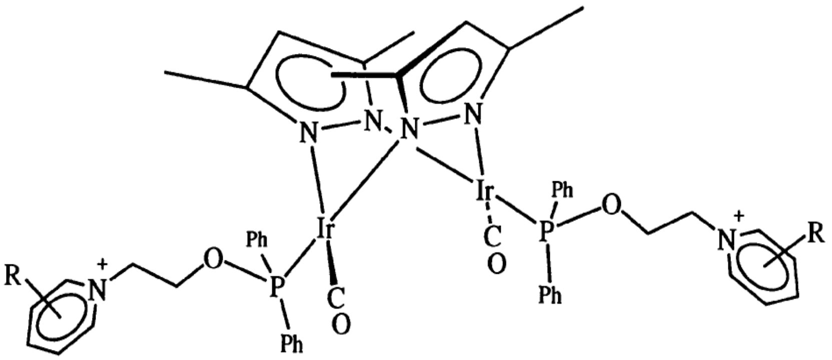
3) The Ti(III) oxidation state is rare in terrestrial minerals due to the comparatively highly oxidizing environment on Earth. Trivalent titanium does occur in extraterrestrial materials; one example is a titanium pyroxene found in the Allende meteorite. The empirical formula for this mineral is $Ca_{1.01}Mg_{0.38}(Ti^{3+})_{0.34}(Ti^{4+})_{0.14}Al_{0.87}Si_{1.26}O_6$. The crystal structure reveals that this mineral contains chains of edge-shared distorted octahedra with $Ti^{3+/4+}$ ions at the center. The Ti-Ti distance is 3.15 Å. The polarized single-crystal absorption spectra of the Ti^{3+}-Ti^{4+} pyroxene from the Allende meteorite at different pressures are shown below (α and β refer to two different polarization directions).

Propose assignments for the absorption bands at 14,000, 16,000, and 20,000 cm^{-1} (1 bar). On the basis of your assignments, offer explanations for the pressure dependent behavior of the three bands.



Wave number, 10^3 cm^{-1}
25
20
17
15
13
450
400
350
300
250
200
Absorption coefficient, cm^{-1}
400
500
600
700
800
Wavelength, nm
B
α 40 kb
α 20 kb
α 1 bar
β 1 bar
β 20 kb
β 40 kb

4) 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 rates is shown below, and a data table is shown on the following page.

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

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

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→$(R\text{–}py)^+$ charge transfer absorption bands for the four Ir compounds used in this study.

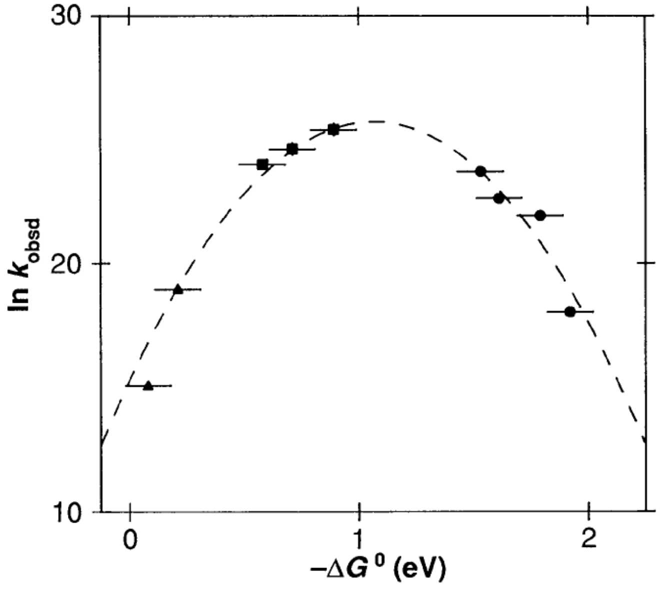


Table 2. Driving forces and rate constants for ET. Standard errors are 0.1 eV for $-\Delta G°$ and ±10% for k_{ET}, except where noted.

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-$Phpy^•$	Ir_2^+	1.53	2.0×10^{10}
4-$Mepy^•$	Ir_2^+	1.61	6.7×10^9
$py^•$	Ir_2^+	1.79	3.3×10^9
2,4,6-$Me_3py^•$	Ir_2^+	1.92	6.7×10^7

*±30%.