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Title: ELECTRONIC STRUCTURES OF YTTERBOCENE-IMINE COMPLEXES

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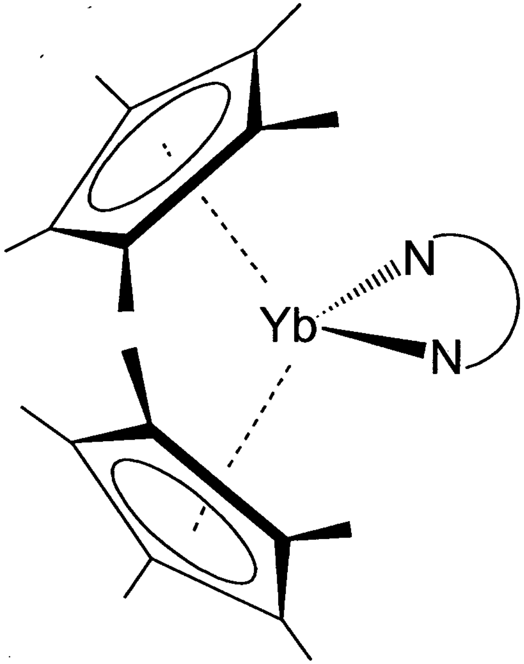
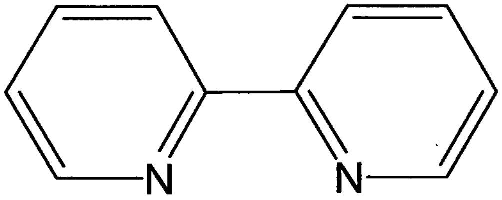
Electronic Structures of Ytterbocene-Imine Complexes. Ryan E. Da Re, Christopher J. Kuehl, Kevin D. John, and David E. Morris

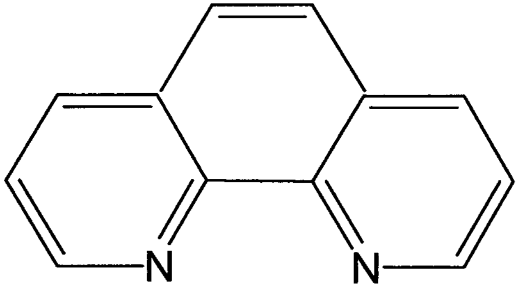
The electronic structures of complexes of the form $[(C_5Me_5)_2Yb(L)]^{+/0}$ (L = bipyridine, phenanthroline, terpyridine) have been probed using cyclic voltammetry and electronic spectroscopy. Remarkably, the voltammetric data reveal that the imine-based LUMO is stabilized and the redox-active metal f orbital is destabilized by ca. 1 V each upon formation of the ytterbocene–imine adduct, which is presumably responsible for the $[(f)^{13}(\pi^*(L))^1]$ charge-transfer ground state characteristic of these complexes. The ca. 0.8 V separation between ligand-based oxidation and metal-based reduction waves for each ytterbocene adduct correlates with the energy of its optically promoted $\pi^*(L)$–f(Yb) charge transfer (LMCT) transition (ca. 5000 cm^{-1}). The coupling between this LMCT excited state and the $^2F_{7/2}$ ground and $^2F_{5/2}$ excited states of Yb(III) leads to unusually large intensities ($\varepsilon \sim 1000$) for the metal-localized f–f bands, which will be discussed in the context of an intensity borrowing mechanism that invokes exchange between the ligand-based ^2S and metal-based ^2F spin states.

Electronic Structures of α,α'-Diimine Adducts of $(Cp^*)_2Yb$





bpy

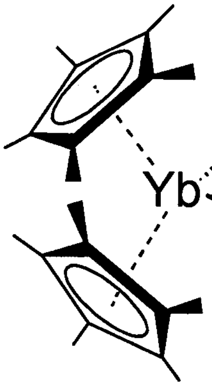


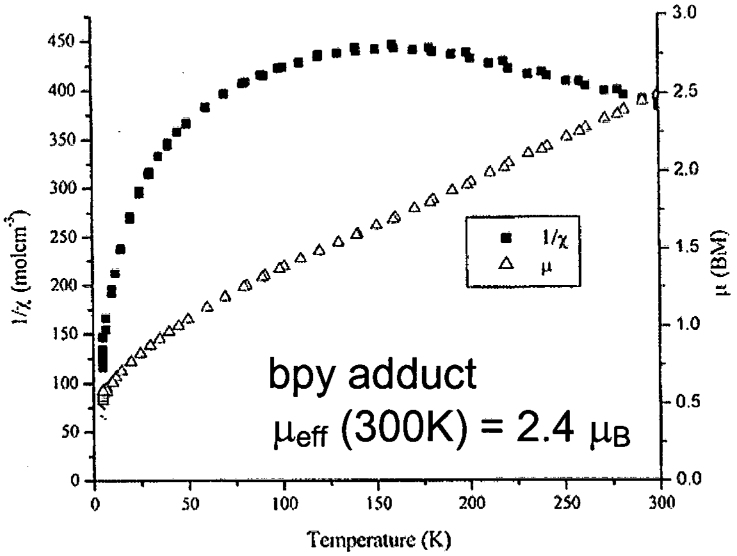
phen

Schultz, Boncella, Berg, Tilley, Andersen *Organometallics*, **2002**, *21*, 460–472

- An electron is spontaneously transferred from the f^{14} Yb center to the diimine ligand to yield an $[(f)^{13}(\pi^*)^1]$ ground state
- Physical properties are consistent with a radical-anion diimine ligand: IR, NMR, UV-Vis

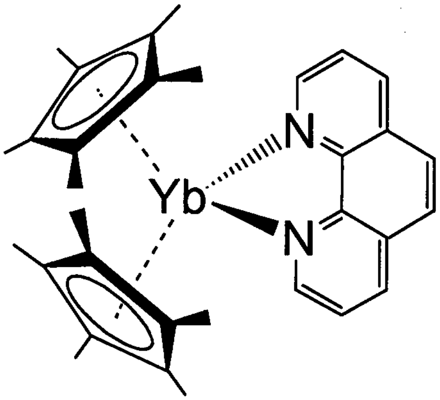
Magnetic Properties of Ytterbocene Adducts

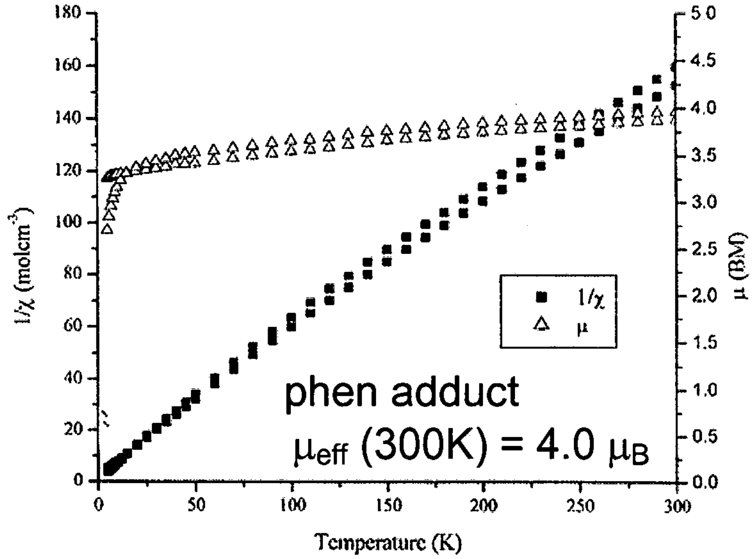




bpy adduct

μ_{eff} (300K) = 2.4 μ_B





phen adduct

μ_{eff} (300K) = 4.0 μ_B

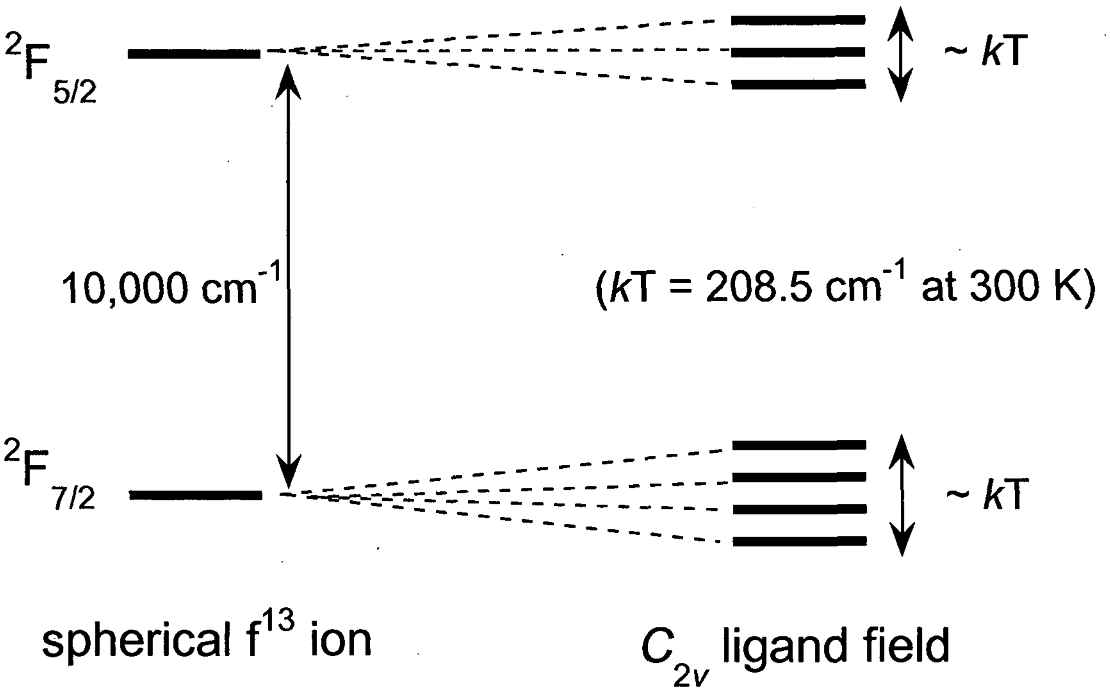
Theoretical μ_{eff} Values for $[(f)^{13}(\pi^*)^1]$ Ground State

uncoupled spins	4.8 μ_B
antiferromagnetically coupled spins	3.4 μ_B
ferromagnetically coupled spins	5.6 μ_B

Schultz, Boncella, Berg, Tilley, Andersen *Organometallics*, **2002**, *21*, 460–472

Experimental Determination of the Sign of *J*

Deducing the coupling between the Yb-based and ligand-based spins is difficult due to the splitting of the $^2F_{7/2}$ ground-state term of Yb(III)



$^2F_{5/2}$

~ kT

10,000 cm^{-1}

(kT = 208.5 cm^{-1} at 300 K)

$^2F_{7/2}$

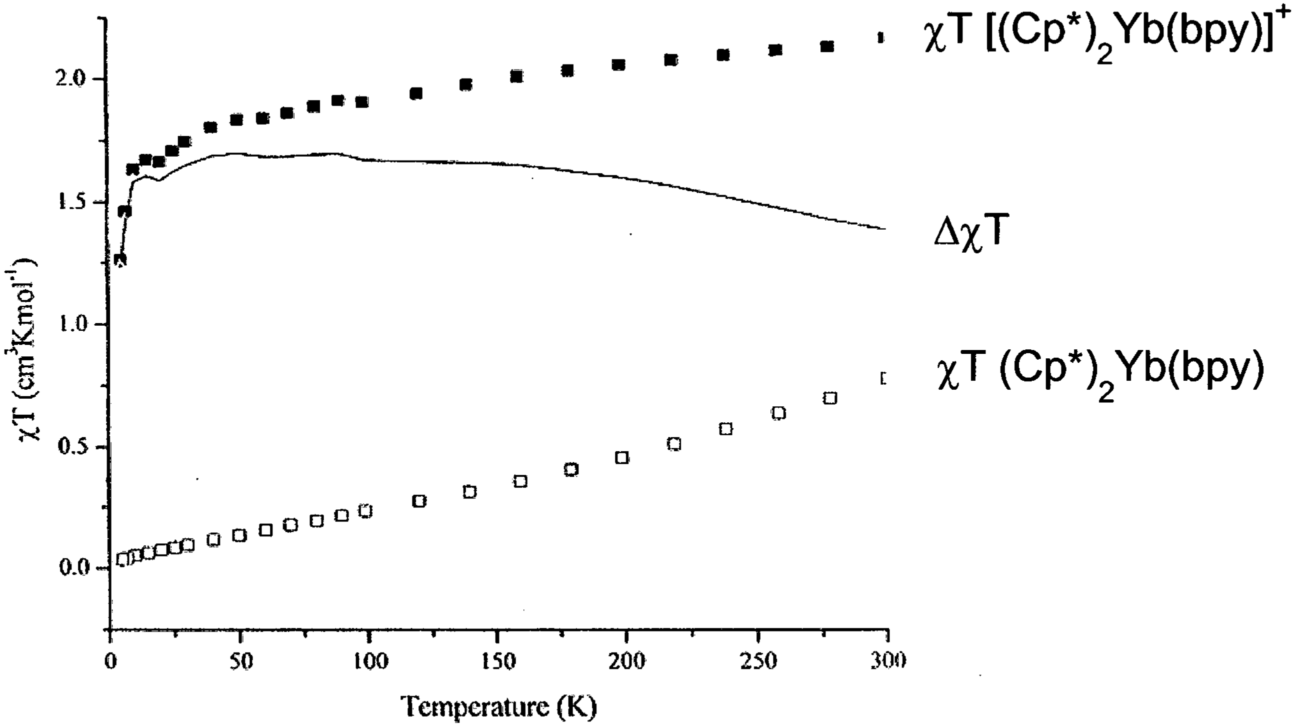
~ kT

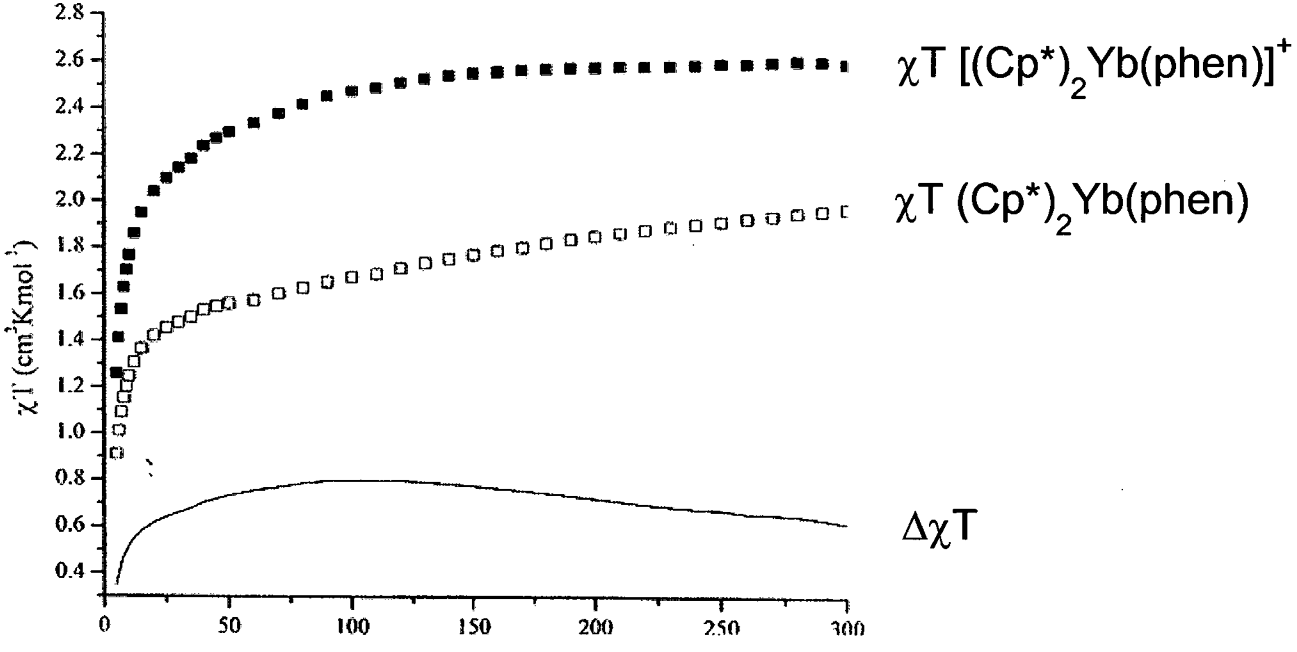
spherical f^{13} ion

C_{2v} ligand field

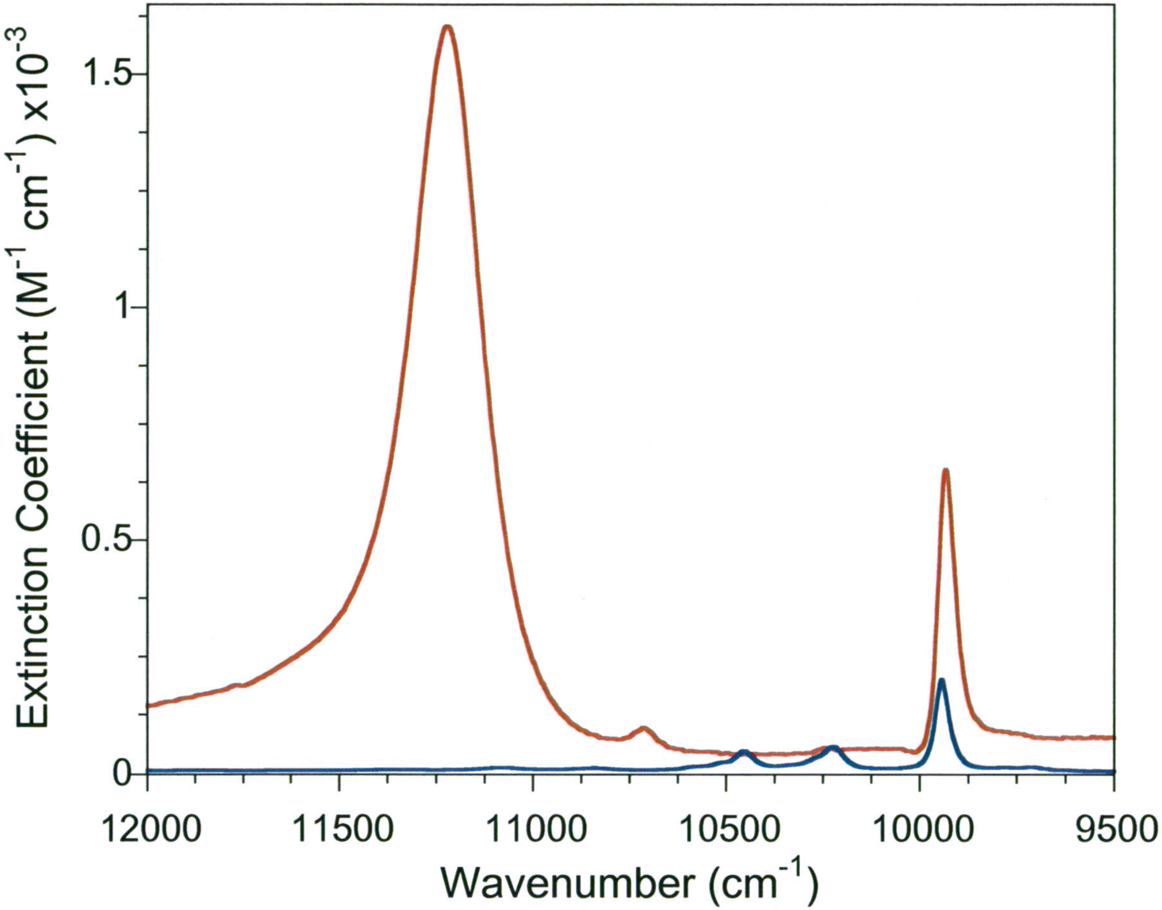
Each level of the $^2F_{7/2}$ term couples differently with the ligand-based spin, so the coupling varies with thermal populations of these levels

Experimental Determination of the Sign of *J*





f→f Bands of $(Cp^*)_2Yb(phen)$ and $[(Cp^*)_2Yb(phen)]^+$



The Kahn method assumes that the ligand-field splitting of the $^2F_{7/2}$ term is identical for $(Cp^*)_2Yb(L)$ and $[(Cp^*)_2Yb(L)]^+$

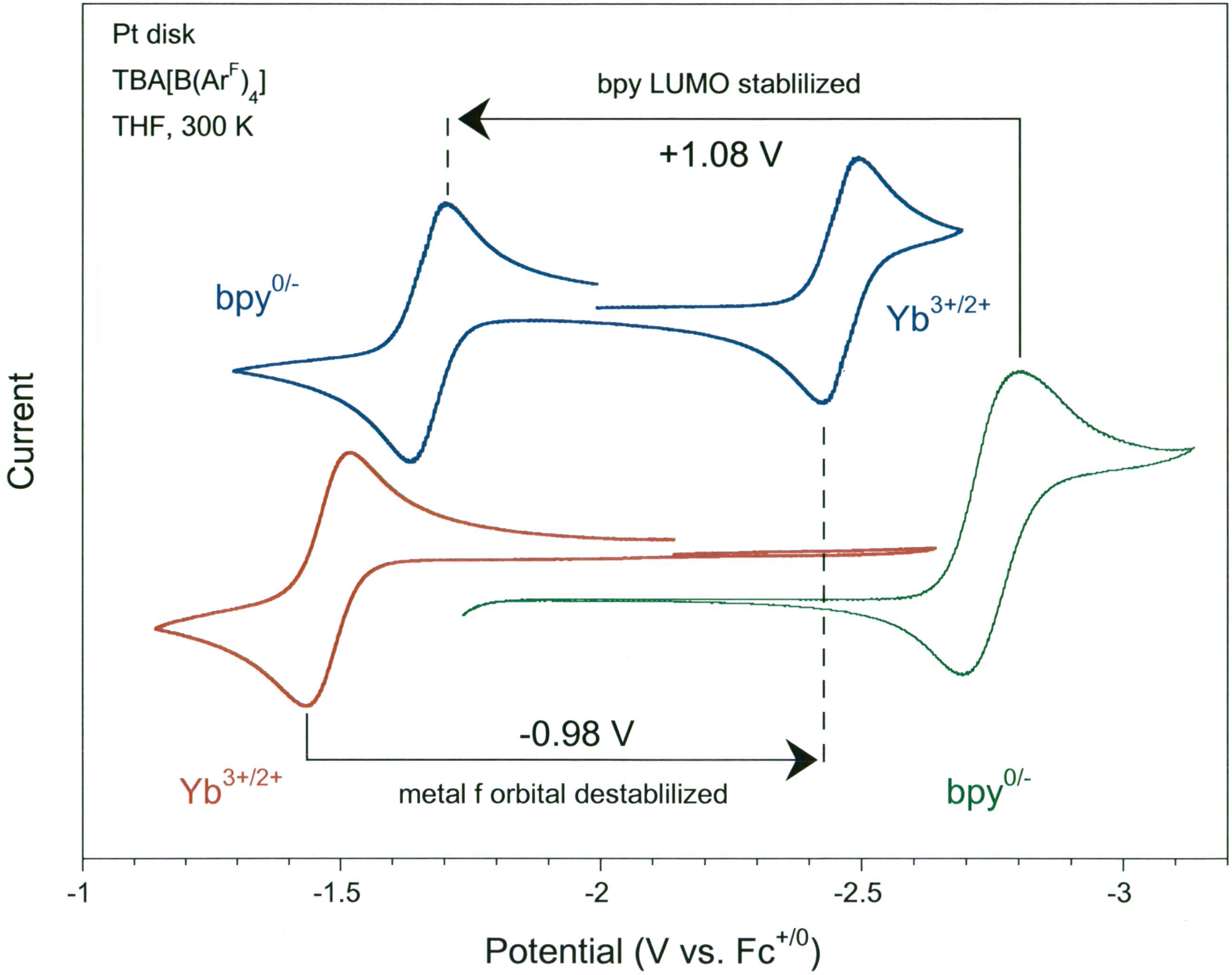
2 2

Goals of this Work

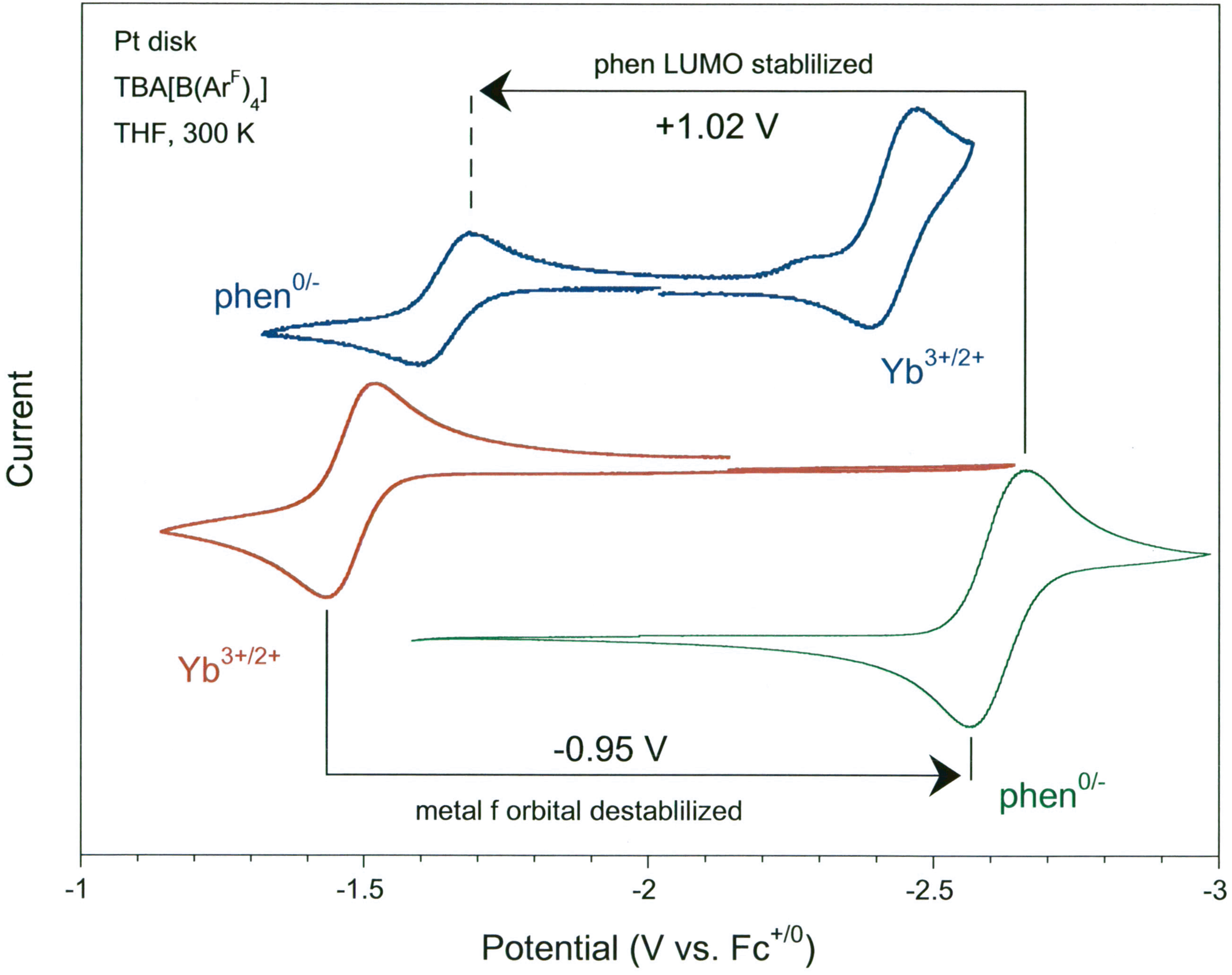
- Probe the charge-transfer ground states found in the bpy and phen adducts of ytterbocene using electrochemistry and electronic spectroscopy
- Characterize the ligand-field splittings of the $^2F_{7/2}$ ground-state term of Yb(III) for the bpy and phen adducts of ytterbocene
- Correlate the intensities of the $f \rightarrow f$ bands in the phen adduct with the spin–spin coupling
- Extend this electronic structural model to the newly prepared class of terpyridyl-based complexes $(Cp^*)_2Yb(tpy)$ and $(Cp^*)_2Yb(tpp)Yb(Cp^*)_2$

Da Re, Kuehl, Brown, Rocha, Bauer, John, Morris, Shreve, Sarrao *Inorg. Chem.*, **2003**, *42*, 5551–5559

Cyclic Voltammograms of $(Cp^*)_2Yb(THF)_n$, bpy, and $(Cp^*)_2Yb(bpy)$



Cyclic Voltammograms of $(Cp^*)_2Yb(THF)_n$, phen, and $(Cp^*)_2Yb(phen)$



Summary of Electrochemical Data for Ytterbocene–Imine Complexes

- The oxidation potential of f^{14} $(C_5Me_5)_2Yb(THF)_n$ is insufficient to reduce bpy or phen

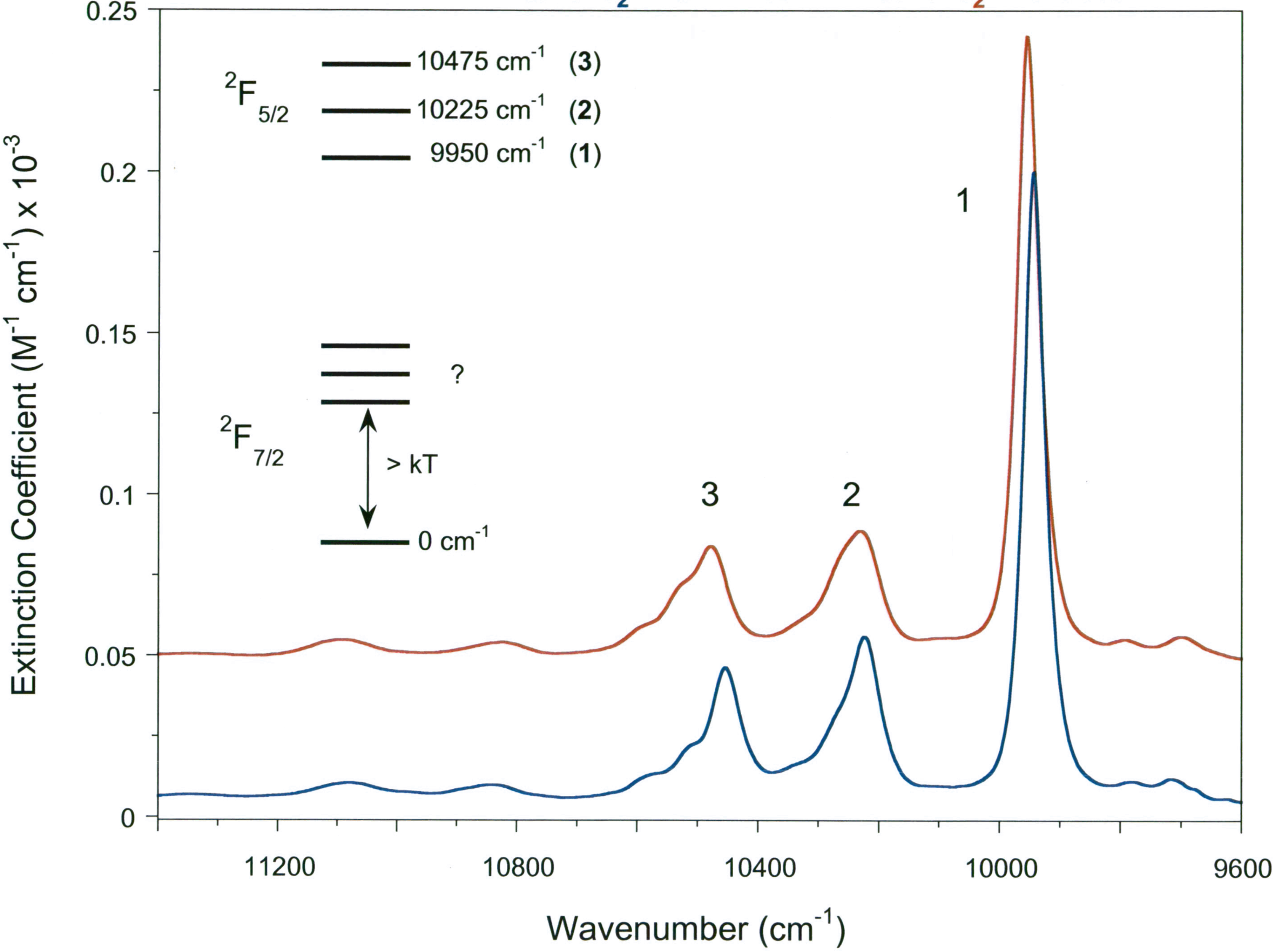
- The separation between the $L^{0/-}$ and $Yb^{3+/2+}$ redox waves (~ 0.8 V) for the bpy and phen adducts yields a comproportionation constant of $10^{13.4}$ for the following reaction between the fully oxidized and fully reduced forms:

$$(C_5Me_5)_2Yb^{III}(L^0) + (C_5Me_5)_2Yb^{II}(L^{1-}) = 2(C_5Me_5)_2Yb^{III}(L^{1-}) \qquad K_c = 10^{13.4}$$

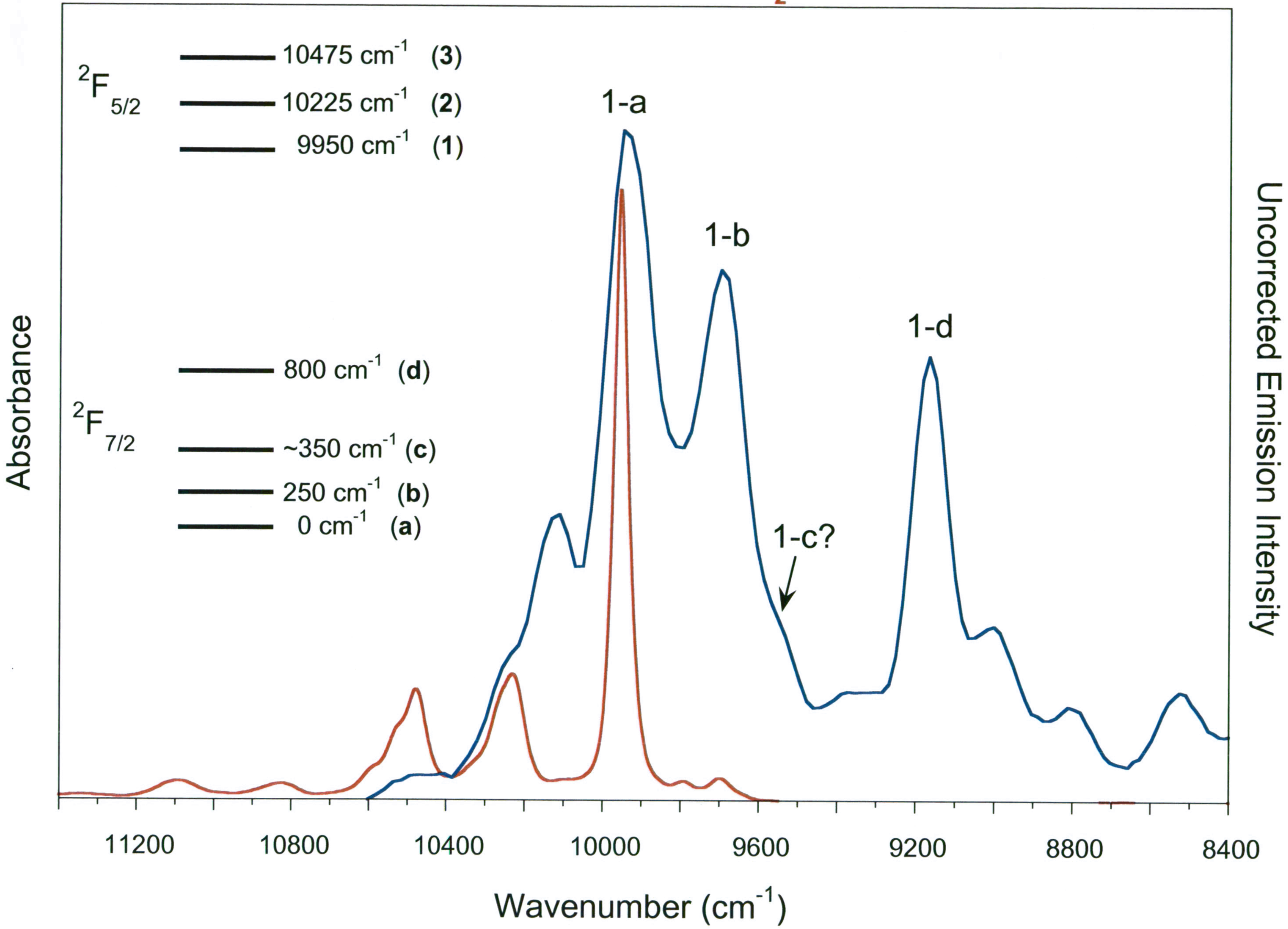
- This separation (~ 0.8 V) indicates that the $[(f)^{14}(\pi^*)^0]$ excited state lies less than 7000 cm^{-1} above the $[(f)^{13}(\pi^*)^1]$ ground state:

$$\Delta[|E_{1/2}(\text{diimine}^{0/1-}) - E_{1/2}(Yb^{3+/2+})|] \quad \approx \quad \Delta E\ \{[(f)^{13}(\pi^*)^1] \rightarrow [(f)^{14}(\pi^*)^0]\}$$

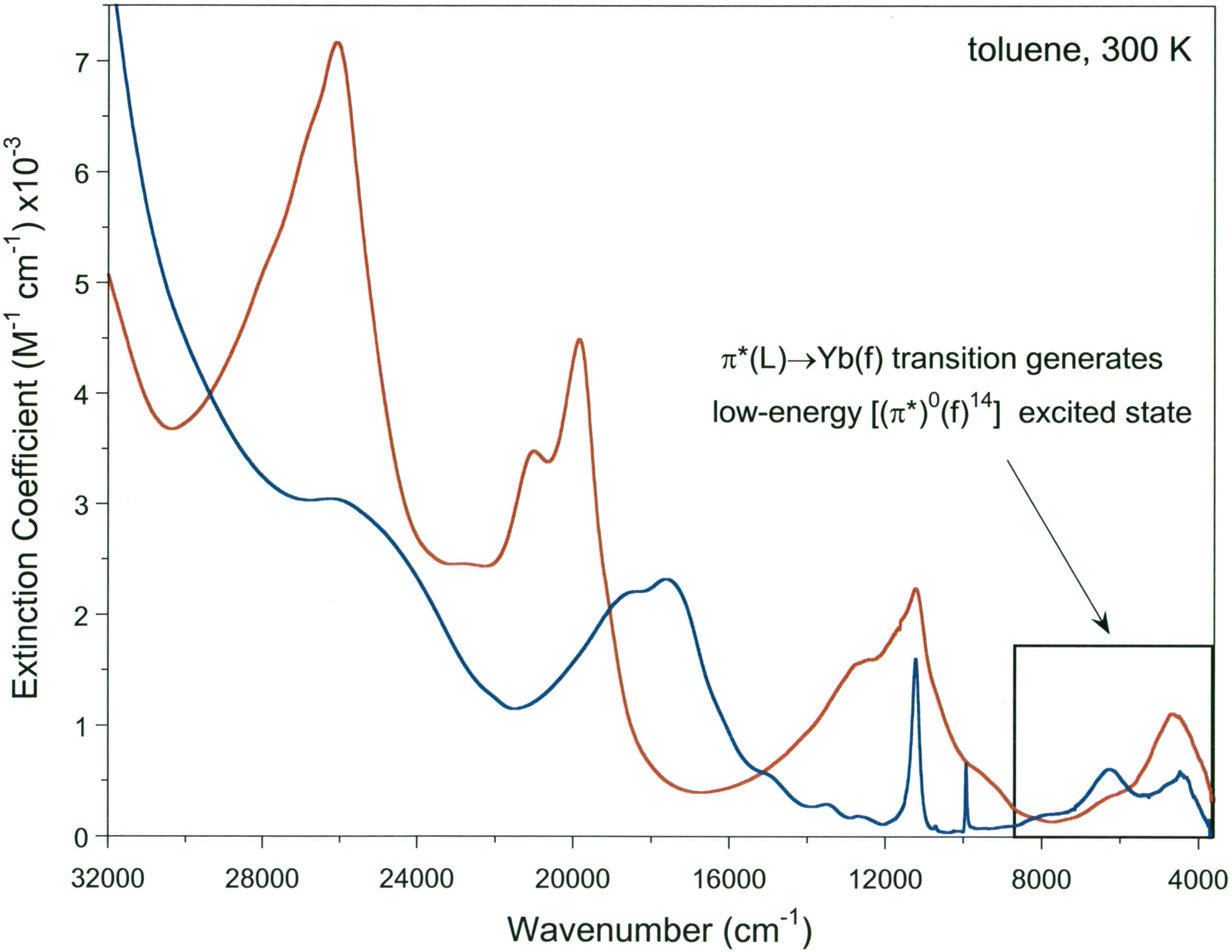
f → f Bands of $[(Cp^*)_2Yb(phen)]^+$ and $[(Cp^*)_2Yb(bpy)]^+$



f → f Bands of $[(Cp^*)_2Yb(bpy)]^+$

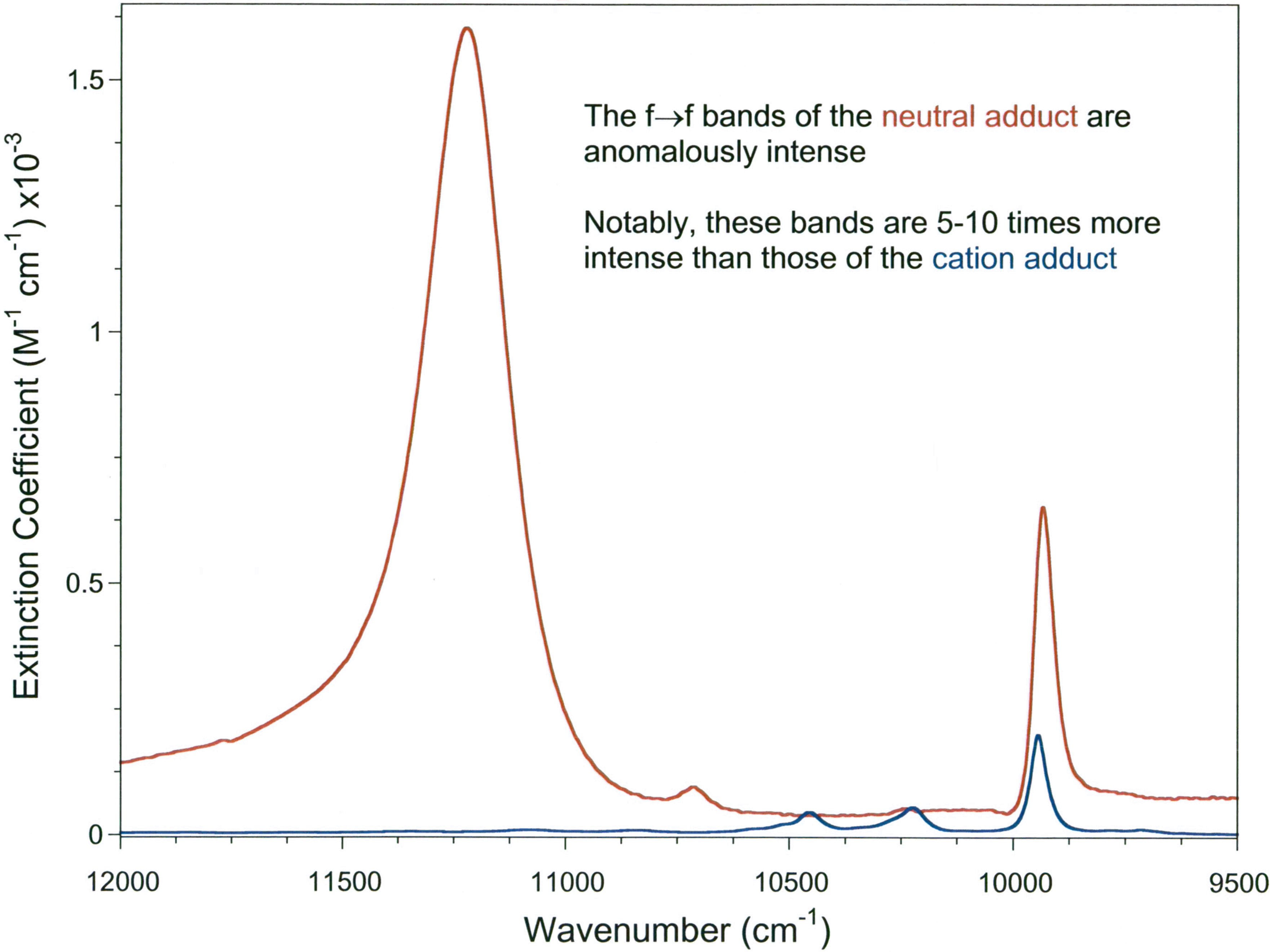


UV-Vis-NIR Absorption Spectra of (Cp*)$_2$Yb(bpy) and (Cp*)$_2$Yb(phen)



π*(L)→Yb(f) transition generates low-energy [(π*)^0(f)^{14}] excited state

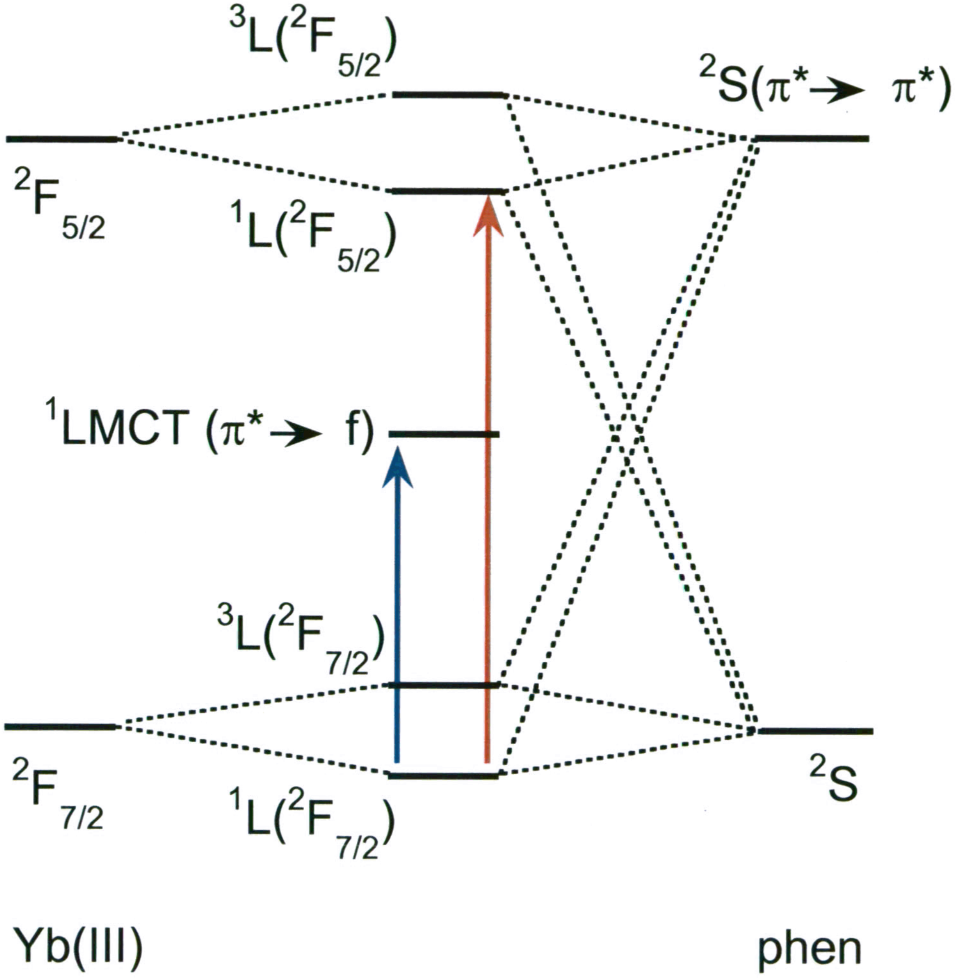
f→f Bands of $(Cp^*)_2Yb(phen)$ and $[(Cp^*)_2Yb(phen)]^+$

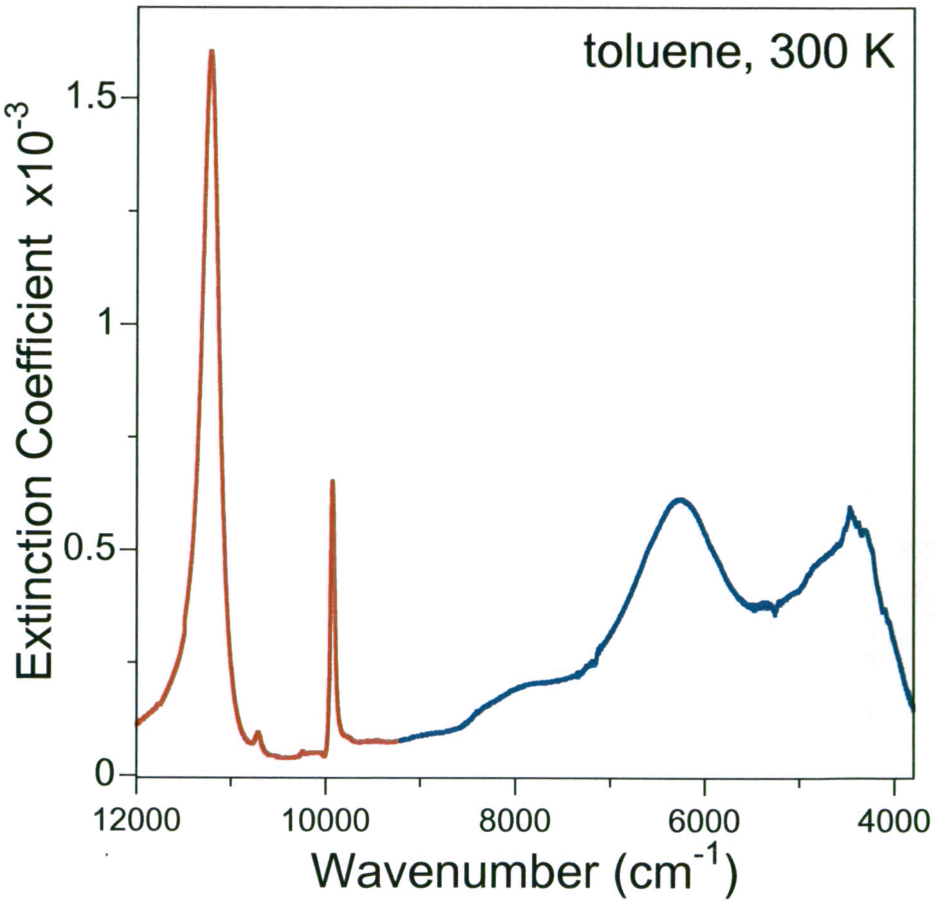


The f→f bands of the neutral adduct are anomalously intense

Notably, these bands are 5-10 times more intense than those of the cation adduct

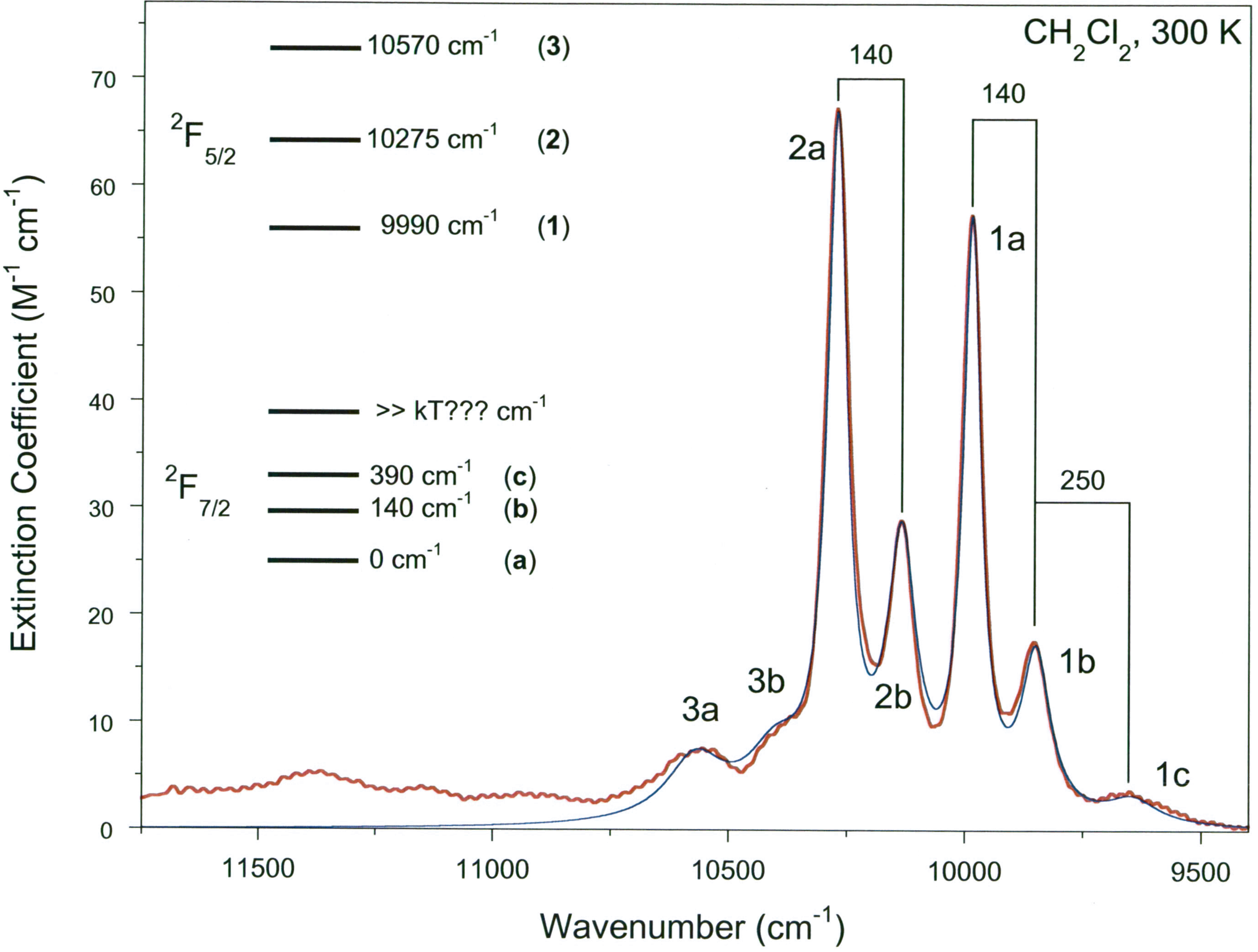
Proposed Intensity-Stealing Mechanism for the f →f Bands of $(Cp^*)_2Yb(phen)$



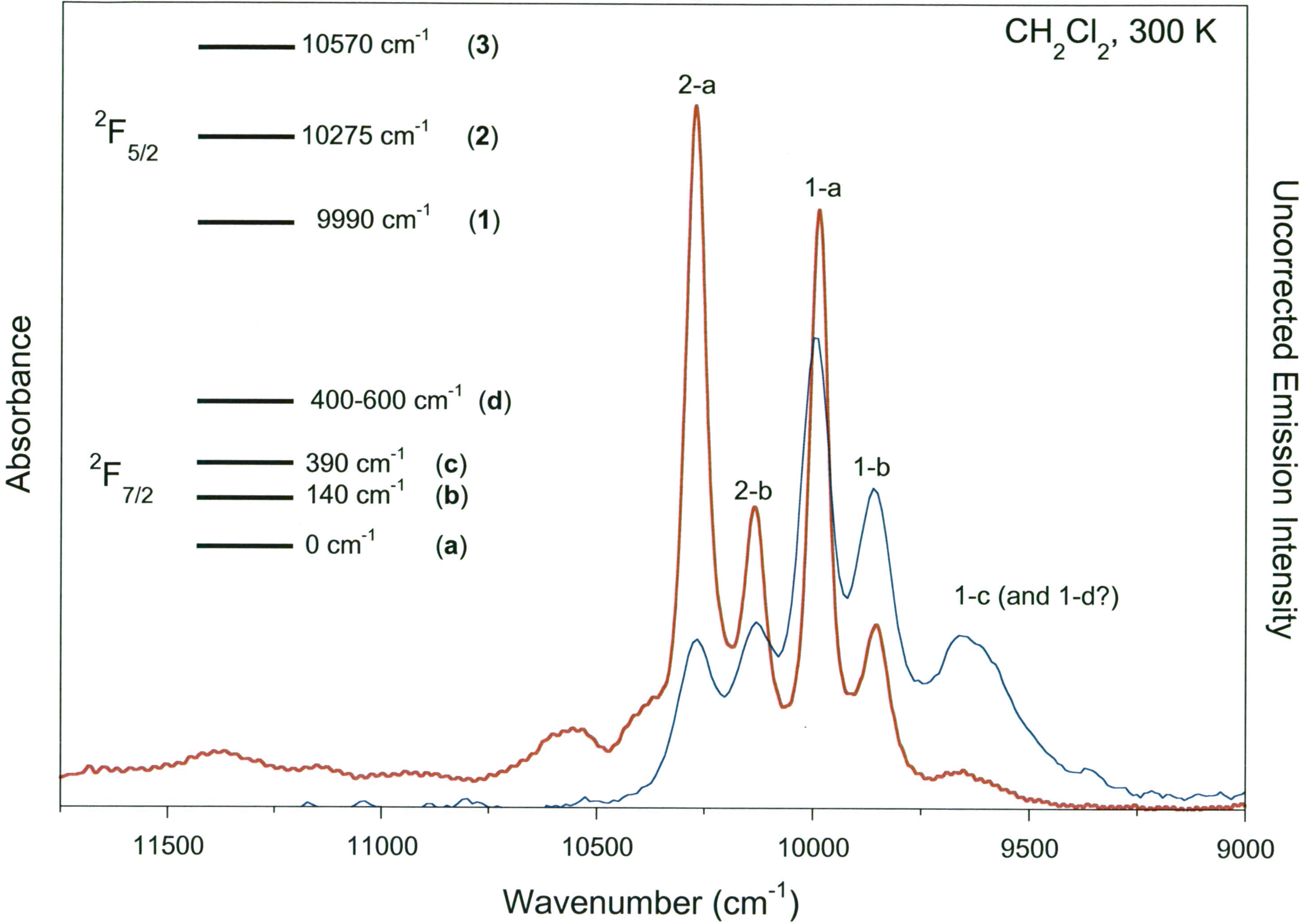


The f→f bands steal intensity from the π*(phen)→f(Yb) LMCT transition through mixing between ^2F and ^2S spin states

f → f Bands of $[(Cp^*)_2Yb(tpy)]^+$



f → f Bands of $[(Cp^*)_2Yb(tpy)]^+$



Conclusions

- The electrochemical data indicate that the diimine LUMO is stabilized and the Yb f orbital is destabilized each by ~1.0 V in the bpy and phen adducts of ytterbocene

- The ligand-field splitting of the ${}^2F_{7/2}$ term for the phen adduct is sensitive to the unpaired electron on the phen ligand

- The anomalous intensities of the f→ f bands can be explained using a model in which coupling between the ${}^2F$ and ${}^2S$ spins states allows the f→ f transitions to steal intensity from the low-energy π^*→ f LMCT transition

Da Re, Kuehl, Brown, Rocha, Bauer, John, Morris, Shreve, Sarrao *Inorg. Chem.*, **2003**, *42*, 5551–5559

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