Design and Applications
of
Luminescent Inorganic Complexes

Thesis by

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Abstract A series of Au(I) phosphine complexes were designed and synthesized to investigate the possibility of room temperature phosphorescence in solution from three different types of transitions: metal-to-ligand-charge-transfer in four coordinate monomers, $d\sigma^* \rightarrow p\sigma$ in Au(I) dimers, and $d \rightarrow p$ in two and three coordinate monomers. Solution emission was only observed from the three coordinate Au(I) complexes. The complex $Au_2(dcpe)_3^{2+}$ (dcpe = 1,2-bis-dicyclohexylphosphinoethane) has two isolated AuP_3 units and emits at 508 nm in acetonitrile solution with a lifetime of 21 μs and a quantum yield of 0.8 (366 nm excitation). The emission has been assigned as a $^1A_1 \leftarrow E'(^3E'')$ transition with the corresponding absorption band at 370 nm. The excited state is a powerful reductant capable of reducing aryl halides.

Electron transfer (ET) rates were studied from the excited $Au_2(dcpe)_3^{2+*}$ to a series of substituted pyridiniums (py^+). The low excited state reduction potential (Au(II)/Au(I)) of -2.3 V made it possible to study ET rates at driving forces as high as 2.1 eV. High driving force, bimolecular ET rates were also studied with $[Ir(cod)(pz)]_2$ (Ir_2; cod = cyclooctadiene, pz = pyrazole). The forward ET rates from Ir_2 to py^+ increase to the diffusion limit and remain diffusion limited at driving forces as high as 1.60 eV. The recombination ET rates from $py\cdot$ to Ir_2^+ show inverted behavior (rates decrease as the driving force increases) at driving forces > 0.85 eV, representing the first observation of inverted behavior for a bimolecular system. The discrepancy between the forward ET and recombination ET rates is explained by ET to low lying excited states.

On the basis of the emission observed from three coordinate Au(I) complexes, Au(I) was used as a probe for the coordination environment of the active site in *Pseudomonas auruginosa* azurin. The active site consists a copper center strongly bound to two histidines and a cysteine in a trigonal plane with a disputed axial interaction to Met121 3.1Å away. The Au(I)-WT-azurin is stable and emits at 580 nm, indicating that there is little or no interaction with the Met121.

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Chapter 1.

Design and Applications of Luminescent Inorganic Complexes: An Introduction

Introduction.

Luminescent complexes have provided a fascinating and diverse area of research. There are over 2000 papers on the classic inorganic complex $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) alone. The great interest in this complex varies from use as a means for transferring light energy into useful chemical energy[1] to a photo-activated trigger for studying reactions on a fast time scale[2] to a luminescent probe of the environment.[3] The extensive studies on $Ru(bpy)_3^{2+}$ and other luminescent inorganic complexes has produced a wealth of information concerning the fundamental process of emission, making it feasible to design luminescent complexes. This thesis will focus on the design and characterization of a luminescent gold complex and examine the application of such a luminescent inorganic species to photo-reduce substrates, study the fundamental process of electron transfer, and probe the nature of the geometry in the active site of a protein.

The desire to harness the light energy by photo-reducing a substrate places a few requirements on the emission characteristics. In order for the excited state of the luminescent species to interact with other compounds it is necessary that the complex emit in solution with a lifetime which exceeds the time required for the two molecules to diffuse together. For most solutions the required lifetime is >1 ns. Emission at room temperature is also beneficial to facilitate both the study and possible applications of the luminophore. To purposely design a compound with such characteristics it is necessary to understand some of the basic aspects of luminescence.

Luminescence occurs when an electron decays from an excited state to the ground state by emitting a photon. The electron generally achieves this excited state through the absorption of a photon. The spin states involved in the transition have a large effect on the lifetime of the excited state. The complexes addressed in this thesis have diamagnetic ground states. The excited state will either be a singlet state if the excited electron remains paired with the electron remaining in the highest occupied molecular orbital (HOMO) of the ground state or a triplet if the electrons have the same spin. The spin

allowed singlet to singlet process (fluorescence) occurs on a shorter time scale (ps-ns) than the spin forbidden triplet to singlet process (phosphorescence; ns-s) in which spin angular momentum is not conserved. Therefore, phosphorescence is the desired decay path for long-lived emission in solution. Accessing the triplet excited state directly is a problem because the spin forbidden nature of the transition means there will be no absorption band. The excited triplet state may be accessed from the higher energy singlet excited state (there will be a strong absorption band for the allowed singlet to singlet transition; ε>10,000), but this spin crossover rate is usually much slower than the allowed fluorescence decay. For these reasons most organic compounds which luminesce fluoresce brightly but show very little phosphorescence. The bright fluorescence makes them useful as laser dies, but they are not capable of bimolecular photochemistry.

Inorganic compounds with large metal centers provide a mechanism where spin angular momentum can couple with the orbital angular momentum. By changing orbital angular momentum concomitant with the spin angular momentum, the total angular momentum is conserved. As the spin change becomes more allowed, the spin crossover rate can become faster than fluorescence and the triplet excited state can be readily populated from the singlet excited state (Figure 1.1). Direct excitation to the triplet state becomes possible with measurable absorption bands (ε>10).[4] The lifetime of the phosphorescence state decreases as the triplet to singlet transition becomes more allowed, offsetting the increased efficiency of populating the triplet excited state. The balance between the lifetime of the triplet state and the quantum yield for phosphorescence can be tuned by varying the metal center. Spin orbit coupling effects increase considerably with the size of the metal atom. Some inorganic species with third row metals display phosphorescence with quantum yields as high as 0.8 and lifetimes in solution as long as 25 μs (substantially longer than the 1 ns required for bimolecular reactions).[5] The compounds in this thesis utilize the third row metals Au and Ir for their spin orbit coupling ability.

Although the presence of the heavy metal atom helps to access the triplet excited state, it does not ensure emission. One must also consider the nature of the orbitals involved in the emission process. When the electron absorbs a photon it may go directly into the lowest unoccupied molecular orbital (LUMO) or into one of many higher lying orbitals. Inter-conversions between different excited states occurs in ≈ 10 fs.[6] Emission on a picosecond or longer time scale will always come from the lowest energy excited state with singly occupied HOMO and LUMO orbitals (Figure 1.1). By engineering the appropriate HOMO and LUMO it is possible to design low-energy transitions which are more likely to lead to long lived excited states. One of the reasons for the vast interest in $Ru(bpy)_3^{2+}$ is that it has a long-lived excited state (600 ns) at room temperature in acetonitrile. The emission of $Ru(bpy)_3^{2+}$ transfers an electron from the ligand centered π^* (LUMO) to the metal centered d orbital (HOMO). The metal to ligand charge transfer (MLCT) transition is vital to the emission. It has been demonstrated that substituent changes on the bpy ligands which raise the ligand π^* orbital and bring the MLCT transition close in energy to the higher lying ligand field transition result in a shorter lifetime and an increase in photo-dissociation.[7] These observations are even more pronounced for the isoelectronic $W(CO)_5X$ (X is a substituted pyridinium) complexes,[8] and are believed to be a result of a thermal equilibrium between the excited MLCT state and the excited ligand field state. As the two excited states become closer in energy, the excited ligand field state becomes occupied and provides the pathway for photo-dissociation.

The fact that d-d absorption transitions often lead to photo-dissociation instead of luminescence is expected from ligand field theory considerations. The energy of the d orbitals is determined by their interactions with the bonding electrons form the ligands. The lower energy orbitals are generally non-bonding and the higher energy d orbitals are M-L anti-bonding. In $Ru(bpy)_3^{2+}$ the octahedral ligand environment splits the d orbitals into two degenerate sets. The low energy non bonding (or π back bonding) orbitals are

Figure 1.1. Jablonski diagram: S_0 is the ground state singlet; S_1 is the lowest energy excited state singlet; S_2 is a higher energy excited state singlet; T_1 is the lowest energy excited state triplet; k_F is the fluorescence decay rate; k_{NR} is the non-radiative decay rate; k_P is the phosphorescence decay rate; k_{SS} is the singlet to singlet interconversion rate; k_{ST} is the singlet to triplet crossover rate.

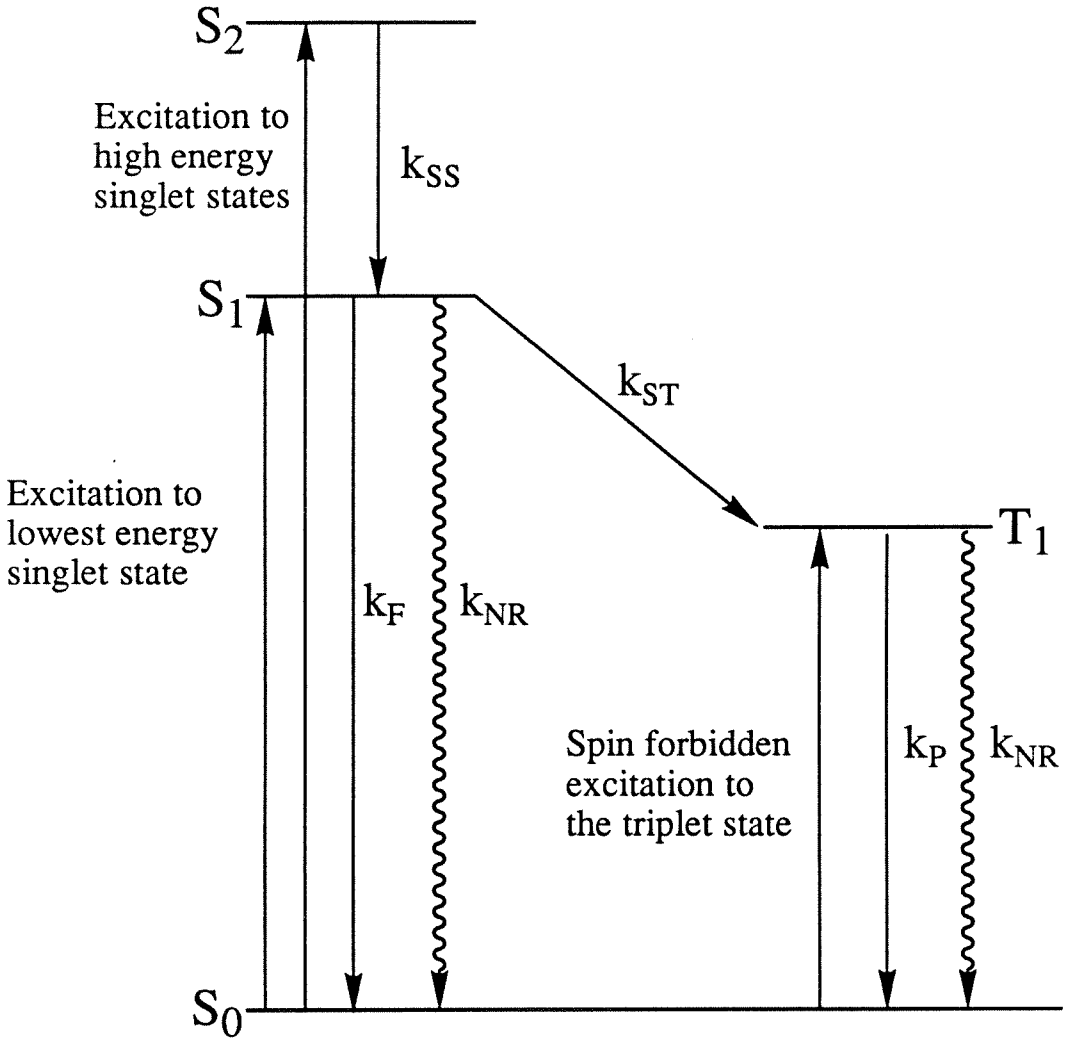
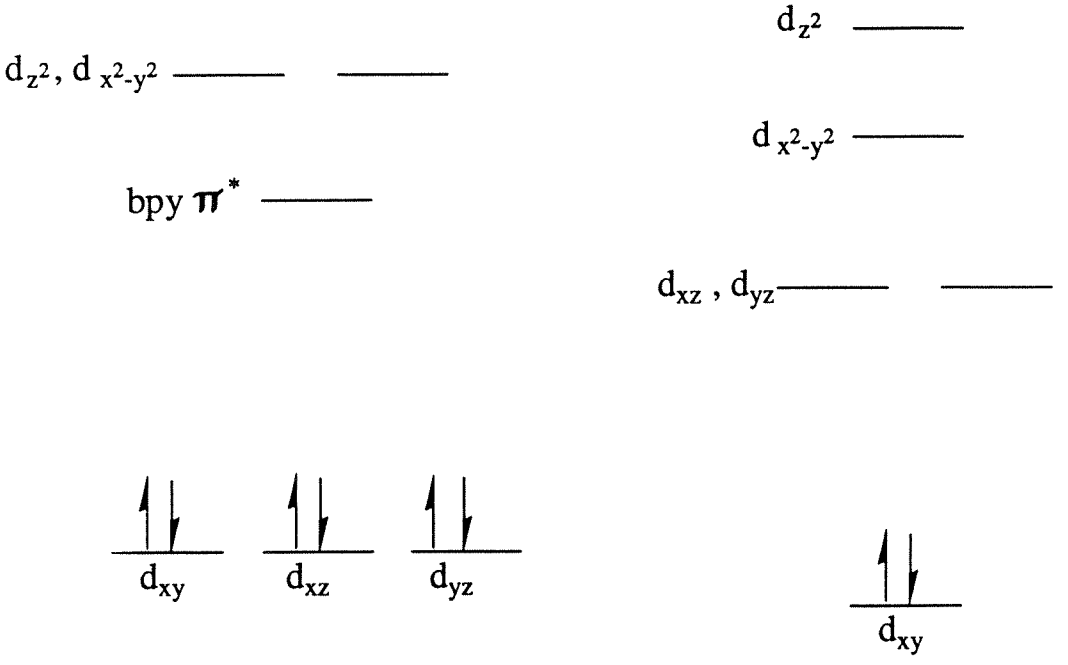

S2
Excitation to high energy singlet states
kSS
S1
kST
Excitation to lowest energy singlet state
kF
kNR
T1
Spin forbidden excitation to the triplet state
kP
kNR
S0

Figure 1.2. Orbital energy diagrams of $Ru(bpy)_3^{2+}$ and $Re(O)_2(py)_4^{+}$.


d_{z^2}
d_{z^2}, $d_{x^2-y^2}$
$d_{x^2-y^2}$
bpy π^*
d_{xz}, d_{yz}
d_{xy}
d_{xz}
d_{yz}
d_{xy}
2+
+
Ru
Re
N
O
py

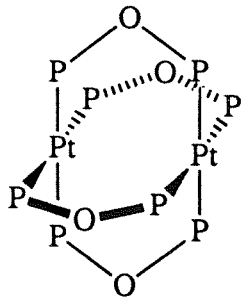
d_{xz}, d_{yz}, and d_{xy}. The high lying d_z^2 and $d_{x^2-y^2}$ orbitals are σ anti-bonding (Figure 1.2). The six d electrons of the Ru^{2+} center completely fill the non-bonding d orbitals. Ligand field excitation takes a d electron from a non-bonding orbital and places it into an anti-bonding orbital, causing the metal ligand bond to weaken enough to dissociate.

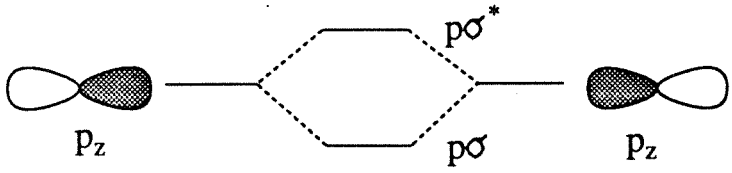
Emission in solution from a d-d transition is observed in multiply bonded species such as metal oxos (M=O) and metal nitridos (M=N). The compound $Re(py)_4O_2$ emits in acetonitrile solution with a lifetime of 10 μs.[8] The emission transition of the d^2 species has been assigned as a $d_{xy} \leftarrow d_{xz}\, d_{yz}$ transition (Figure 1.2). The d_{xy} (HOMO) is a non-bonding orbital and the degenerate d_{xz}, d_{yz} (LUMOs) are π^* anti-bonding orbitals. When the electron is excited into the π^* orbital the π bond of the strong metal oxo double bond is weakened, but the σ bond remains intact preventing dissociation.

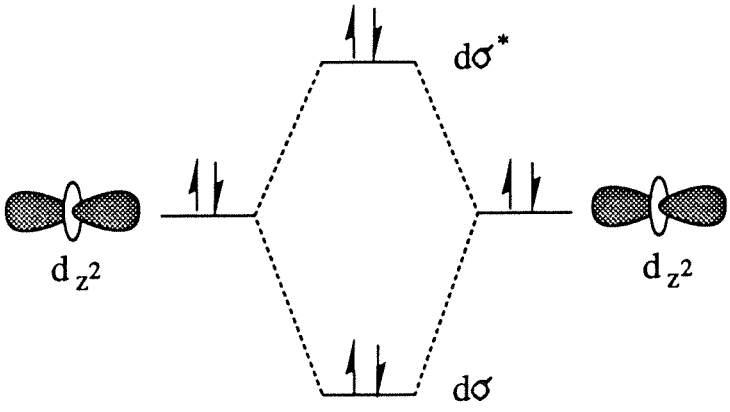
Room temperature luminescence in solution has been observed for a variety of d^8-d^8 dimers. One such dimer is the completely inorganic complex PtPOP.[5] The complex consists of two square planar Pt d^8 centers brought together in a face-to-face arrangement. The filled d_z^2 orbitals interact to form a bonding $d\sigma$ orbital and an anti-bonding $d\sigma^*$ orbital. The empty p_z orbitals interact in an analogous manner to form a bonding $p\sigma$ and an anti-bonding $p\sigma^*$ orbital (Figure 1.3). The lowest energy absorption transition is a $d\sigma^* \rightarrow p\sigma$ transition. This transition formally removes an electron from an anti-bonding orbital and places it into a bonding orbital, resulting in a stronger metal - metal bond. One can observe the increase in bond strength by excited state raman; the metal -metal bond stretch shifts from 118 cm^{-1} for the ground state to 156 cm^{-1} for the excited state.[10] The Pt dimer emits in solution with a lifetime of 25 μs.

Two other types of transitions commonly observed are ligand to metal charge transfer (LMCT) transitions and intraligand transitions. The LMCT transition promotes an electron from a ligand based orbital to a metal centered orbital. The excited state orbital of an LMCT transition is usually a metal centered d orbital. As in the d-d transitions one must be careful to ensure that the metal orbital is non-bonding to observe

Figure 1.3. Orbital energy diagram of PtPOP.


O
P
P
O
P
P
P
Pt
Pt
P
O
P
P
P
O


pσ*
pz
pσ
pz

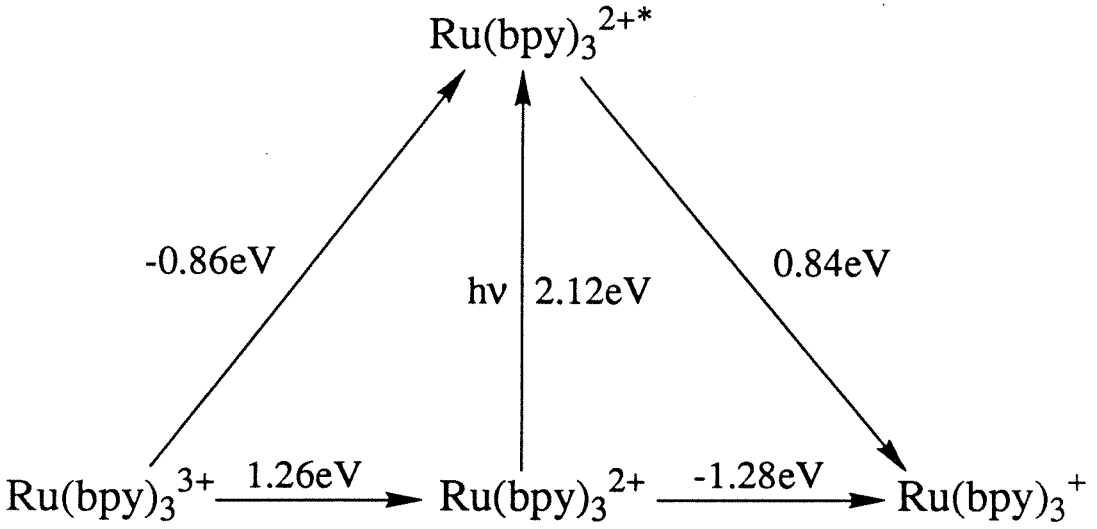

dσ*
dz2
dz2
dσ


Pt
Pt

long-lived luminescence. Metals are also known to perturb intraligand transitions. In terms of luminescence, ligands that only fluoresce on their own have been observed to phosphoresce when ligated to a metal center. This heavy atom effect is a result of the spin orbit coupling mentioned earlier.

The research discussed in the second chapter started with the goal of designing a luminescent inorganic complex capable of using the absorbed light energy to reduce a substrate. Gold(I) was chosen as the metal center for a number of reasons: it is a third row metal with efficient spin orbit coupling for accessing the triplet excited state; gold(I) has a d^{10} configuration so none of the dissociative d-d transitions are possible; the oxidation of Au(I) produces Au(III) in a two electron process. Understanding the benefits of this last feature requires an examination of the process of photo-reduction. When a molecule absorbs a photon, the light energy stored in the excited state makes the complex both a better oxidant and a better reductant than the ground state. When the ground state acts as an oxidant the electron from the substrate must go into the LUMO, but in the excited state the substrate electron can fill the hole in the HOMO. In a similar manner the excited state acts as a better reductant because the electron transferred from the complex is the excited electron in the LUMO; the ground state must transfer an electron from the lower energy HOMO. Ruthenium trisbipyridine is an example of a complex which is stable in the ground state with respect to both oxidation to Ru^{3+} (ΔG (Ru^{2+}/Ru^{3+}) = 1.26 eV) and reduction to Ru^{1+} (ΔG (Ru^{2+}/Ru^{+}) = 1.28 eV). In the excited state it can act as both an oxidant (ΔG (Ru^{2+*}/Ru^{+}) = -0.84 eV) and a reductant (ΔG (Ru^{2+*}/Ru^{3+}) = -0.86 eV; Figure 1.4).[3] The products of the photo-induced electron transfer can thermally react to regenerate the original ground state reactants, posing a major problem for converting sunlight energy into storable chemical energy. This unwanted back electron transfer will always be exoergonic for solar energy conversion processes, so the reaction must somehow be slowed kinetically. The two electron reduction capacity of Au(I) is one way to slow the back reaction. An excited Au(I) species can reduce a substrate by

Figure 1.4. Modified Latimer Diagram of $Ru(bpy)_3^{2+}$.


Ru(bpy)3 2+*
-0.86eV
hν 2.12eV
0.84eV
Ru(bpy)3 3+
1.26eV
Ru(bpy)3 2+
-1.28eV
Ru(bpy)3 +

one electron and generate transient unstable Au(II) complex. The Au(II) complex rapidly disproportionates to Au(I) and Au(III) or donates a second electron to another molecule of substrate before back electron transfer to the Au(II) can occur (Figure 1.5). The two electron transfer to Au(III) is kinetically slow since it must proceed through the unstable Au(II) state. Alternatively, the two electron transfer from Au(I) can be carried out on a single substrate molecule in conjunction with transfer of an atom, such as Cl, from the substrate (R1). Such atom abstraction has a slow back rate because the atom must

$$R\text{-}Cl + M^n \rightarrow R\text{-}Cl^- + M^{n+1}$$

$$R\text{-}Cl^- + M^{n+1} \rightarrow Cl\text{-}M^n + R$$

$$Cl\text{-}M^n + R\cdot \rightarrow Cl\text{-}M^{n+1} + R^- \qquad \text{R1}$$

dissociate from the metal center.

Chapter three takes advantage of luminescence by using it as a trigger to initiate electron transfer. Electron transfer (ET) is the fundamental process by which all molecules are reduced or oxidized. Mammalian respiration, nitrogen fixation and photosynthesis are just three of the myriad of biological processes which require ET.

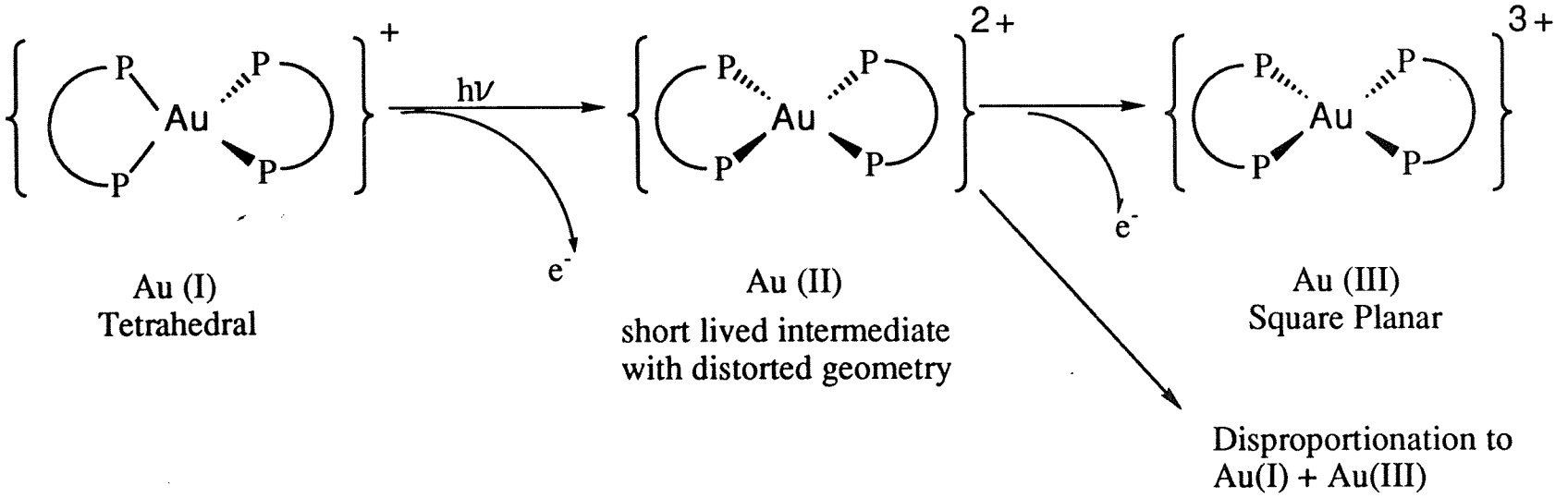
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$N_2 + 10H^+ + 8e^- \rightarrow 2NH_4^+ + H_2$$

$$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$$

The ET rates can take place in less than a nanosecond, so conventional stop flow techniques that require mixing time for the reaction mixture to become homogeneous are too slow for studying ET. Long-lived excited states, however, provide a way to generate a homogeneous reaction mixture in the time required to absorb a photon ≈ fs. As an example, one can study ET from $Ru(bpy)_3^{2+*}$ to N-methyl pyridinium by first making a solution of $Ru(bpy)_3^{2+}$ and N-methyl pyridinium; no reaction occurs initially because the ground state ruthenium complex is not a powerful enough reductant to reduce the pyridinium. Absorption of light from a laser pulse produces $Ru(bpy)_3^{2+*}$ in ≈ fs, allowing one to study the subsequent ET to the pyridinium. The limitation for observing

Figure 1.5. Scheme for the two electron transfer from Au(I).



Step 1) Absorption of light leads to an excited state complex that transfers one electron to produce an unstable gold (II) compound

Step 2) The unstable gold (II) compound thermally transfers a second electron

fast ET now becomes the duration of the laser pulse. This type of photo-triggering has enabled researchers to study ET in proteins[11] as well as many of the short-lived intermediates in photosynthesis.[12]

Photosynthesis begins with the absorption of light by a chlorophyll molecule. The excited electron then travels 17 Å to a bacteria pheophiton in 3 ps. The electron quickly moves on to quinone A in 200 ps (Figure 1.6).[12] This second step must compete with the highly exoergonic back reaction which produces the original ground states. The remarkable aspect of photosynthesis is that the reaction to the ground state is much slower (12 ns) than either of the first two forward ET steps despite the fact that there is a higher driving force, $-\Delta G$, for the back reaction. Understanding the long-lived charge transfer state which results from the slow back ET rate is crucial to the development of artificial photosynthesis. One hypothesis suggests poor coupling between the HOMO of the chlorophyll and the orbital of the bacteria pheophiton is responsible for the slow back rate. To account for the fast forward ET rate, the LUMO of the chlorophyll must be highly coupled to the bacteria pheophiton orbital. The difference in rates would require the coupling of the bacteria pheophiton orbital to the π^* orbital of the chlorophyll to be an order of magnitude greater than the coupling to the π orbital of the chlorophyll. The large coupling difference between two spatially similar orbitals is difficult to imagine.

A second explanation comes from the Marcus theory for ET,[13] which predicts that the ET rates will increase exponentially as the driving force increase, reach a maximum, and then decrease exponentially as the driving force continues to increase (Figure 1.7). If the forward ET reaction is near the maximum of the Marcus curve then the higher driving force back reaction will be much slower. The maximum of the Marcus curve occurs when the driving force is equal to the reorganization energy. The reorganization energy is comprised of the energy required for the solvent dipoles to reorient as the charge transfers and the energy required for any bond length or bond angle changes (Figure 1.8). The photosynthetic center lies within the cell membrane so that the "solvent" is

Figure 1.6. Reaction steps of photosynthesis: P is the chlorophyll; Bph is the bacteria pheophiton; Q_a is quinone A; Q_b is quinone B.

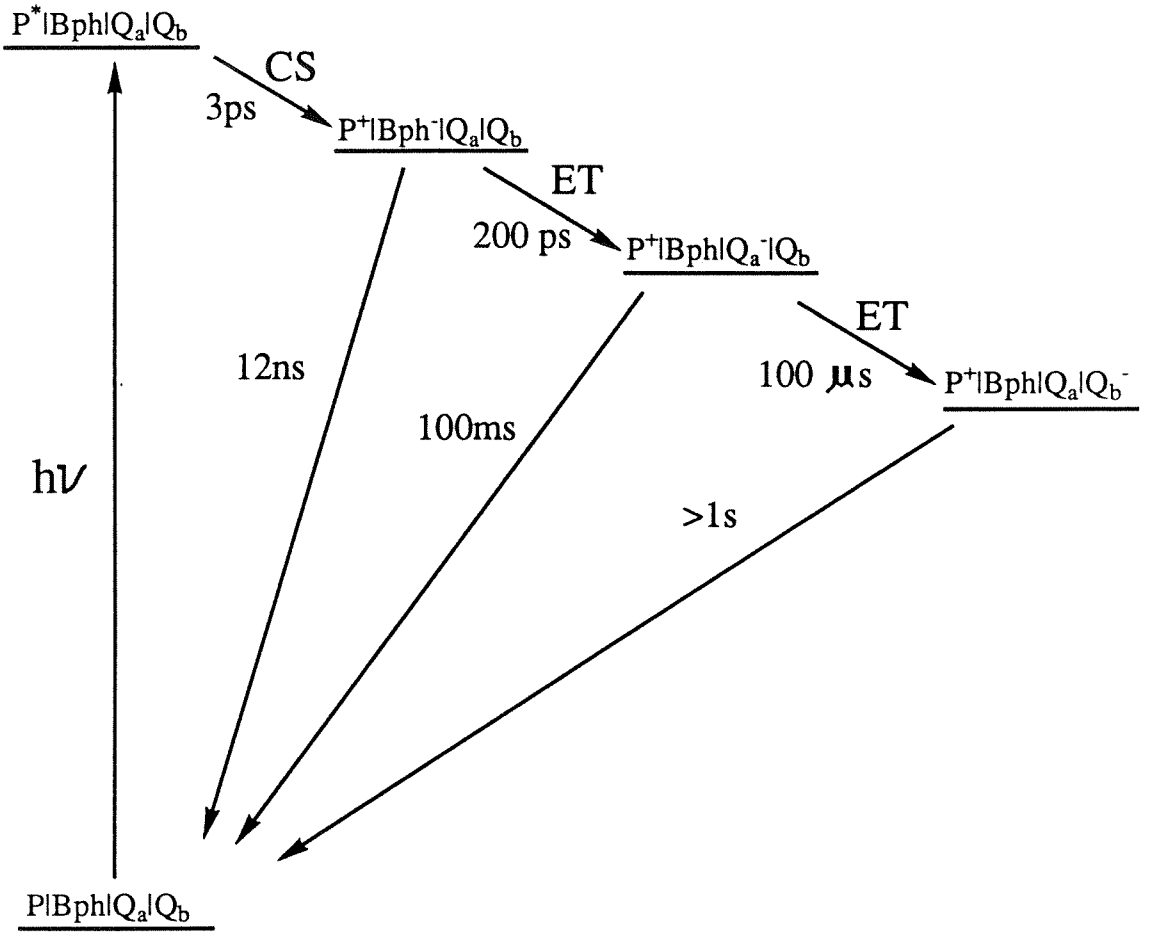

P*|Bph|Qa|Qb
CS
3ps
P+|Bph-|Qa|Qb
ET
200 ps
P+|Bph|Qa-|Qb
ET
100 μs
P+|Bph|Qa|Qb-
12ns
100ms
>1s
hν
P|Bph|Qa|Qb

Figure 1.7. Marcus curve: k_{max} is the maximum electron transfer rate.

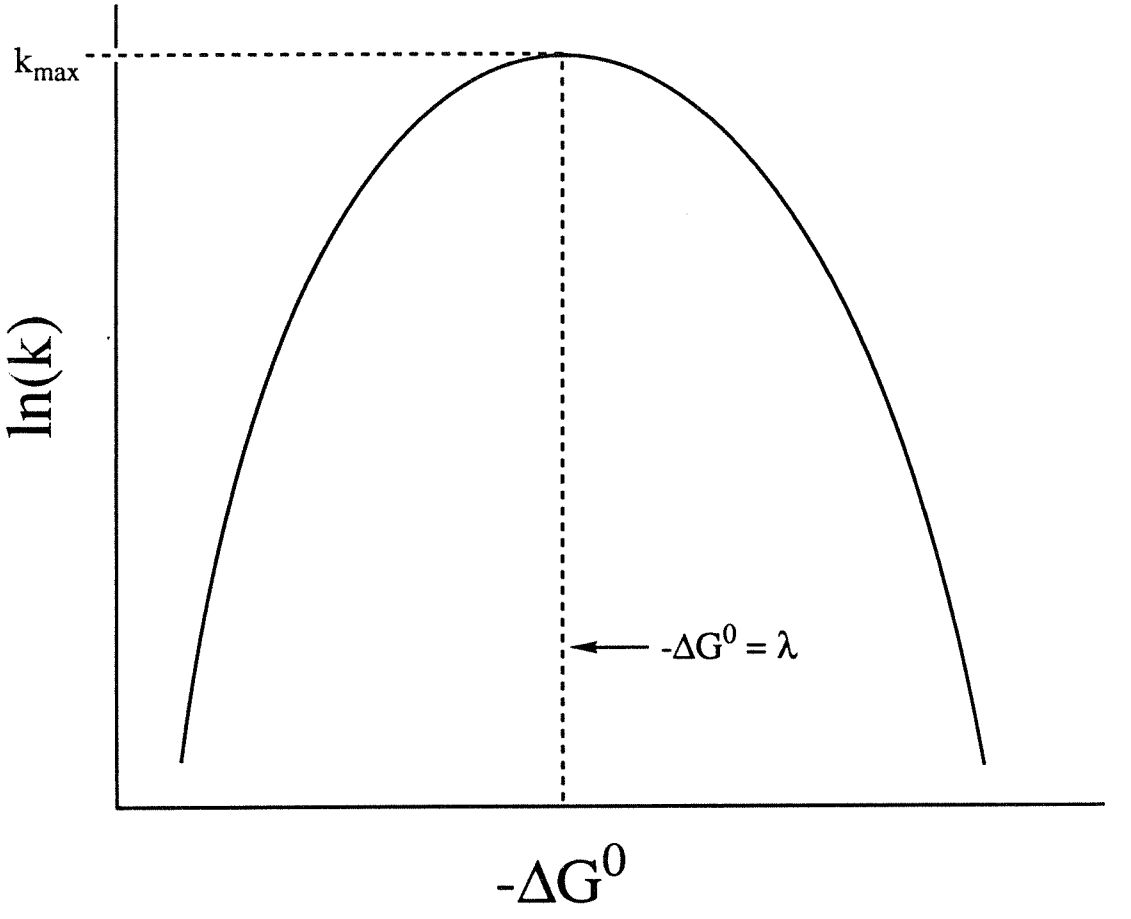
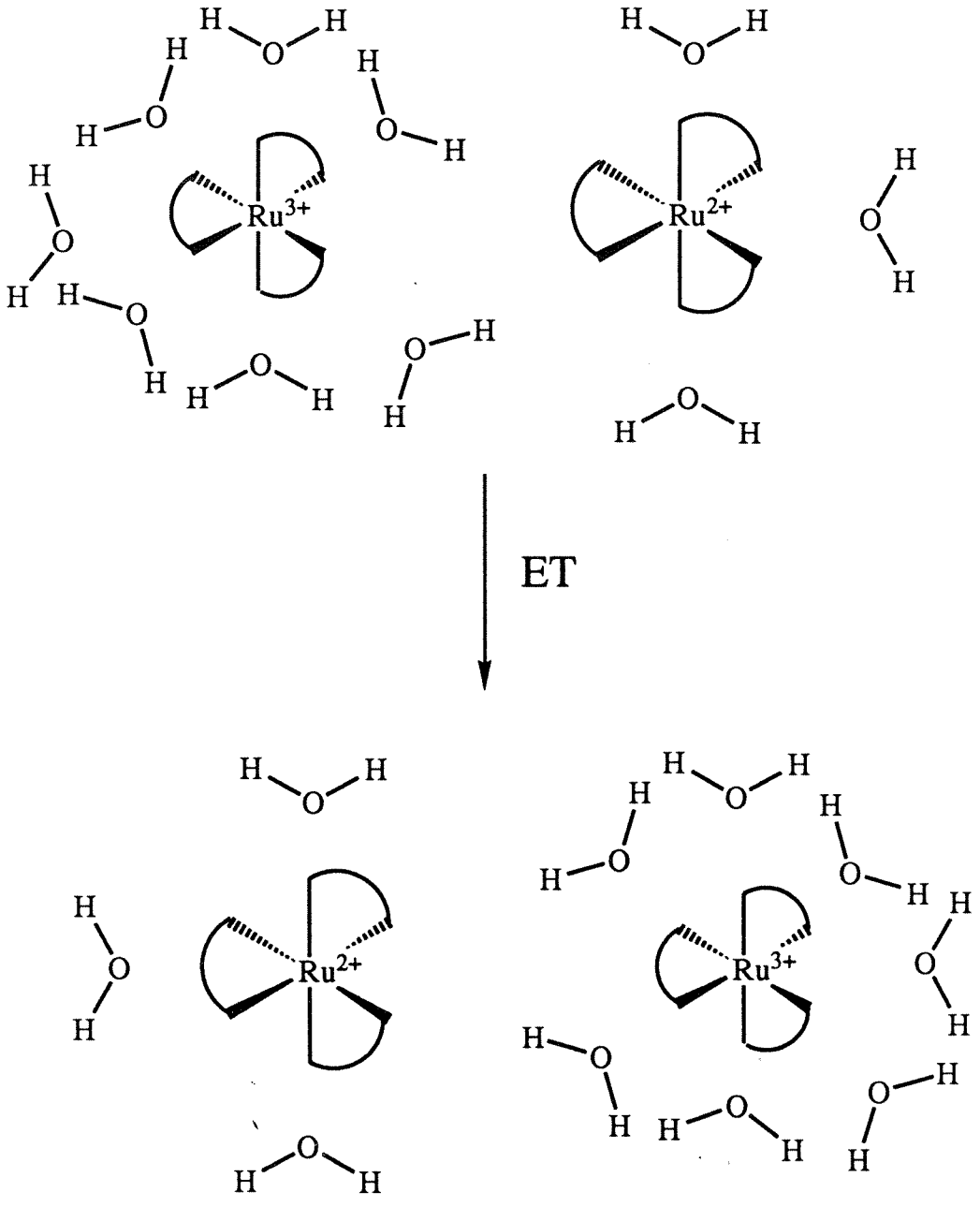

k_{max}
ln(k)
$-\Delta G^0 = \lambda$
$-\Delta G^0$

Figure 1.8. Reorganization energy.


Ru3+
Ru2+
ET
Ru2+
Ru3+

essentially fixed in place. The lack of solvent reorganization leads to a low total reorganization energy (λ) and a very narrow Marcus curve (Figure 1.9). The fast initial ET step in photosynthesis can now be explained if the relatively low driving force is $\approx \lambda$ and lies at the top of the Marcus curve. The slow back rate is explained by the fact that it has a much higher driving force and will lie deep in the inverted part of the curve. Chapter three discusses the use of luminescent metal complexes to experimentally investigate ET rates at high driving force and verify the predicted inverted region.

For a luminescent complex, the lifetime, the emission maximum, and the intensity of the emission are all affected by the environment around the compound. The $ReO_2(py)_4^+$ complex mentioned earlier emits strongly in an acetonitrile solution, but shows no evidence of emission in water; it is believed that the excited is deactivated through hydrogen bonding between a water proton and the oxo of the $ReO_2(py)_4^+$. The phosphorescence lifetime of many inorganic complexes is drastically shortened in the presence of oxygen.[14] The fact that luminescence can change drastically depending on the environment makes luminescent compounds useful as probes. Ethidium bromide is used as a marker for the presence of DNA in DNA gel separations because it fluoresces brightly when intercalated into DNA, but does not emit in water. Chapter four discusses the use of an emissive gold complex to probe the coordination site of azurin. Azurin is a small blue copper protein that functions as an ET protein (Figure 1.10). The active site is a type I copper site with a Cu^{2+} ion strongly bound to a cysteine and two histidines. The blue color arises from a cysteine to copper charge transfer band at 628 nm.[9] When the protein accepts an electron the Cu^{2+} is reduced to Cu^+, and the protein loses its blue color as the cysteine to copper charge transfer band moves to the UV. Despite crystal structures of both the reduced an oxidized forms of the protein,[14] there is still some controversy in the literature as to how much the copper center interacts with the methionine at position 121. The crystal structure places the methionine 3.1 Å from the copper. Solomon and coworkers have used the crystal structure coordinates to perform

Figure 1.9. Theoretical Marcus curve for the photosynthetic center.

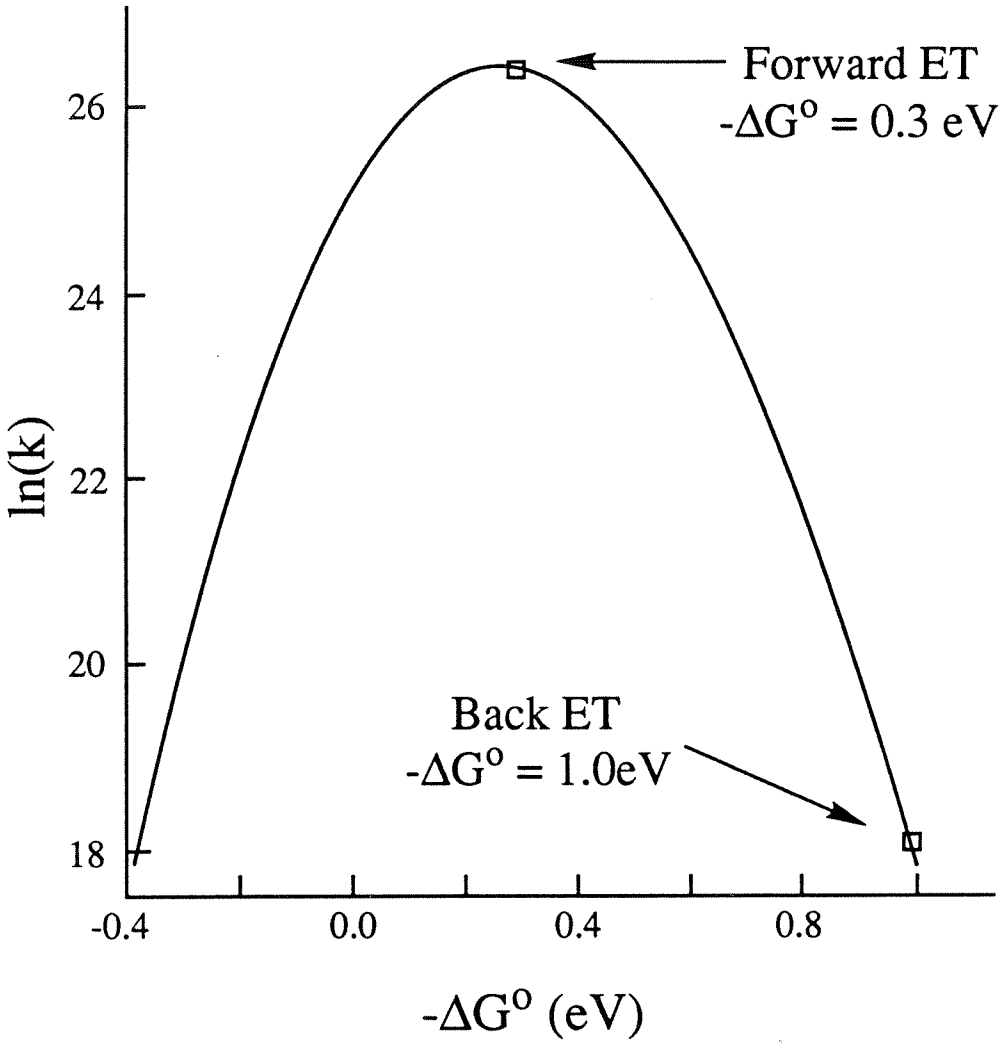
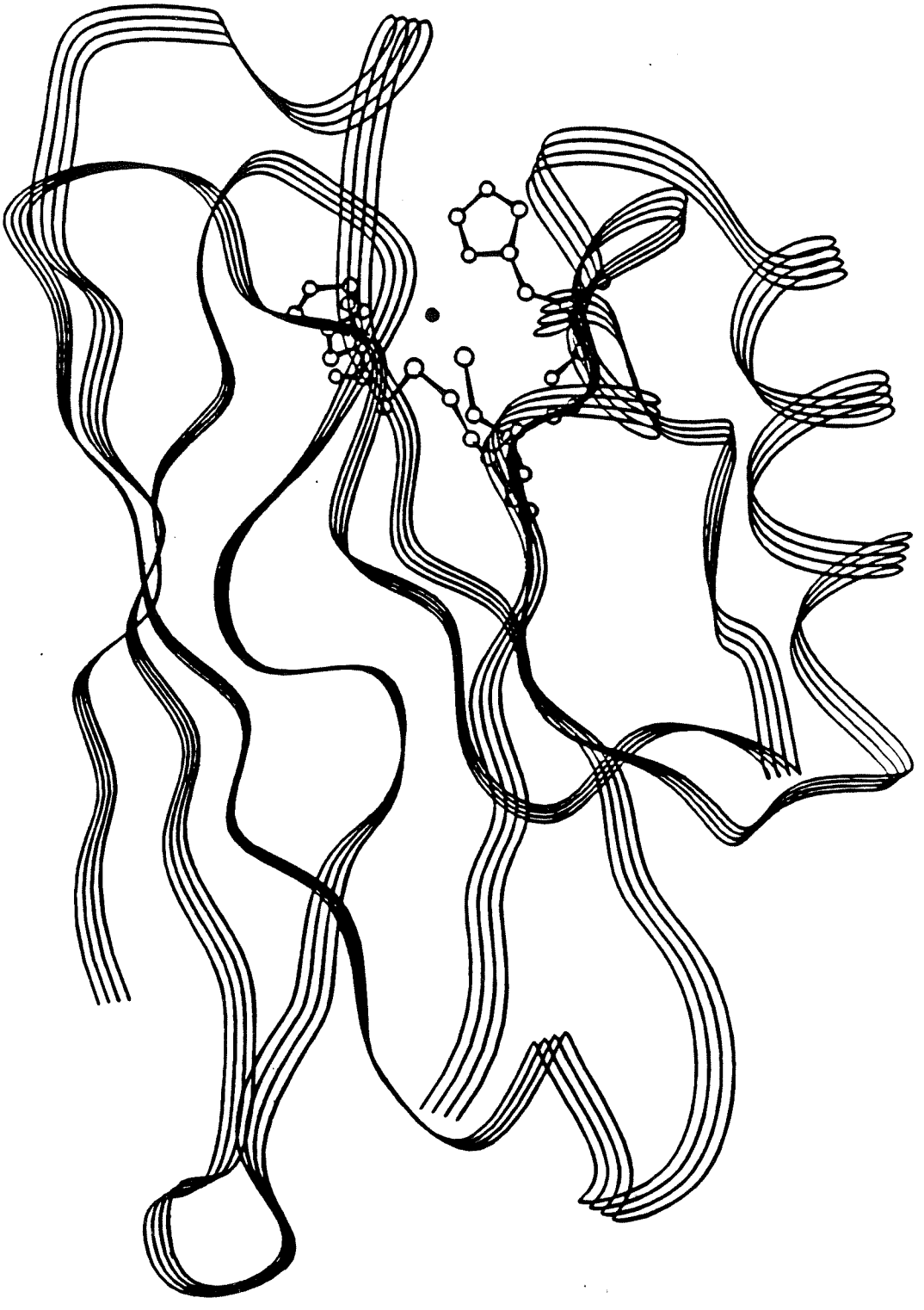

Forward ET
-ΔG° = 0.3 eV
Back ET
-ΔG° = 1.0eV
ln(k)
26
24
22
20
18
-0.4
0.0
0.4
0.8
-ΔG° (eV)

Figure 1.10. Ribbon diagram of *Pseudomonas* aeruginosa.



XCF-Xalpha calculations and report a 30% bond to the methionine.[15] Chapter four reports a series of gold substituted azurins and their luminescence properties. Gold was placed in the active site because results on the emission from gold phosphines (see chapter two) show that three coordinate gold phosphoresces strongly, but four coordinate gold does not emit. Strong bonding with the methionine would lead to a non-emissive four coordinate gold(I) site. Little or no bonding interaction with the methionine would produce an emissive three coordinate gold(I) site.

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Characterization and Photophysics of Gold(I) Phosphine Complexes

Background

Luminescence has been reported for a few dinuclear gold(I) complexes in solution.[1-4] Formulations of the electronic structures of the emissive states have emphasized the importance of Au-Au interactions by analogy to d^8-d^8 Pt_2[5-6] and d^{10}-d^{10} Pt_2[7] species. A crystal structure of the luminescent $[Au_2(dppm)_2]$ $[BF_4]_2$ (dppm = bis-(diphenylphosphino) methane) reports a Au-Au distance of 2.962 Å, significantly shorter than the sum of the van der Waals radii, 3.40 Å.[1] When the two d^{10} centers are brought together, the filled d_z^2 orbitals and the empty p_z orbitals interact in the same manner as discussed for PtPOP (Figure 1.3). The resulting $d\sigma^* \rightarrow p\sigma$ singlet transition is observed in the electronic absorption spectrum at 293 nm for $[Au_2(dppm)_2]$ $[BF_4]_2$. The emission in solution (λ_{max} = 593 nm) has been assigned as the triplet $d\sigma^* \leftarrow p\sigma$ transition.[3] The large Stokes shift of 17,300 cm^{-1} is similar to the shift (16,600 cm^{-1}) observed by Che et al. in the complex $Au_2(dmb)(CN)_2$ (dmb=1,8-di-isocyano-p-menthane).[2a] The excitation spectrum reported by Che for the dmb compound is extremely intriguing because it differs markedly from the absorption spectrum. In general the excitation spectrum is expected to be nearly identical to the absorption spectrum. The excitation spectrum of $Au_2(dmb)(CN)_2$ shows only a single intense band at 350 nm which is lower in energy than any observable feature in the absorption spectrum, indicating that a small amount of a luminescent impurity may be responsible for the emission..

Introduction

Gold complexes have the potential to be strong photo-reductants. The Au(I) metal center has several advantageous features: it is a third row metal with efficient spin orbit coupling for accessing the triplet excited state, Au(I) has a d^{10} configuration so none of the dissociative d→ d transitions are possible, and the oxidation of most Au(I) species produces a transient, unstable Au(II) moiety which will disproportionate or thermally transfer a second electron before back electron transfer can occur. Design of luminescent

complexes focused on three types of transitions: MLCT transitions, $d\sigma^* \rightarrow p\sigma$ transitions associated with the dimers, and $d \rightarrow p$ transitions in gold monomers.

The MLCT transition was chosen based on the long-lived luminescence of the MLCT state of $Ru(bpy)_3^{2+}$. The complex Au(bis-(diphenylphosphino) ethane)$_2^+$ was synthesized to generate a low-lying MLCT state. The d Au-P σ^* orbitals are pushed up in energy by the four highly-donating, bound phosphines and there exists a potentially accessible π^* orbital as the LUMO on the phosphine ligand. This type of MLCT transition should be more stabilizing than the MLCT of $Ru(bpy)_3^{2+}$ since the electron is being removed from a metal centered d σ^* orbital as opposed to a non-bonding metal centered d orbital.

The d Au-Au $\sigma^* \rightarrow$ p Au-Au σ transition was investigated, because previous literature reported the emission in solution from Au d^{10}-d^{10} dimers as being analogous to the d^8-d^8 systems such as PtPOP. Dimers with ethyl butyl bridged chelating phosphines were synthesized for comparison to the literature methyl bridged chelating phosphines. Presumably the longer bridge would lead to a longer Au-Au distance, causing both the absorption and emission bands to move to higher energy.

Although there were no reports in literature of long-lived emission in solution from a $d \leftarrow p$ transition, the bonding character of the HOMO and LUMO justified investigation of the transition. The $d \rightarrow p$ transition involves removing an electron from the highest energy d Au-L σ^* orbital and placing it into a non-bonding p orbital; such transitions should lead to a contraction of the Au-L bonds as opposed to the dissociation associated with $d \rightarrow d$ transitions. The absence of a pathway for photo-dissociation enhances the possibility that the $d \rightarrow p$ excited state could be long-lived. Two and three coordinate gold phosphine complexes were prepared to generate low energy d Au-P $\sigma^* \rightarrow$ p transitions. Four coordinate complexes were considered undesirable for d Au-P $\sigma^* \rightarrow$ p transitions, because the p LUMO would be a M-L σ^* type orbital as opposed to a non-bonding orbital.

Possible LMCT states were not investigated, because they would generate a Au(0) species which could plate out as metallic gold. Intraligand transitions were considered disadvantageous for photo reduction, because electron transfer produces a radical on the ligand which could lead to unwanted side reactions; the three transitions investigated all produce Au(II) centers upon oxidation and leave the ligands unperturbed.

Experimental Section

Materials Bis-(dicyclohexylphosphino)ethane, Bis-(dichlorophosphino)-ethane, Au shot, and hydrogen tetrachloroaurate (II) hydrate were purchased from Strem chemicals. All other solvents and materials were reagent grade and purchased from Aldrich Chemical Company unless otherwise noted. Distilled solvents were dried over CaH_2, except for tetrahydrofuran which was dried over sodium. Lifetime measurements, emission spectra and excitation spectra were all performed with degassed solutions. Solutions were degassed by cycling the solution through a freeze (10 minutes), pump (vacuum of 1 x 10^{-5} torr for 5 minutes), thaw (with a room temperature water bath) procedure at least four times.

X-ray Data Collection and Reduction for [Au_2(bis-(diphenylphosphino) ethane)$_2$] [$(PF_6)_2$] Crystals for X-ray diffraction were grown by recrystallization from CH_3CN/Et_2O. Crystal: square prism with cross-section 0.26 x 0.26 mm, 0.3 mm long with skewed ends; CAD-4 diffractometer; cell dimensions from 25 reflections with $39^o < 2h < 43^o$; no absorption correction (lr_{max}=1.2, 2 data sets merged satisfactorily); $(\sin h/k)_{max}$ =0.66; data collected to 2h = 56°, h from 0 to 21, k from 0 to 21, l from -16 to 6; three standard reflections, 230, 140, 22$\bar{2}$, showed no variations greater than expected from counting statistics; 8221 reflections measured, 3805 independent; goodness of fit for merging 1.08; $(GOF=[\sum_{n} w(F^2_{o(hkl)}-F^2_{avg(hkl)})^2/(n-1)]^{1/2}$ for n observations of reflection hkl; $GOF_{merge}= [\sum_{m} w(GOF_{hkl})^2/m]^{1/2}$, for m reflections with more than one contributor); R_{merge}(point group, $\bar{4}$m2) for 3386 reflections with exactly 2 observations = 0.042; all

reflections used in solution and refinement of the structure; gold atom coordinates found from Patterson map, remainder of structure by successive structure factor-Fourier calculations; full matrix least squares refinement using F^2 values; hydrogen atoms placed by calculation 0.95 Å from their carbon atoms, with isotropic B's of 10.0 $Å^2$, hydrogen coordinates not refined but adjusted once near conclusion of refinement; 165 parameters refined, including scale factor, all refineable coordinates of non-hydrogen atoms and their anisotropic U_{ij}'s; final R 0.064 for 3525 reflections with $F_o^2 > 0$, 0.038 for 2440 reflections with $F_o^2 > 3\sigma(F_o^2)$, final goodness of fit 1.46. The absolute configuration for the structure was confirmed by refining both alternatives; the incorrect one gives R = 0.087 compared to R = 0.064 for the correct one . Variances ($\sigma^2(F_o^2)$), derived from counting statistics plus an additional term, $(0.014I)^2$, variances of the merged data by propagation of error plus another additional term, $(0.014I)^2$; ratio of maximum shift to error in final least squares cycle, 0.07 for cation, 0.36 for fluorine atoms of PF_6^- anion; one peak 2.7e$Å^{-3}$ between the two gold atoms, another 1.8 e$Å^{-3}$ 0.3Å from the gold atom, all other peaks less than 1.5 e$Å^3$, most negative peaks in the vicinity of PF_6^- ion; atomic scattering factors and dispersion corrections taken from Cromer and Waber; programs used were those of the CRYRM crystallographic computing system and ORTEP. Table 2.1 gives a list of selected bond distances and bond angles.

X-ray Data Collection and Reduction for [Au_2(bis-(dicyclohexylphosphino) ethane)$_3$] [$(Au(CN)_2)_2$] The crystal was prepared by the slow evaporation of methanol. Crystal: prism with cross section 0.08 x 0.16 x 0.22 mm, CAD-4 diffractometer; cell dimensions from 25 reflections with $30^o < 2\theta < 33^o$; $(\sin\theta/\lambda)_{max} = 0.59$; data collected to $2\theta = 50^o$, h from -14 to 14, k from -15 to 15, l from -18 to 18; three standard reflections, $03\bar{3}$, $\bar{4}0\bar{1}$ and 013, showed no variations greater than expected from counting statistics; 15196 reflections measured, 7486 independent; goodness of fit for merging 1.02 $(GOF=[\sum_n w(F^2_{o(hkl)}-F^2_{avg(hkl)})^2/(n-1)]^{1/2}$ for n

Table 2.1 Selected bond distances and bond angles for $[Au_2(dcpe)_2]$ $(PF_6)_2$.

Distance (Å)		Angle (°)	
Au - Au	2.935(1)	P1 - Au - P1	160.6(1)
Au - P1	2.314(2)	Au - P1 - C1	120.7(2)
P1 - C1	1.848(7)	Au - P1 - C10	109.1(3)
P1 - C10	1.819(10)	Au - P1 - C20	107.4(2)
P1 - C20	1.825(8)	C10 - P1 - C1	103.8(4)
C1 - C1	1.463(9)	C20 - P1 - C1	108.2(3)
		C20 - P1 - C10	107.0(4)
		C1 - C1 - P1	117.8(5)
		C11 - C10 - P1	109.4(6)
		C15 - C10 - P1	111.2(6)
		C21 - C20 - P1	112.8(6)
		C25 - C20 - P1	115.9(6)

Table 2.2 Selected bond distances and bond angles for $[Au_2(dcpe)_3]$ $[Au(CN)_2]_2$.

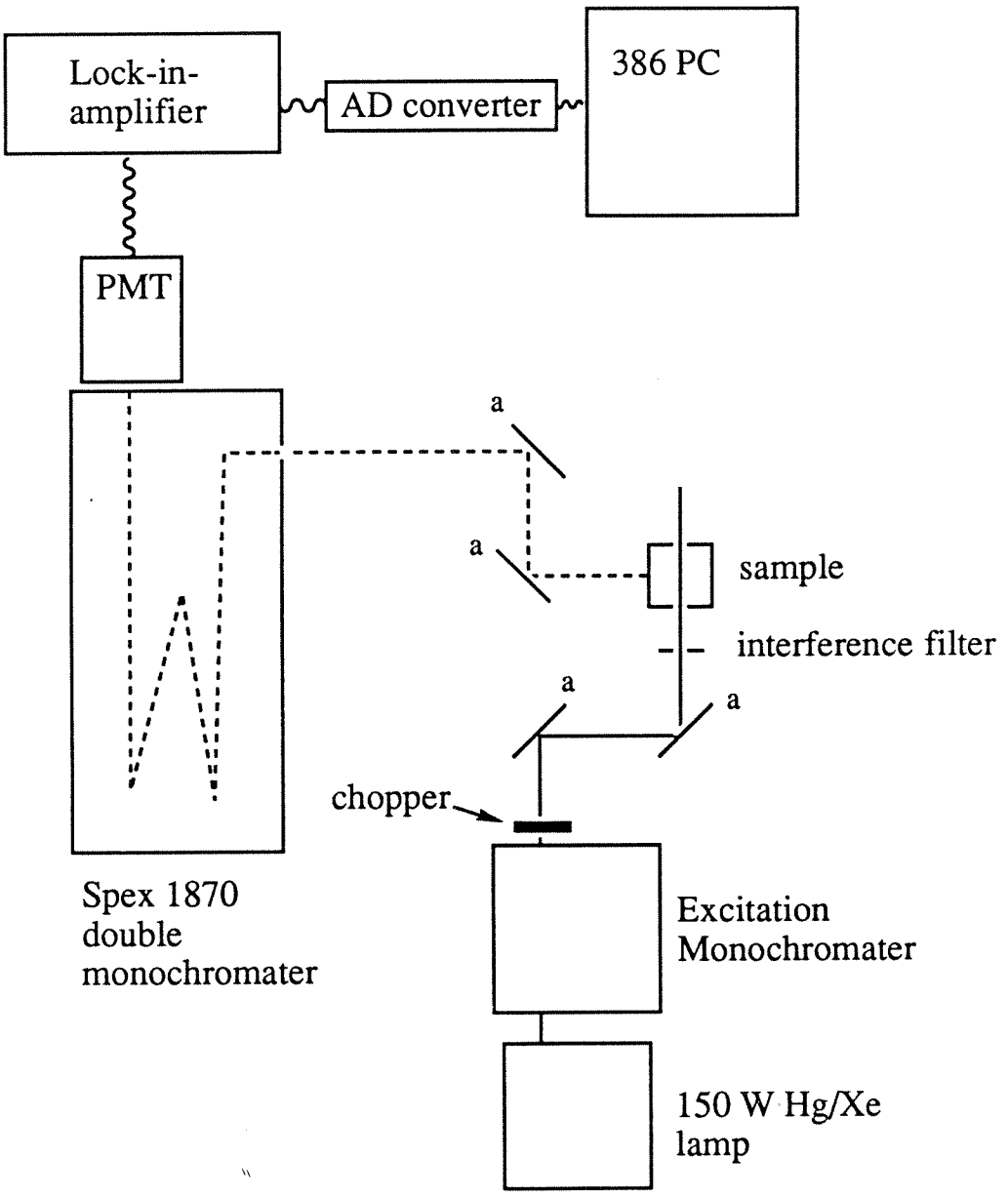
Distance (Å)		Angle (°)	
Au1 - P1	2.440(2)	P1 - Au1 - P2	87.4(1)
Au1 - P2	2.422(2)	P1 - Au1 - P3	136.9(1)
Au1 - P3	2.318(1)	P2 - Au1 - P3	135.3(1)
P1 - C1	1.849(6)	Au1 - P1 - C1	103.9(2)
P1 - C10	1.851(6)	Au1 - P1 - C16	118.0(2)
P1 - C16	1.846(6)	Au1 - P1 - C10	119.2(2)
P2 - C2	1.839(6)	C1 - P1 - C10	103.3(3)
P2 - C22	1.847(6)	C1 - P1 - C16	103.5(3)
P2 - C28	1.833(6)	C10 - P1 - C16	106.6(3)
P3 - C3	1.846(6)	Au1 - P2 - C2	103.9(2)
P3 - C34	1.846(6)	Au1 - P2 - C22	117.8(2)
P3 - C40	1.844(6)	Au1 - P2 - C28	119.4(2)
C1 - C2	1.531(8)	C2 - P2 - C22	103.6(3)
C3 - C3'	1.502(8)	C2 - P2 - C28	104.9(3)
		C22 - P2 - C28	105.4(3)
		Au1 - P3 - C3	116.4(2)
		Au1 - P3 - C34	113.6(2)
		Au1 - P3 - C40	112.3(2)
		C3 - P3 - C34	105.2(3)
		C3 - P3 - C40	103.5(3)
		C34 - P3 - C40	104.7(3)
		P1 - C1 - C2	114.8(4)
		P2 - C2 - C1	116.0(4)
		P3 - C3 - C3'	114.3(4)

observations of reflection hkl; $GOF_{merge}= [\sum_{m} w(GOF_{hkl})^2/m]^{1/2}$, or m reflections with more than one contributor); R_{merge}(point group $\bar{1}$) for 6605 reflections with exactly 2 observations = 0.027; the final R for $F^2_o > 3\sigma$ was 0.0301; the final wR was 0.0030. Table 2.2 gives a list of selected bond angles and bond distances.

Spectroscopic Measurements All electronic absorption spectra were measured with a Cary-14 spectrophotometer. The ^{31}P NMR spectra were obtained with a JOEL 400 MHz NMR equipped with a broad band probe, except for the ^{31}P NMR spectrum of $Au_2(dcpe)_3^{2+}$ which was also measured on a Brucker AMX 500 MHz NMR and a JOEL 90 MHz NMR. All ^{31}P NMR shifts were measured in CD_3CN and are reported relative to phosphoric acid. A Beckman 4240 infrared spectrometer was used for IR measurements. Electrochemistry was performed with a model 173 potentiastat and a model 175 universal programmer form EG and G Princeton Applied Research. The experimental equipment for the emission spectra included: a 200W Xe/Hg lamp from Oriel as the source; a Spex 1681 monochrometer for the excitation monochrometer; an Oriel narrow bandpass interference filter; a Spex 1870 monochrometer as the emission monochrometer; a Hamamatsu R955 PMT as the detector; a model 186A lock in amplifier from EG and G Princeton Applied Research which was used to ratio the sample signal to a blank signal; an 386 PC to analyze the data (Figure 2.1).[9] Excitation spectra were recorded with a SLM 8000 Fluorimeter.

Lifetime Measurements and Analyses Analyses for C, H and N were done at the Caltech Analysis Facility; analyses of all other elements were done at Galbraith Laboratories. The experimental apparatus for the lifetime measurements is described in chapter 3. The excitation source for the lifetime measurements was the third harmonic (355 nm) of a Quanta-Ray Nd-YAG laser with a 20 ns pulse width. The TBA salt of PtPOP was used as a standard for quantum yield measurements . Solutions of PtPOP and the gold complex to be measured were prepared with an absorbance of 0.1 at 366 nm to

Figure 2.1. Instrument configuration for emission spectra; "a" indicates an off axis parabolic broad band mirror with a focal length of 15 cm; the chopper enables the lock-in amplifier to reference the signal to a blank; the operating computer program was written Jim Bailey.


Lock-in-
amplifier
AD converter
386 PC
PMT
a
a
sample
interference filter
a
a
chopper
Spex 1870
double
monochromater
Excitation
Monochromater
150 W Hg/Xe
lamp

avoid self quenching of the emission. Emission spectra were taken using the equipment described above. The integrated areas under the emission bands were used to calculate the quantum yield, ϕ. The quantum yield of PtPOP in acetonitrile has been previously

$$\phi = \frac{\text{integrated area for sample}}{\text{integrated area for PtPOP}} * 0.8$$

reported as 0.8.[10]

Bis-(diisopropylphosphino)ethane (1)[11] A solution of 2 M isopropyl magnesium chloride (29 mL) was added dropwise under an argon atmosphere to a schlenk flask containing 55 mL of freshly distilled tetrahydrofuran (THF) and 2.0 g of 1,2-bis-(dichlorophosphino) ethane. The mixture was refluxed for ninety minutes and then allowed to cool to room temperature. Excess Grignard reagent was quenched by the slow, dropwise addition of saturated aqueous ammonium chloride. The resulting solution containing copious amounts of solid lithium chloride was extracted with 3 times with 60 mL portions of ether. The ether layers were combined and the ether was removed by rotary evaporation under reduced pressure. The product was then purified by vacuum distillation to yield a clear oil (2 mL) which was stored in an inert atmosphere. ^{31}P NMR: 9.0 ppm (s).

1,3-Bis-(dicyclohexylphosphino)propane (2)[12] A solution of 2.5 M N-butyl lithium (20 mL) was added to a schlenk flask charged with 60 mL of Ar purged ether at -78°C. Following the slow addition (1 drop per second) of a solution of dicyclohexyl-phosphine (10 g) in 30 mL of ether, the mixture was allowed to stir for two hours. A solution of 1,3- dichloropropane (2.4 mL) in 30 mL of ether was added dropwise and the solution was warmed to room temperature. Removal of the solvent by rotary evaporation followed by vacuum distillation yielded a clear oil, which was stored in an inert atmosphere. ^{31}P NMR: -5.3 ppm (s).

Au(SCH)(Cl) (3) Gold shot (1.48 g) was dissolved in 150 mL of aqua regia. Once dissolved (heating the mixture slightly sped up the dissolution process for large ingots of gold) the solution was concentrated to 5 mL by boiling. To remove any nitrates

the mixture was washed twice with 50 mL portions of concentrated HCl and reduced in volume to 5 mL by boiling after each addition of HCl. The resulting bright orange solution of auric acid ($HAuCl_4$) was then dissolved in 400 mL of ethanol and an excess (4 mL) of tetrahydrathiophene was added to solution. The solution turned bright orange for a few seconds and then clear as the white, product precipitated out of solution. The product was collected by vacuum filtration (2.18 g Yield: 91%). The isolated product can be stored for months in a freezer.

$[Au(PPh_3)_2]$ $[PF_6]$ (4) Compound **3** was suspended in 50 mL of freshly distilled dichloromethane. Two equivalents of triphenylphosphine were added and the mixture was stirred for 45 minutes. The solvent was removed by rotary evaporation under reduced pressure, yielding the solid Cl salt. The solid was then dissolved in 30 mL of water and a minimum of methanol. Addition of a solution of ammonium hexafluorophosphate in methanol lead to the precipitation of the product as a white solid. The solid was collected by vacuum filtration and dried overnight in a vacuum oven. Analysis Calculated for $AuClP_2C_{36}H_{30}$: C, 57.12 ; H, 3.99. Found: C, 56.63; H, 4.09. ^{31}P NMR: 42.64 ppm (s). Analysis calculated for $AuP_3F_6C_{36}H_{30}$: C, 49.90; H, 3.49. Found: C, 50.13; H, 3.62.

$[Au(P(C_6H_{11})_3)_2]$ $[PF_6]$ (5) This compound was made by a procedure analogous to that described for $[Au(PPh_3)_2]$ $[PF_6]$. ^{31}P NMR: 63.8 ppm (s).

[Au(1,2-bis-(diphenylphosphino)ethane)$_2$] $[PF_6]$ A round-bottom flask was filled with 50 mL of freshly distilled dichloromethane, 200 mg (0.624 mmol) of **3** and 525 mg (1.320 mmol) of dppe. The solution was stirred for two hours. The solvent was then reduced in volume to 25 mL by rotary evaporation under reduced pressure. Addition of 50 mL of ether precipitated the product as a white powder which was collected by vacuum filtration (500 mg; Yield 71%) . The powder was dissolved in 25 mL of methanol and water was added until the solution became slightly cloudy. Addition of a solution of ammonium hexafluorophosphate in methanol lead to the precipitation of the

PF_6 salt in product as a white solid. The solid was collected by vacuum filtration and dried overnight in a vacuum oven. ^{31}P NMR: 44.76 ppm (s). Analysis calculated for $AuP_5F_6C_{52}H_{48}$: C, 54.85; H, 4.25. Found: C, 54.80; H, 4.33.

[Au(bis-(dicyclohexylphosphino)ethane)$_2$] [PF_6] A mixture of compound **3** (100 mg ; 0.31 mmol) and an excess of dcpe (920 mg; 2.1 mmol) in 50 mL of freshly distilled dichloromethane was stirred under argon at room temperature for one hour. The solvent was removed by rotary evaporation under reduced pressure to give a white powder. The powder was dissolved in a minimum of a 60:40 solution of methanol: water, and an excess of ammonium hexafluorophosphate in 1 mL of methanol was added to precipitate the PF_6 salt. The product was collected by vacuum filtration. ^{31}P NMR: 30.01 ppm (s). Analysis calculated for $AuP_5F_6C_{52}H_{96}$: P, 13.05; F, 9.60; C, 52.61; H, 8.15. Found: P, 13.27; F, 9.33; C, 52.98; H, 8.20.

[Au$_2$(bis-(dicyclohexylphosphino)ethane)$_2$] [(PF_6)$_2$] A mixture of compound **3** (150 mg ; 0.47 mmol) and one equivalent of dcpe (210 mg; 0.50 mmol) in 50 mL of freshly distilled dichloromethane was stirred under argon at room temperature for one hour. The solvent was removed by rotary evaporation under reduced pressure to give a white powder. The powder was dissolved in a minimum of a 60:40 solution of methanol: water, and an excess of ammonium hexafluorophosphate in 1 mL of methanol was added to precipitate the PF_6 salt. The product was collected by vacuum filtration. ^{31}P NMR: 51.39 ppm (s). Analysis calculated for $Au_2P_6F_{12}C_{52}H_{96}$: P, 12.15; F, 14.90; C, 40.85; H, 6.33. Found: P, 11.76; F, 14.61; C, 40.54; H, 6.27.

[Au$_2$(bis-(dicyclohexylphosphino)ethane)$_3$] [(PF_6)$_2$] A mixture of compound **3** (1.2 g; 3.75 mmol) and one and one half to two equivalents of dcpe (3.00 g; 7.1 mmol) in 50 mL of freshly distilled dichloromethane was stirred under argon at room temperature for one hour. The solvent was removed by rotary evaporation under reduced pressure to give a thick oil. Sonication in ether followed by rotary evaporation of the solvent yielded a white powder which may have a green tinge due to luminescence

(Yield: 95%). Metathesis to the PF_6 salt was accomplished quantitatively by dissolving the solid in a minimum amount of a 50:50 solution of methanol: water followed by addition of excess ammonium hexafluorophosphate in 1 mL of methanol. ^{31}P NMR: 64.4 ppm (d); 57.6 ppm (t) (Figure 2.2). Fine splitting in the doublet and triplet patterns due to the $A_2BA'_2B'$ is expected for the molecule. Spectra taken on a 400 MHz or 90 MHz NMR have increasingly complex patterns as the chemical shift difference between the two types of phosphines approaches the coupling value. Analysis calculated for $Au_2P_8F_{12}C_{78}H_{144}$: P, 12.70; F, 11.68; C, 48.00; H, 7.44. Found: P, 12.72; F, 11.42; C, 48.14; H, 7.13.

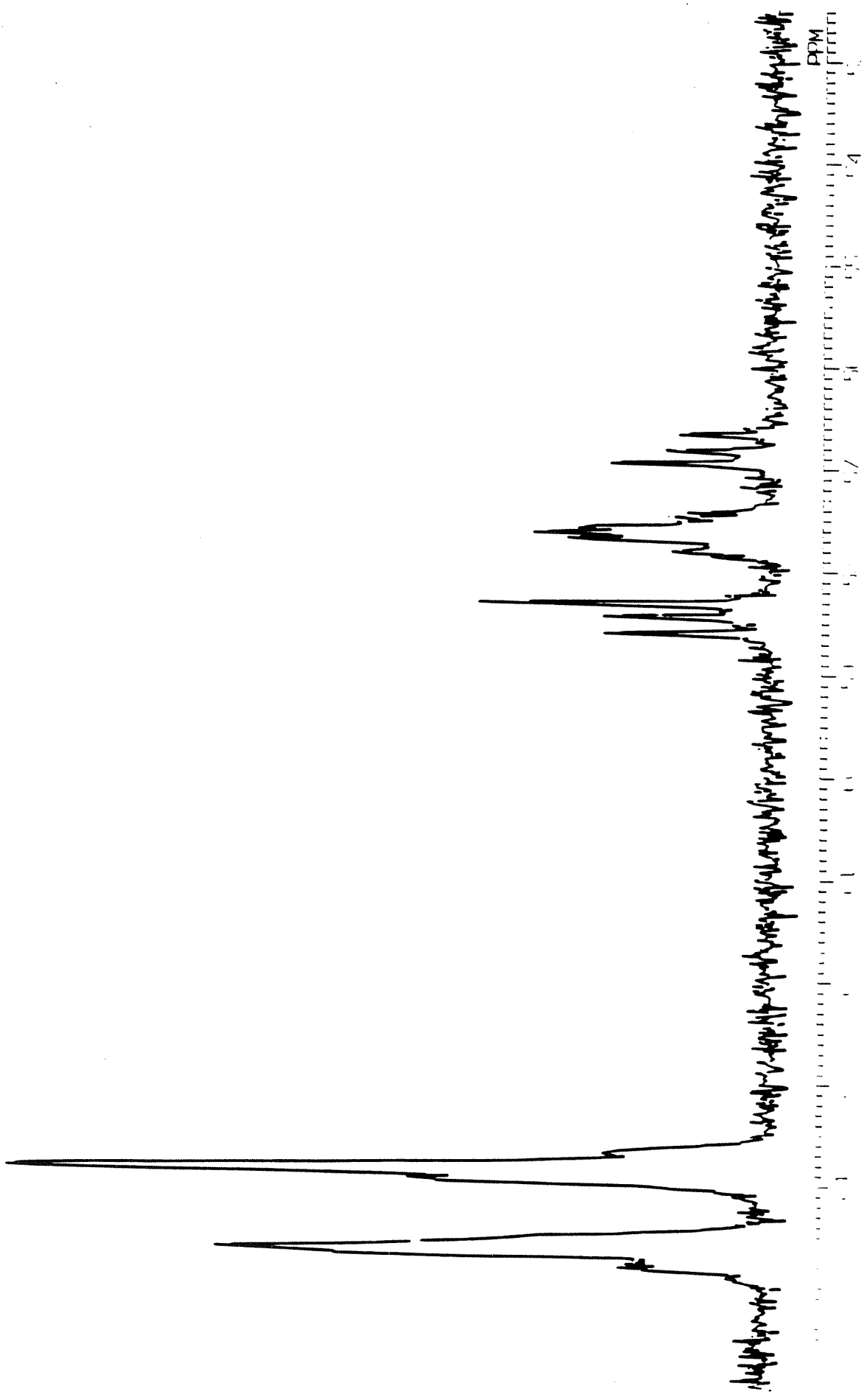
AuCN[13] Gold powder (500 mg) was stirred in a solution of 400 mg KCN and 20 mL of distilled water overnight. The resulting clear solution was combined with 10 mL of concentrated HCl and brought to a boil. The product precipitated out as a yellow solid and was collected by vacuum filtration.

[Au_2(bis-(dicyclohexylphosphino)ethane)$_3$] [$(Au(CN)_2)_2$] A 100 mL round-bottom flask was filled with 50 mL of methanol, 223 mg AuCN and 423 mg of dcpe. The yellow solution was stirred until it turned clear, and the solvent was then removed by rotary evaporation under reduced pressure. The resulting white powder was dried overnight in a vacuum oven. IR: CN stretch 2125 cm^{-1}. ^{31}P NMR: 64.4 ppm (d); 57.6 ppm (t). Analysis calculated for $Au_4P_6C_{82}H_{144}N_4$: C, 45.60; H, 6,72; N, 2.60. Found: C, 45.20; H, 6.61; N, 2.58.

[Au(bis-(diisopropylphosphino)ethane)$_2$] [PF_6] The 1,2-bis(diisopropyl-phosphino)ethane compounds were made according to procedures analogous to those previously described for the corresponding dcpe complexes. ^{31}P NMR: 41.63 ppm (s). Analysis calculated for $AuP_5F_6C_{28}H_{64}$: C, 38.81; H, 7.44. Found: C, 38.19; H, 7.37.

[Au_2(bis-(diisopropylphosphino)ethane)$_2$] [$(PF_6)_2$] ^{31}P NMR: 60.94 ppm (s). Analysis calculated for $Au_2P_6F_{12}C_{28}H_{64}$: C, 27.83; H, 5.34. Found: C, 28.34; H, 5.37.

Figure 2.2 ^{31}P NMR spectrum of $[Au_2(dcpe)_3]$ $(PF_6)_2$.


PPM

[Au_2(bis-(diisopropylphosphino)ethane)$_3$] [$(PF_6)_2$] ^{31}P NMR: 74.05 ppm (d); 66.95 ppm (t). Analysis calculated for $Au_2P_8F_{12}C_{52}H_{96}$: C, 34.31; H, 6.58. Found: C, 34.51; H, 6.63.

[Au_2(bis-(diphenylphosphino)butane)$_3$] [$(Cl)_2$] A slight excess of 1,4-bis(diphenylphosphino)butane (300 mg) was added to a stirring solution of compound **3** (75 mg) in 50 mL of freshly distilled acetonitrile. The product precipitated out as a white powder and was collected by vacuum filtration. This compound has limited solubility in ethanol. ^{31}P NMR: 30.47 ppm (s). The formulation of this compound as a triply bridged dimer is based on a combination of the analysis results and the singlet ^{31}P NMR signal. The ^{31}P NMR spectrum shows that all of the phosphines are equivalent, ruling out structures involving one chelating bidentate ligand and one bridging bidentate ligand.

Results and Discussion

Crystal Structures

The crystal structure for $Au_2(dcpe)_2^{2+}$ features a binuclear complex bridged by two dcpe bidentate ligands (Figure 2.3). Each AuP_2 unit has a nearly linear geometry with a P-Au-P angle of 160.6°. The ethylene groups in the dcpe bridges are twisted to give a Au-Au separation of 2.936 Å. This distance is shorter than the van der Waals distance of 3.4 Å and is even shorter than that observed for the $Au_2(dppm)_2^{2+}$, indicating a significant metal - metal interaction.

The structure for $Au_2(dcpe)_3^{2+}$ shows each gold atom is bound to one chelating dcpe and one bridging dcpe (Figure 2.4). The slightly distorted trigonal planar geometry is quite unusual. Gold(I) complexes are almost exclusively linear or tetrahedral about the gold atom, with only a few examples of a trigonal planar environment.[14-16] The distortion is due to the constrained, chelating dcpe unit, which binds with a P-Au-P angle of 87.4°. The other two P-Au-P angles are which involve the bridging dcpe are 136.9°, and 135.3°. The bridging dcpe unit is extended to give a Au-Au distance of 7.050 Å; clearly no Au-Au interaction is present in this molecule.

Figure 2.3. Ortep drawing of $[Au_2(dcpe)_2]$ $(PF_6)_2$; elipses drawn at 50 % probability.

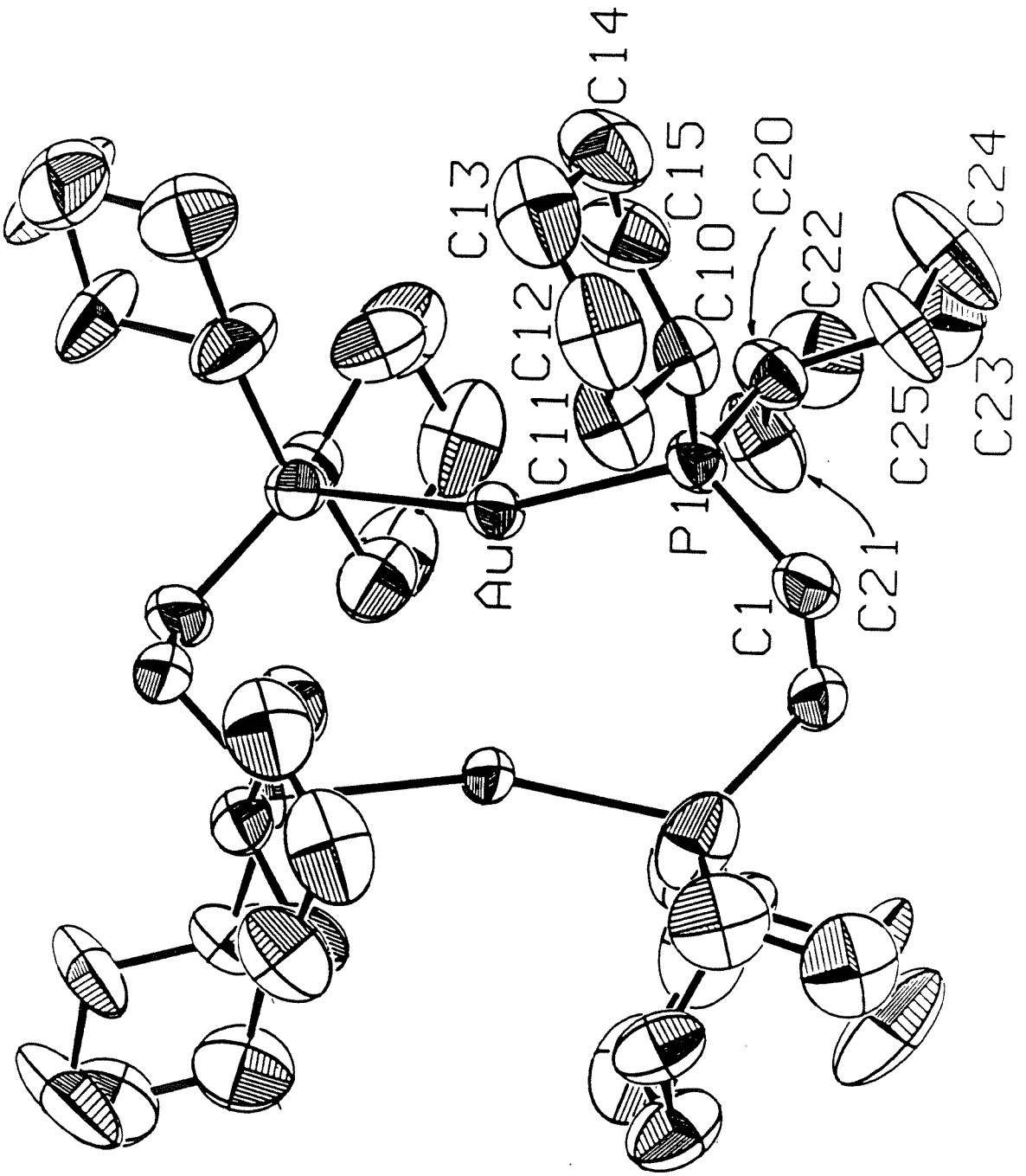
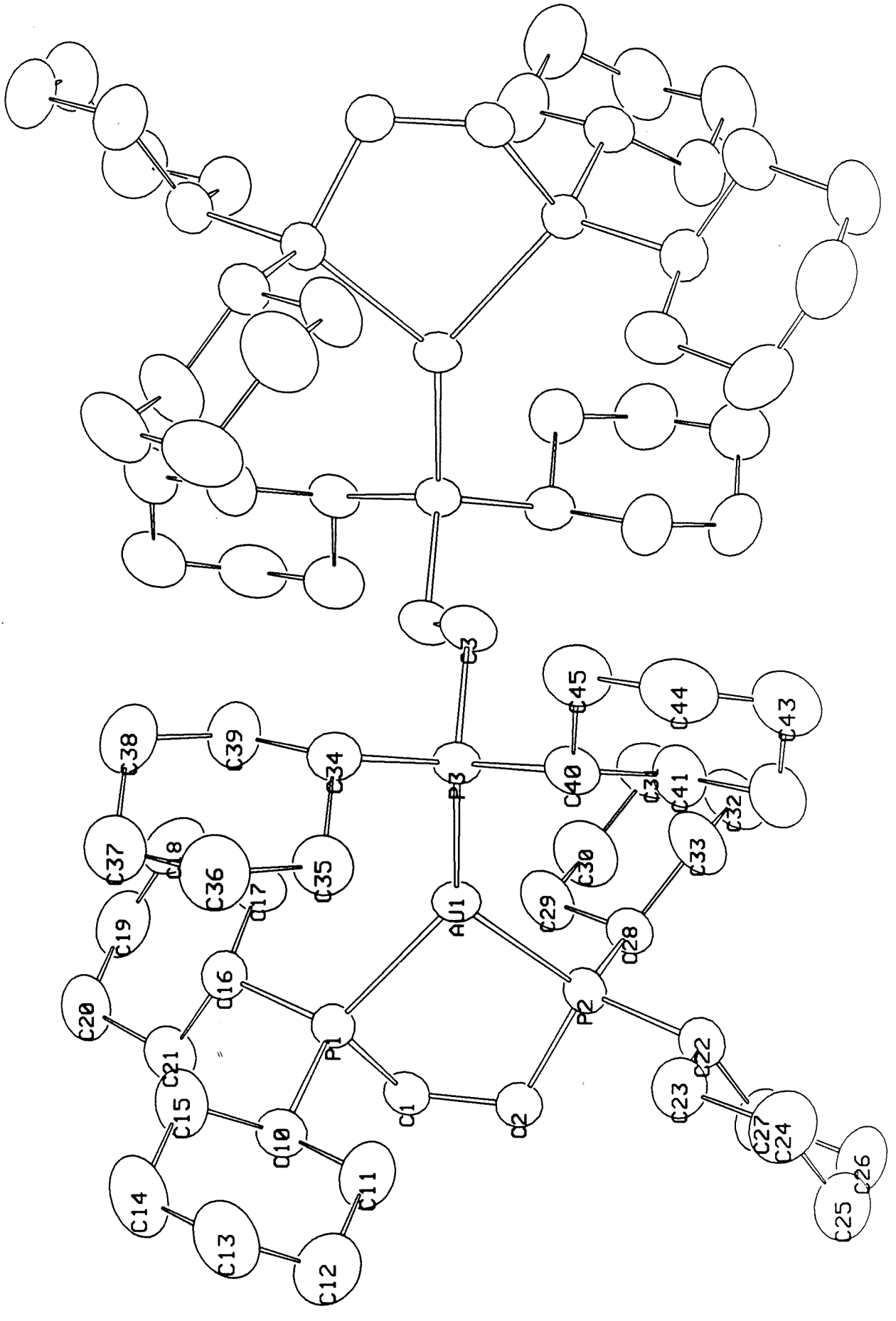

C14
C13
C15
C20
C24
C12
C10
C22
C11
C25
C23
P1
C21
Au
C1

Figure 2.4. Ortep drawing of $[Au_2(dcpe)_3]$ $[Au(CN)_2]_2$; elipses drawn at 50 % probability.


C38
C39
C34
C3
C45
C44
C43
C37
C18
C36
C17
C35
P3
C40
C31
C41
C32
C19
AU1
C30
C33
C29
C20
C16
C28
P1
P2
C21
C15
C1
C2
C22
C23
C10
C27
C24
C14
C11
C26
C13
C25
C12

Electronic Absorption and Emission Spectra The complexes $Au(PPh_3)_2^+$, and $Au(P(C_6H_{11})_3)_2^+$ have similar electronic absorption spectra (Figures 2.5-2.6). The two lowest energy features appear at 275 nm (ε = 9,200 $M^{-1}cm^{-1}$) and 268 nm (ε = 11,800 $M^{-1}cm^{-1}$) for the triphenylphosphine complex and at 250 nm and 236 nm for the tricyclohexylphosphine complex. These two bands are attributed to $^1\Sigma_g \rightarrow {}^1\Pi_u$ ($d_z^2 \rightarrow p_x, p_y$) and $^1\Sigma_g \rightarrow {}^1\Pi_u$ ($d_{xz}, d_{yz} \rightarrow p_x, p_y$) transitions respectively. The d orbitals are pushed up in energy by the two phosphine ligands along the z axis, so the d_z2 (σ^*) will be the HOMO and the d_{xz}, d_{yz} (π^*) will be slightly lower in energy. These assignments agree with analogous assignments made by Mason et al. for $Au(PEt_3)_2^+$ (PEt_3 is triethyl-phosphine).[17]

The electronic absorption spectra of the free ligand dppe and the four coordinate complex $Au(dppe)_2^+$ are shown in Figure 2.7. The ligand spectrum has an absorption band at 252 nm (ε = 17,000 $M^{-1}cm^{-1}$) which can be assigned as a $\pi \rightarrow \pi^*$ transition. Upon coordination of two ligands to the Au center this transition moves to lower energy (λ_{max} = 280 nm, ε = 34,700 $M^{-1}cm^{-1}$), and broadens substantially. At higher energy is the metal centered d $\rightarrow$ p transition, $^1A_1 \rightarrow {}^1B_2$ ($d_{xz}, d_{yz} \rightarrow p_x, p_y$) , which is both spin allowed and dipole allowed in the D_{2d} symmetry. The d $\rightarrow$ p transition is extremely high in energy since both p_x and p_y are σ anti-bonding for a four coordinate Au(I) complex. Mason and coworkers have observed a similar high energy metal centered transition with four monodentate phosphines bound to gold, and have assigned the transition as the analogous T_d transition $^1A_1 \rightarrow {}^1T_2$ (d_{xy},d_{xz}, $d_{yz} \rightarrow p_x, p_y, p_z$).[18] In the D_{2d} symmetry the added electron density from the bridge between the chelating phosphines raises the energy of the p_z, d_{xz}, and d_{yz} orbitals. The solid emits at (λ_{max} = 570 nm) room temperature (Figure 2.8); no emission is observed in solution at room temperature. Based on the assignment of the electronic absorption spectrum the emission has been ascribed to a ligand centered $\pi \leftarrow \pi^*$ emission. The large Stokes shift (18,200 cm^{-1}) between the

Figure 2.5. Absorption spectrum of $Au(PPh_3)_2$ (PF_6), 21 μM.

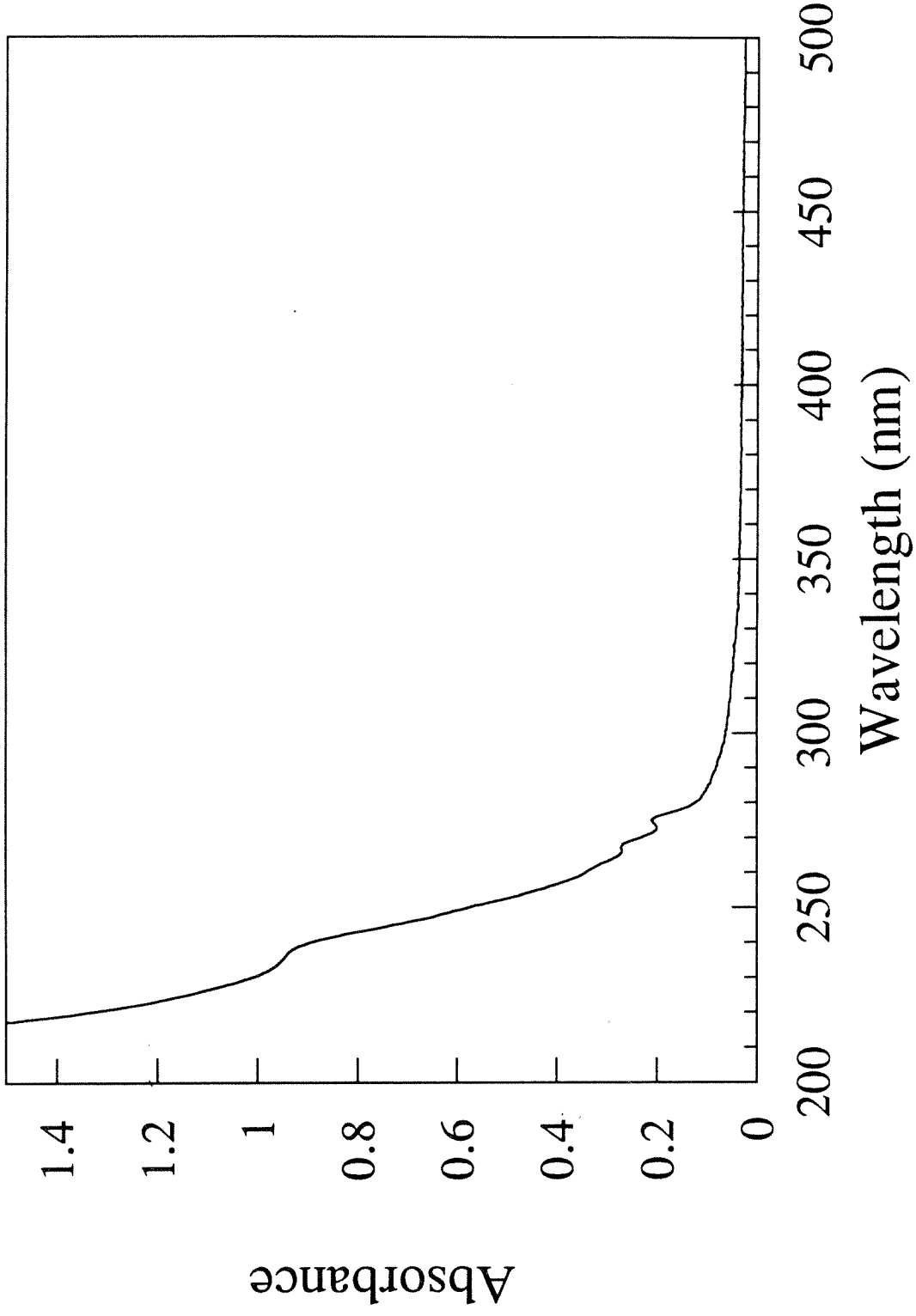

Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.6. Absorption spectrum of $Au(PCy_3)_2$ (PF_6), 100 μM.

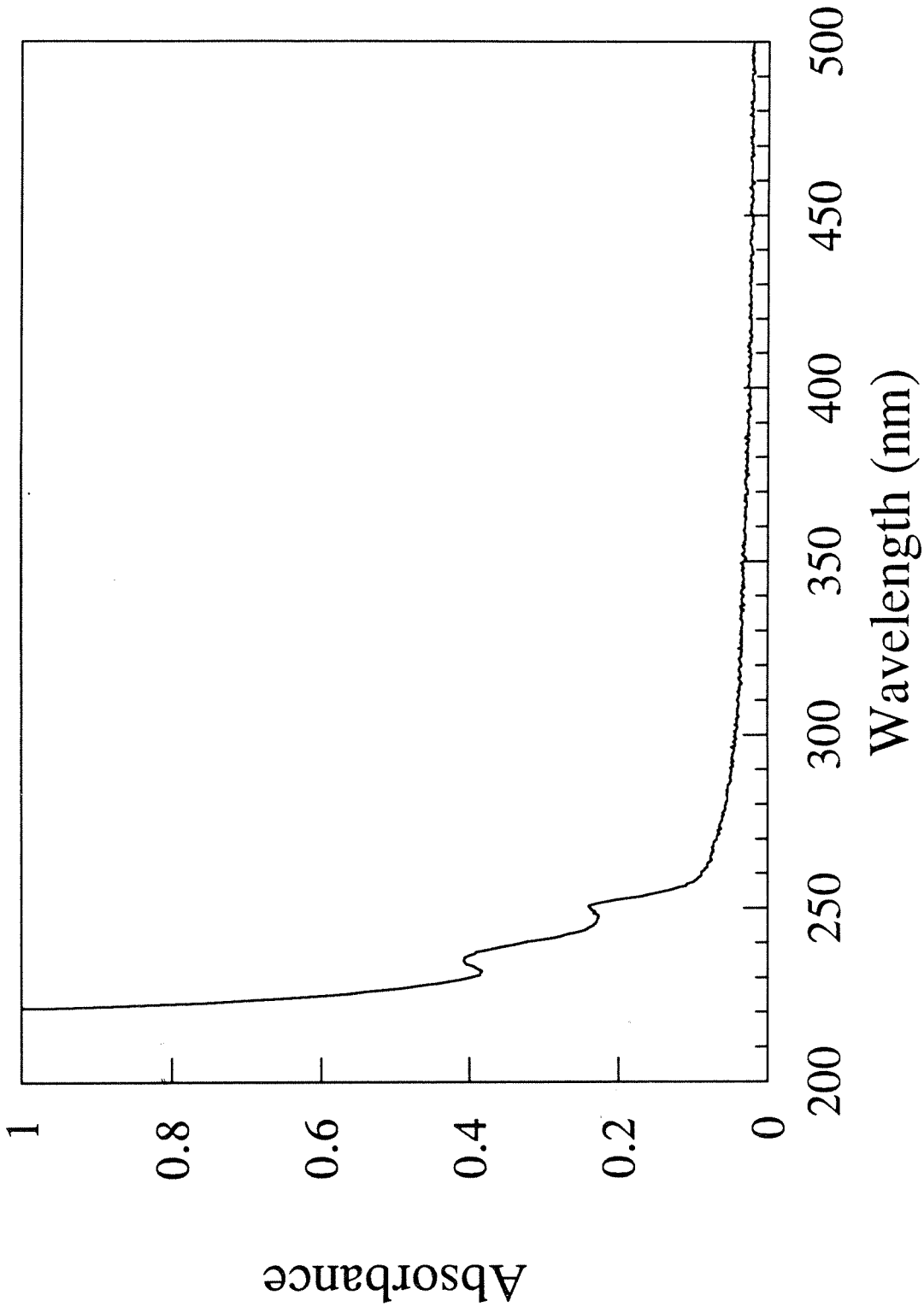

Absorbance
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.7. Absorption spectra of dppe(---), and $Au(dppe)_2$ (PF_6), 20 μM.

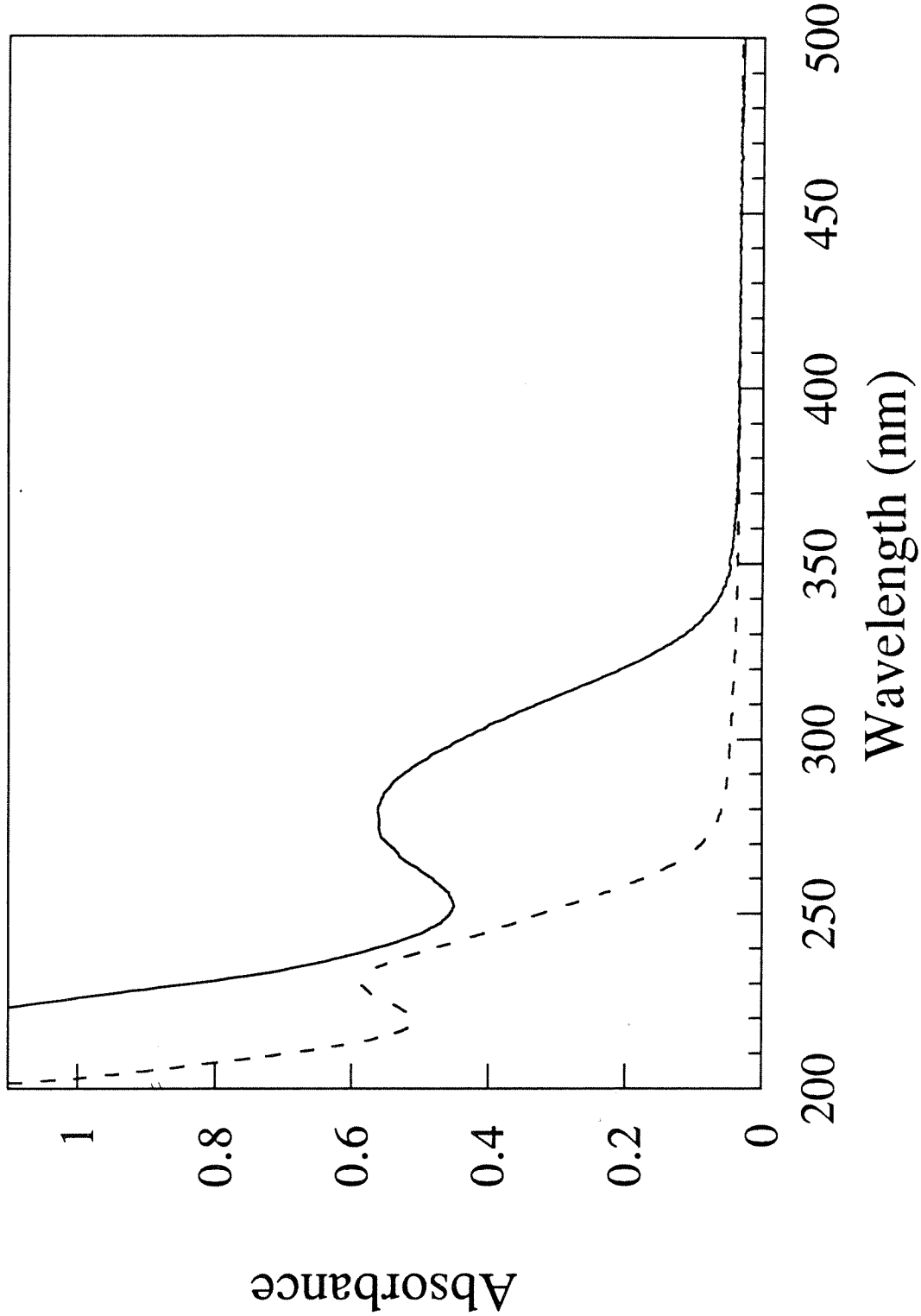
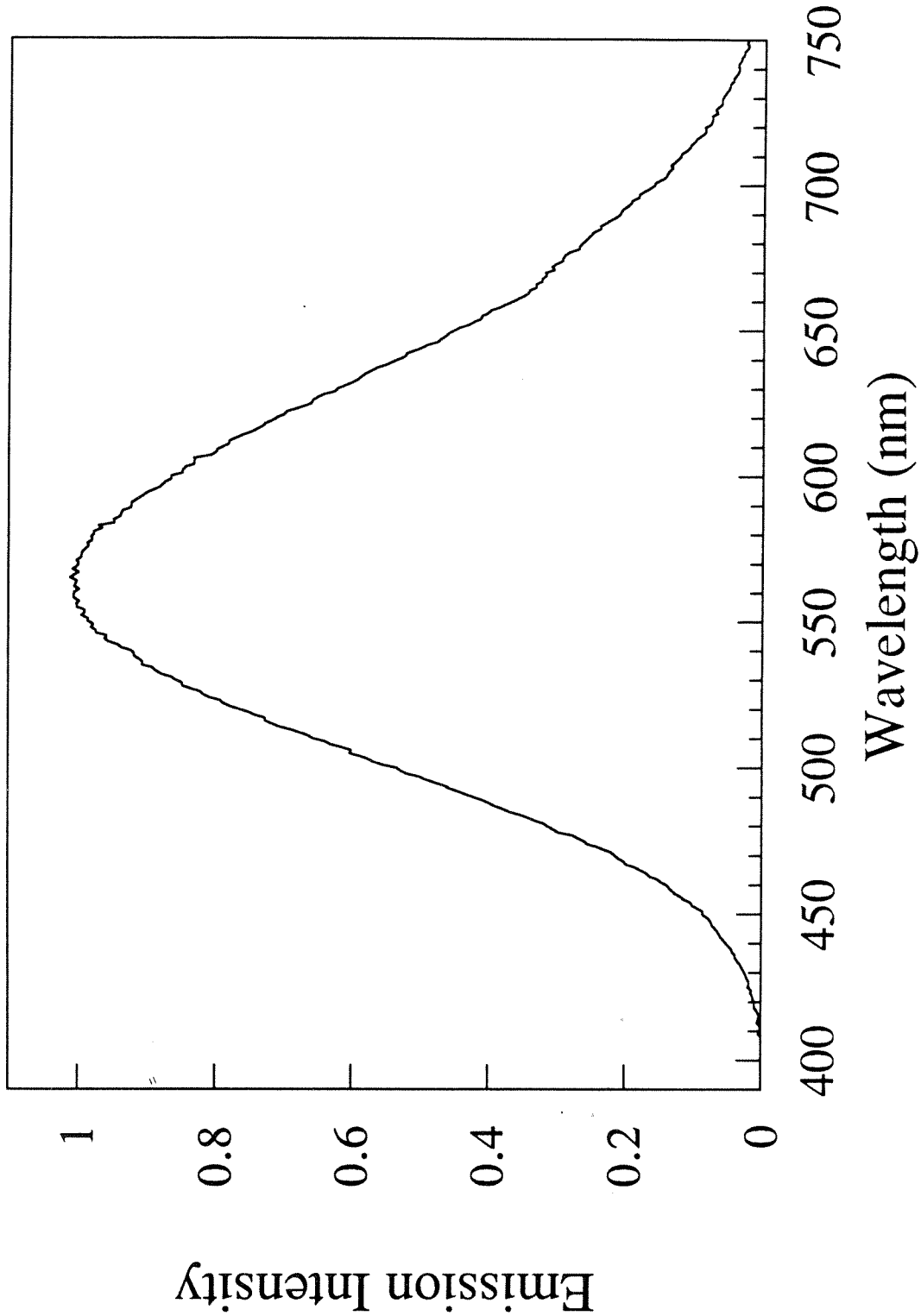

Absorbance
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.8. Solid-state emission spectrum of $Au(dppe)_2$ (PF_6).


Emission Intensity
0
0.2
0.4
0.6
0.8
1
400
450
500
550
600
650
700
750
Wavelength (nm)

absorption band and the emission band identifies the emission as triplet to singlet phosphorescence. The dramatic increase in the intensity of phosphorescence compared to the free ligand is attributed to the heavy atom effect discussed in chapter one.

The electronic absorption spectra for the three dcpe complexes are shown in figures 2.9-2.11. The monomeric $Au(dcpe)_2^+$ species absorbs only in the UV with the lowest energy absorption band occurring at 234 nm (with a shoulder at 266 nm). This absorption band has been attributed to a metal centered d $\rightarrow$ p transition similar to the 280 nm band in $Au(dppe)_2^+$. The $^1A_1 \rightarrow {}^1B_2$ (d_{xz}, $d_{yz} \rightarrow p_x$, p_y) transition is both dipole allowed and spin allowed (ε = 35,000 $M^{-1}cm^{-1}$). The complex does not emit in solution or as a solid at room temperature.

The dimeric complex $Au_2(dcpe)_2^{2+}$ has an intense band (ε = 10,000 $M^{-1}cm^{-1}$) at 270 nm and a weaker shoulder at 320 nm. The Au-Au distance of 2.936 Å indicates a significant interaction as mentioned previously. This interaction occurs primarily between the orbitals along the z axis of the D_{2h} complex. The filled d_z^2 orbitals mix to produce a filled $d\sigma$, and a filled $d\sigma^*$ as the HOMO; the empty p_z orbitals also mix to generate an empty $p\sigma$ as the LUMO and a higher lying $p\sigma^*$. The low energy band at 270 nm is assigned as the $^1A_g \rightarrow {}^1B_{1u}$ ($d\sigma^* \rightarrow p\sigma$), and the shoulder at 320 nm is ascribed to the corresponding $^1A_g \rightarrow {}^3B_{1u}$ ($d\sigma^* \rightarrow p\sigma$). Both transitions are dipole allowed and z polarized. The dimer emits as a solid at 77K (Figure 2.12), but does not emit at room temperature (either as a solid or in solution) upon excitation at 366 nm. The emission spectrum shows two emission bands: a low-energy band at 628 nm and a more intense band at 493 nm. Changing the excitation source to 313 nm leads to emission of the solid at room temperature with a single emission band at 625 nm (Figure 2.13), and emission in an ethanol:methanol glass (4:1) at 77 K, λ_{max} = 604 nm (Figure 2.14; no emission is observed at room temperature in solution). The low energy emission of the solid is assigned as the $^1A_g \leftarrow {}^3B_{1u}$ ($d\sigma^* \leftarrow p\sigma$) transition. The $E_{\nu_0-\nu_0}$ for the emissive transition in the glass is 418 nm with a Stokes shift of 14,700 cm^{-1}.

Figure 2.9. Absorption spectrum of $Au(dcpe)_2$ (PF_6), 43 μM.

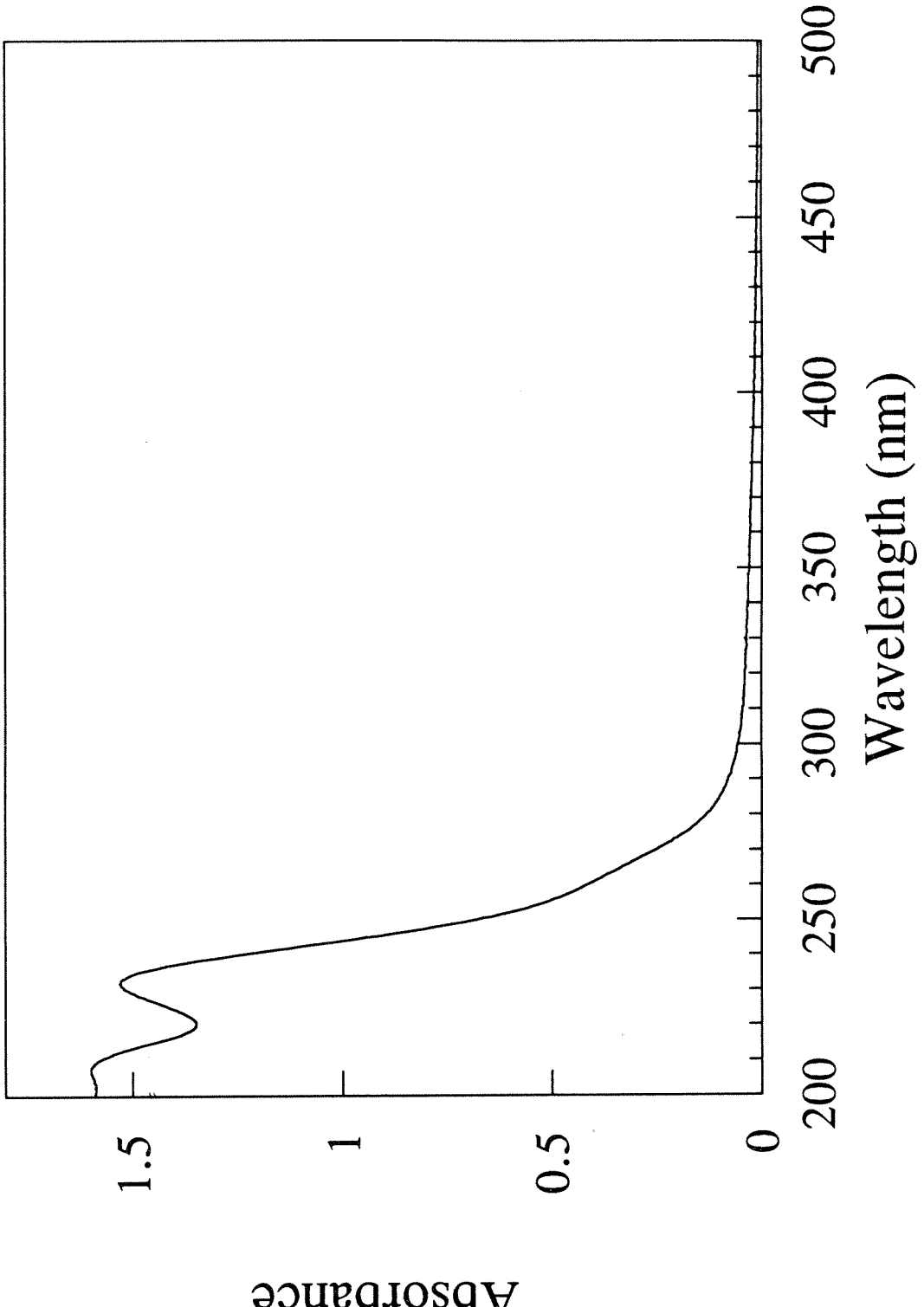

Absorbance
1.5
1
0.5
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.10. Absorption spectrum of $Au_2(dcpe)_2$ $(PF_6)_2$, 73 and 730 μM.

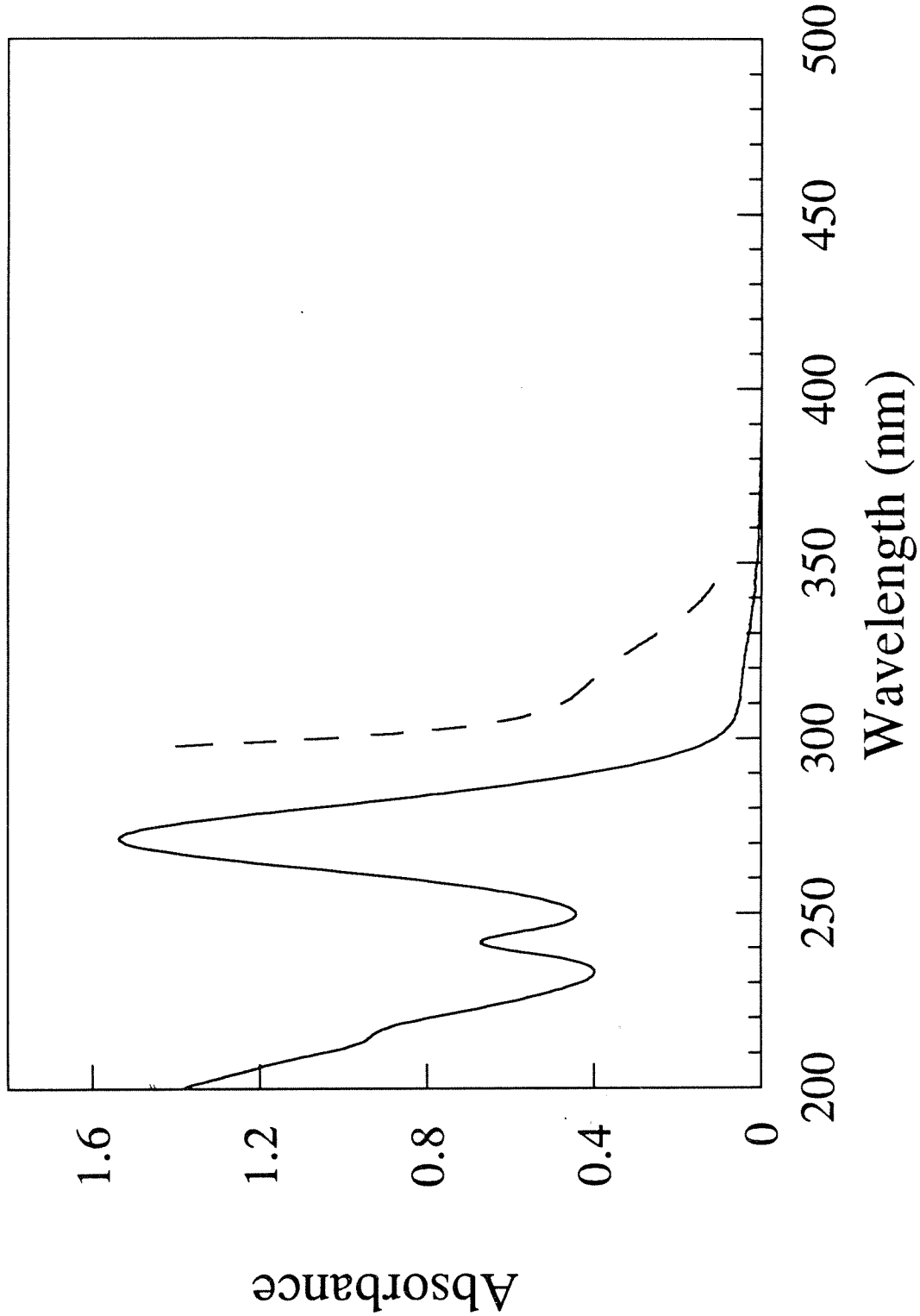

Absorbance
1.6
1.2
0.8
0.4
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.11. Absorption spectrum of $Au_2(dcpe)_3$ $(PF_6)_2$, 5, 50, and 500 μM.

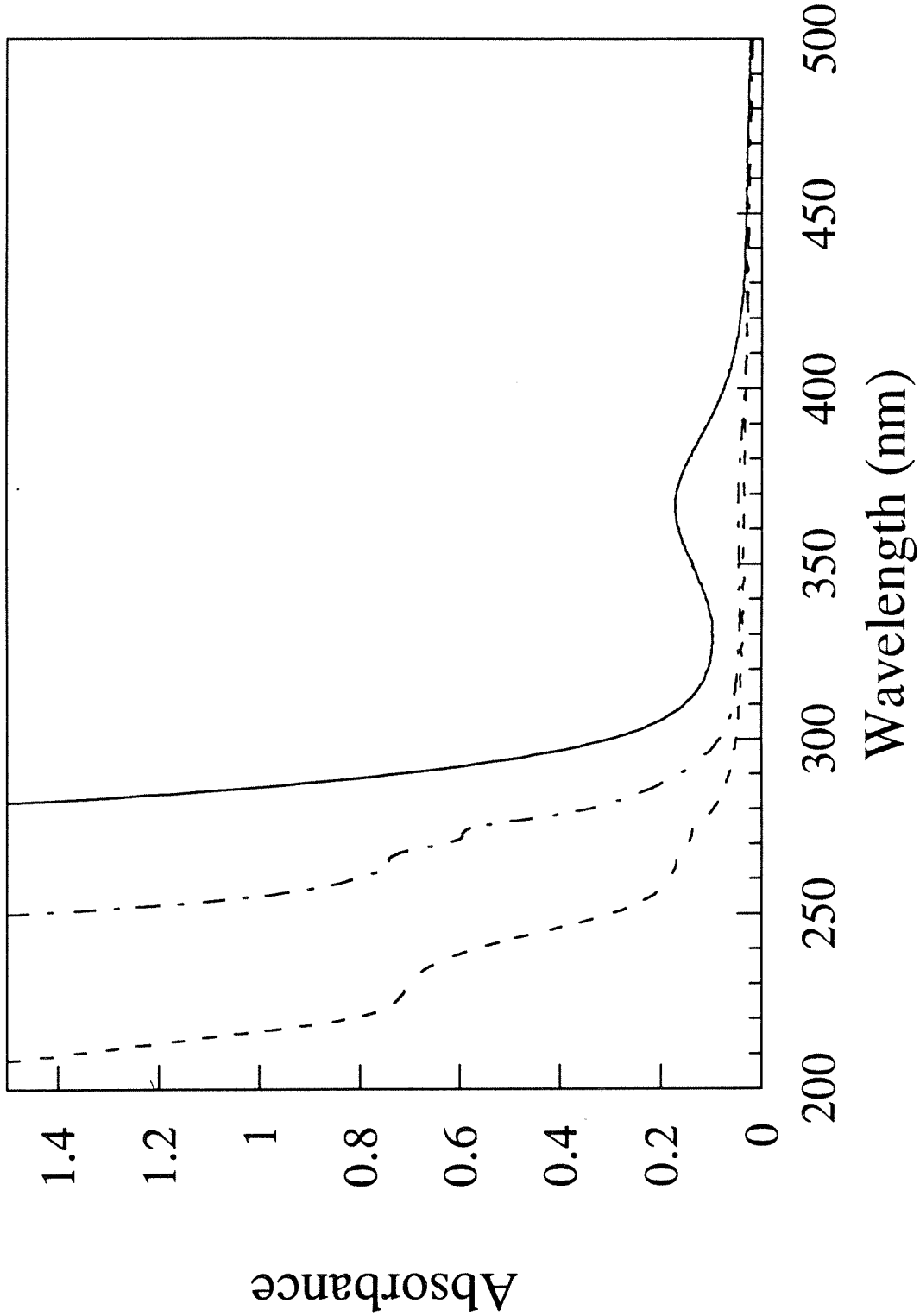

Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.12. Solid-state emission spectrum of $Au_2(dcpe)_2$ $(PF_6)_2$ at 77 K, 366 nm excitation.

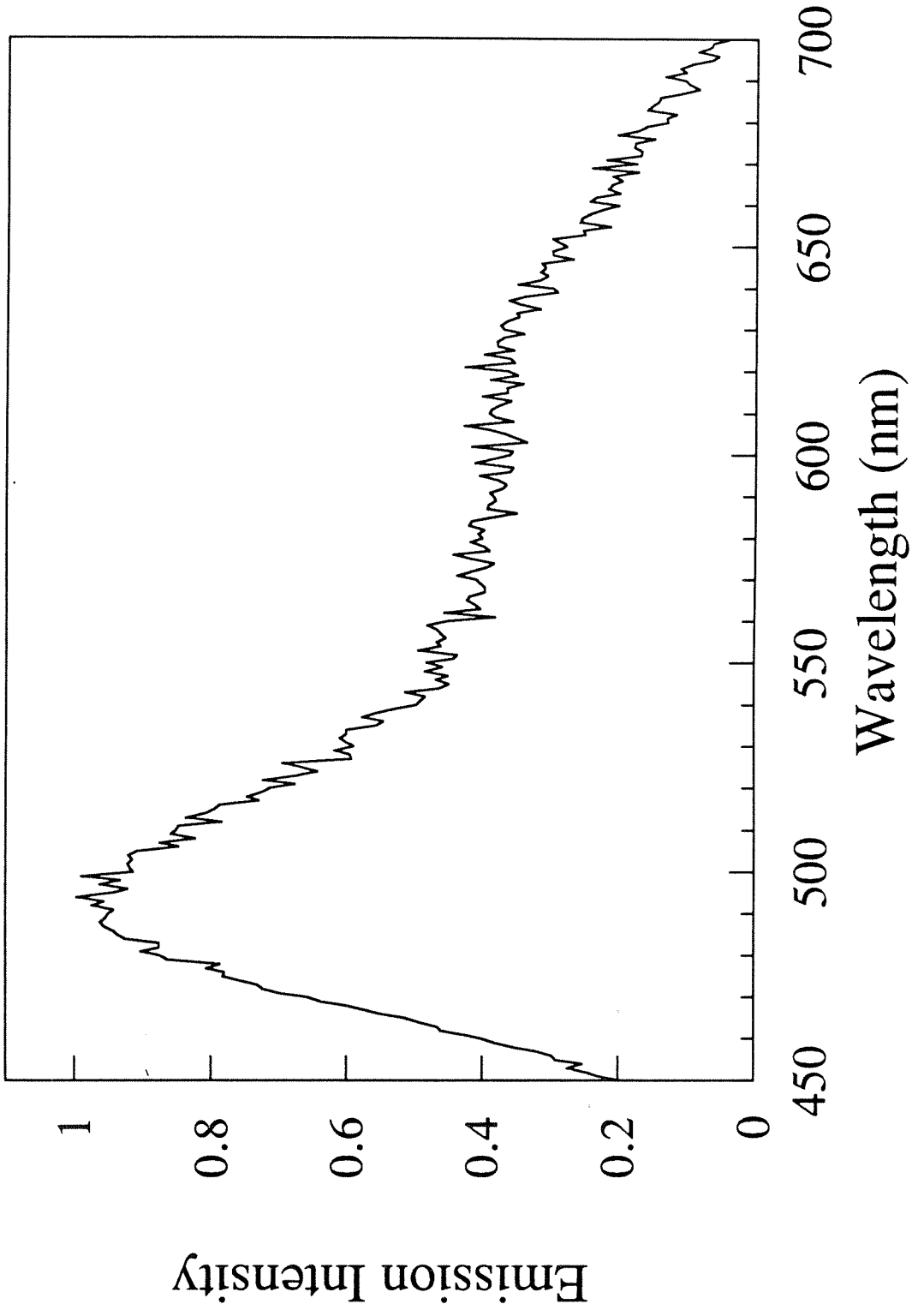

Emission Intensity
1
0.8
0.6
0.4
0.2
0
450
500
550
600
650
700
Wavelength (nm)

Figure 2.13. Solid-state emission spectrum of $Au_2(dcpe)_2$ $(PF_6)_2$ at room temperature, 313 nm excitation.

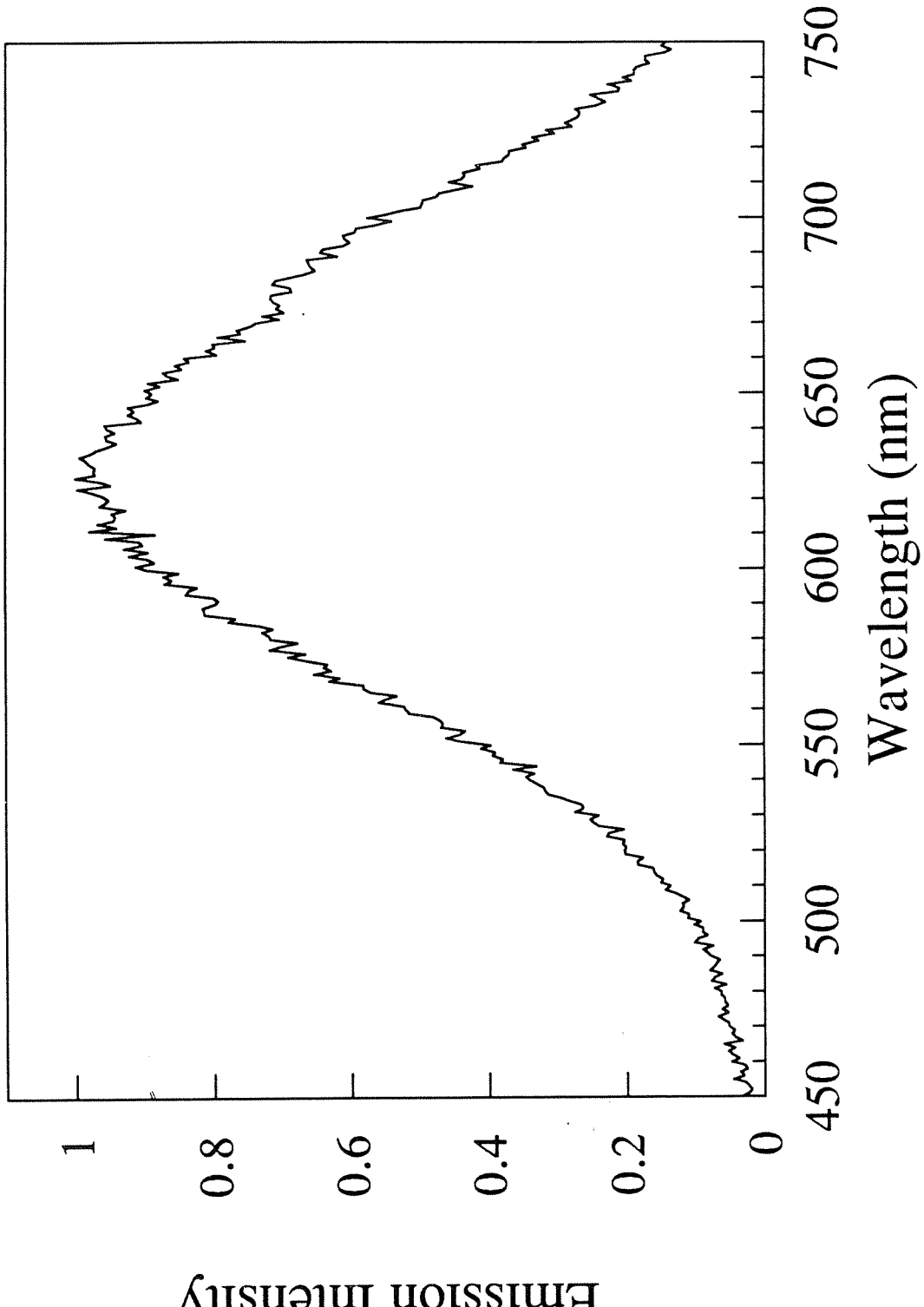

Emission Intensity
0
0.2
0.4
0.6
0.8
1
450
500
550
600
650
700
750
Wavelength (nm)

Figure 2.14. Emission spectrum of $Au_2(dcpe)_2$ $(PF_6)_2$ at 77 K in a 4:1 ethanol:methanol glass, 313 nm excitation.

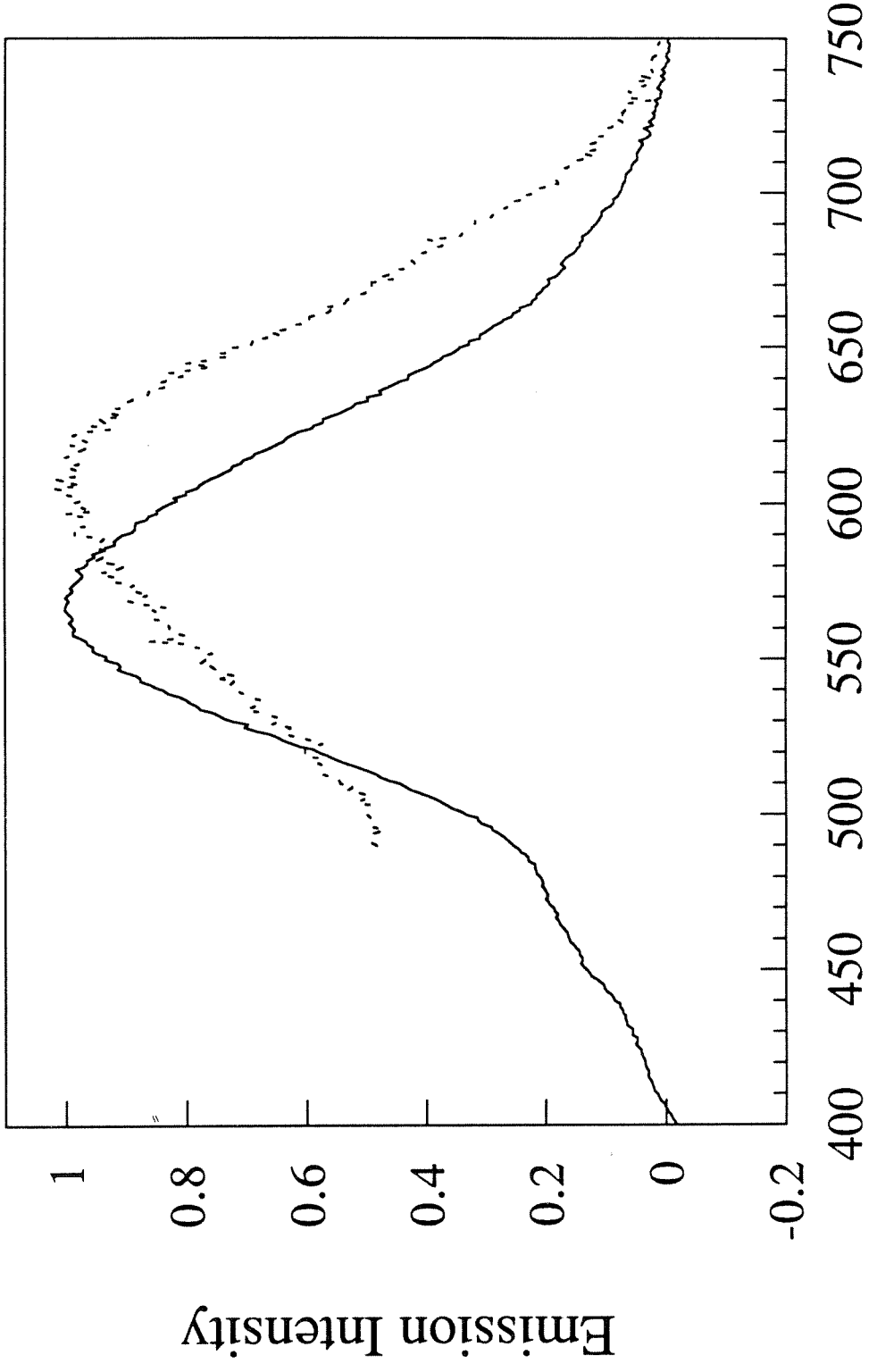

Emission Intensity
1
0.8
0.6
0.4
0.2
0
-0.2
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure 2.15. Emission spectrum of $Au_2(dcpe)_3$ $(PF_6)_2$ in acetonitrile solution at room temperature, 366 nm excitation, 10 μM.

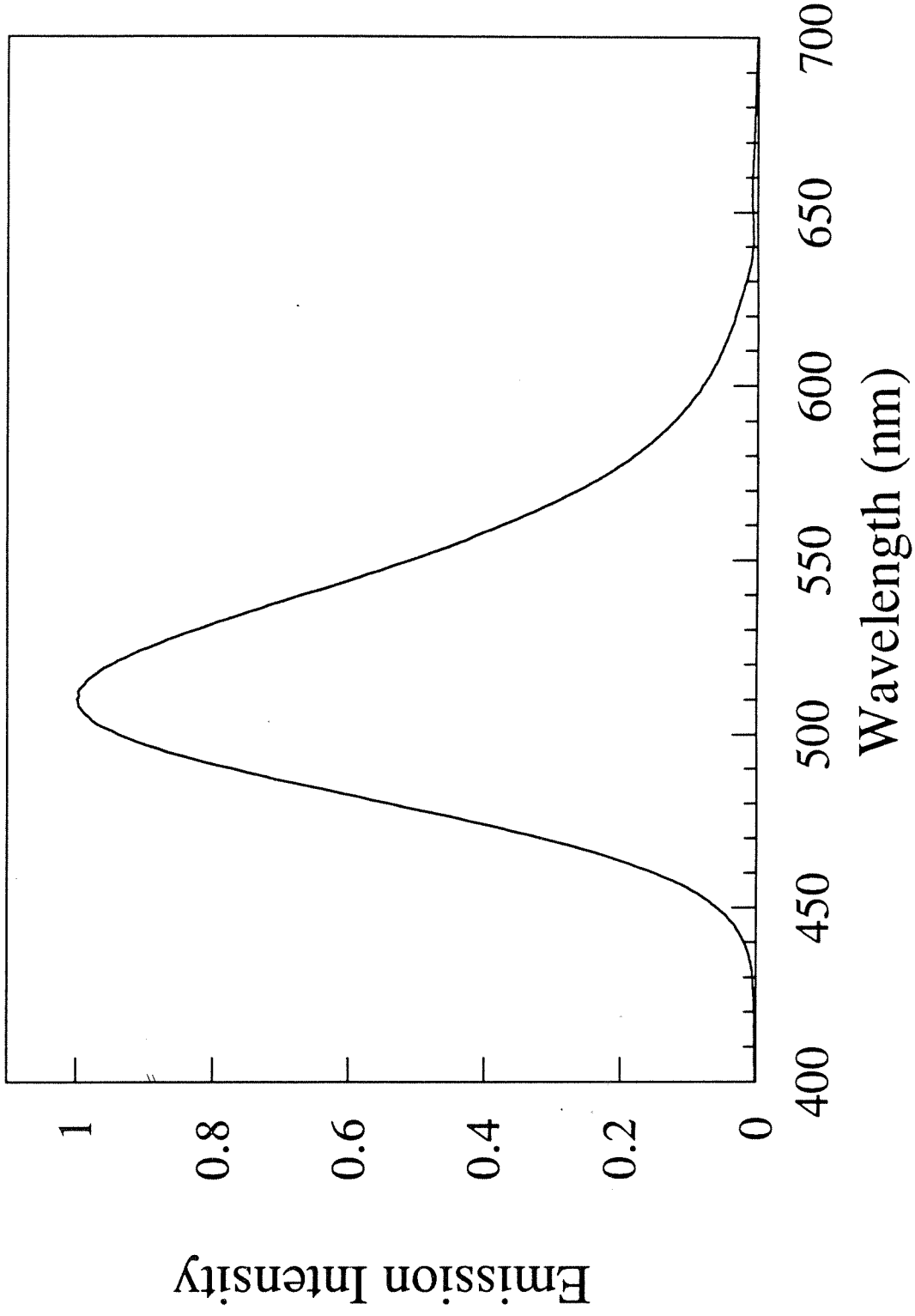
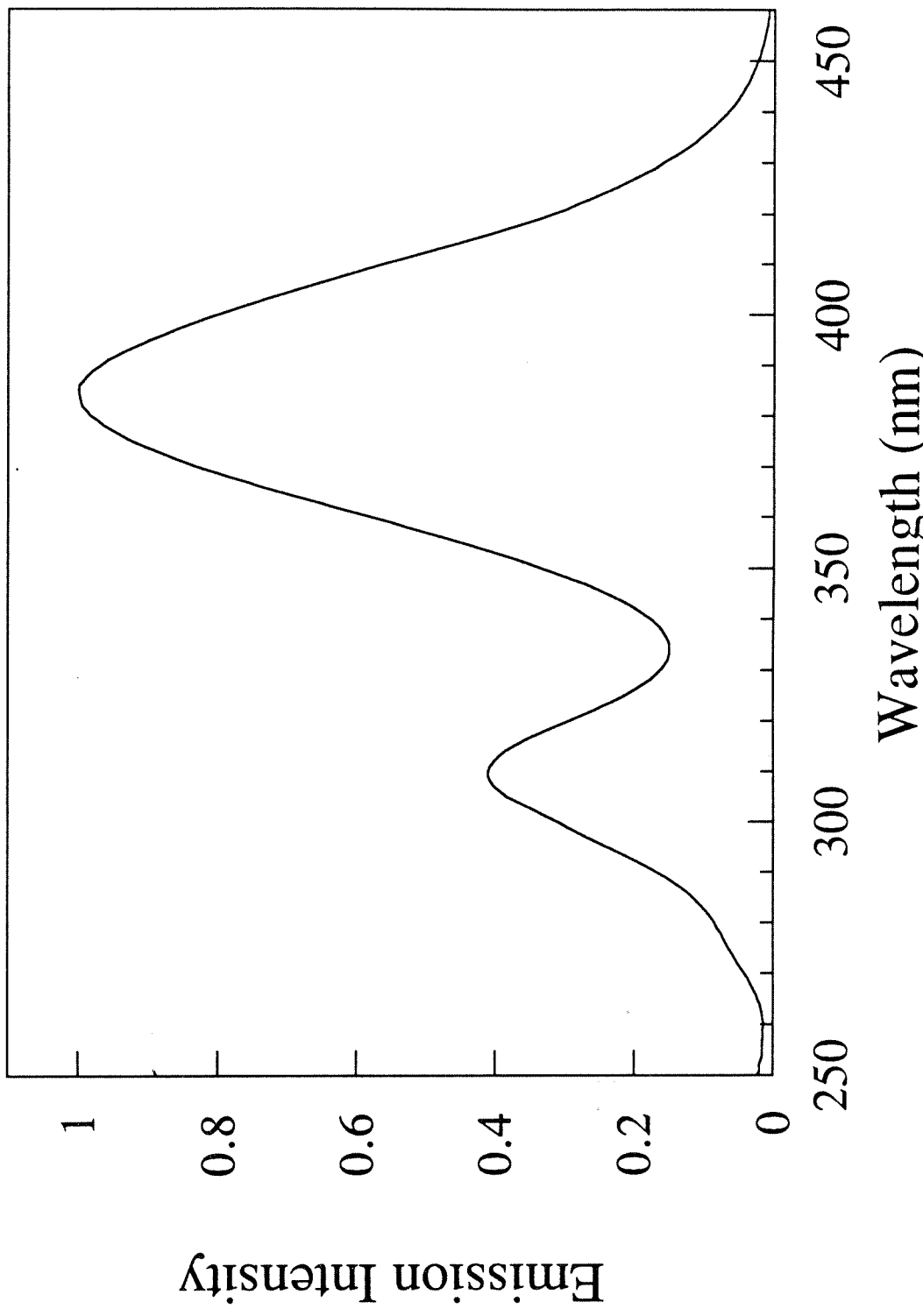

Emission Intensity
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
700
Wavelength (nm)

Figure 2.16. Excitation spectrum of $Au_2(dcpe)_3$ $(PF_6)_2$ in acetonitrile solution at room temperature, 366 nm excitation, 10 μM.


Emission Intensity
1
0.8
0.6
0.4
0.2
0
250
300
350
400
450
Wavelength (nm)

The compound $Au_2(dcpe)_3^{2+}$ has a weak low energy absorption at 370 nm (ε = 300 $M^{-1}cm^{-1}$ per AuP_3 unit). Using the approximate D_{3h} symmetry of the AuP_3 unit, this band is attributable to a $^1A_1' \rightarrow E'$ ($^3E''$) [d_{xy}, $d_{x^2-y^2}$ ($d\sigma^*$) $\rightarrow p_z$] transition. The d_{xy} , $d_{x^2-y^2}$ can be assigned as the HOMO since they lie in the plane of the ligands. Lying perpendicular to the plane of the ligands, the p_z is clearly the lowest energy p orbital and can be assigned as the LUMO since there are no low energy orbitals on the ligand. The resulting HOMO to LUMO, $^1A_1' \rightarrow {}^3E''$ transition is both spin and dipole forbidden. Spin orbit coupling of the gold splits the $^3E''$ state into A_1', A_2', E', and E'' levels; the $^1A_1' \rightarrow E'(^3E'')$ is the only dipole allowed transition. The corresponding singlet transition will be weak since the $^1A_1' \rightarrow {}^1E''$ is dipole forbidden, and is obscured by the allowed bands at 265 nm and 274 nm (ε = 32,500 $M^{-1}cm^{-1}$26,000 $M^{-1}cm^{-1}$ per AuP_3 unit respectively). The two higher energy allowed transitions are assigned as allowed d $\rightarrow$p transitions, but exact orbital assignment is difficult. Both the $^1A_1' \rightarrow {}^1E'$ (d_{xz}, $d_{yz} \rightarrow p_z$) and the $^1A_1' \rightarrow {}^1A_2''$ ($d_z^2 \rightarrow p_z$) are dipole allowed transitions. This complex luminesces intensely both as a solid (λ_{max} = 501 nm) and in acetonitrile solution at room temperature (λ_{max} = 508 nm; t = 21.1 μs (5); ϕ = 0.80 (5); Figure 2.15). The emission corresponds to the $^1A_1' \leftarrow E'(^3E'')$ transition. The excitation spectrum (Figure 2.16) has one very intense low energy band at 383 nm and a weaker band at 310 nm. The strong band at 383 nm confirms the emission assignment as being complementary to the assignment for the absorption at 370 nm. The large quantum yield (ϕ = 0.8 for 366 nm excitation) supports the assignment of the absorption at 370 nm as a direct singlet to triplet transition, and the extremely long lifetime provides further evidence that the emission occurs from a triplet state. The $E_{\nu_0-\nu_0}$ for the emissive transition in acetonitrile solution is 432 nm with a Stokes shift of 7,800 cm^{-1}.

The dipe complexes of gold are structually similar to the dcpe complexes and the assignments for the absorption bands (Figures 2.17-2.19) are as follows: $Au(dipe)_2^+$, $^1A_1 \rightarrow {}^1B_2$ (d_{xz}, $d_{yz} \rightarrow p_x$, p_y) at 233 nm with a shoulder at 255 nm; $Au_2(dipe)_2^{2+}$,

$^1A_g \rightarrow {}^1B_{1u}$ ($d\sigma^* \rightarrow p\sigma$) at 269 nm, $^1A_g \rightarrow {}^3B_{1u}$ ($d\sigma^* \rightarrow p\sigma$) at 315 nm; $Au_2(dipe)_3^{2+}$, $^1A_1' \rightarrow E'$ ($^3E''$) [d_{xy}, $d_{x^2-y^2}$ ($d\sigma^*$) $\rightarrow p_z$] at 368 nm, $^1A_1' \rightarrow {}^1E'$ [d_{xy}, $d_{x^2-y^2}$ ($d\sigma^*$) $\rightarrow p_z$] obscured by the higher energy d $\rightarrow$ p bands at 268 nm and 227 nm. The $Au_2(dipe)_2^{2+}$ complex emits as a solid at room temperature (λ_{max} = 630 nm) upon 313 nm excitation and in a ethanol:methanol (4:1) glass at 77K (λ_{max} = 566 nm), but shows no emission at room temperature with 366 nm excitation (Figure 2.20). Only the $Au_2(dipe)_3^{2+}$ complex emits in acetonitrile solution at room temperature (λ_{max} = 510 nm; Figure 2.21). The excitation spectrum of $Au_2(dipe)_3^{2+}$ has an intense low energy band at 383 nm and a second band at 308 nm (Figure 2.22).

The complex $Au_2(dppb)_3^{2+}$ is only sparingly soluble in any solvent so the absorption spectrum could only be obtained for low concentrations in ethanol. The lowest energy observable absorption band occurs at 270 nm (Figure 2.23). The compound emits both as a solid and in ethanol solution at room temperature (λ_{max} = 534 nm; Figure 2.24) The emission is assigned as a $^1A_1' \leftarrow E'(^3E'')$ transition analogous to the emissive transition observed for $Au_2(dcpe)_3^{2+}$. The excitation spectrum shows two bands at 359 nm and 320 nm (Figure 2.25). The 359 nm band presumably corresponds to the $^1A_1' \rightarrow E'(^3E'')$ transition which is not observable in the absorption spectrum due to solubility limitations. The higher energy band falls on the tail of the 270 nm absorption band and is assigned as the $^1A_1' \rightarrow {}^1E''$ transition.

Low Temperature Spectra To confirm the assignment of the low energy absorption band and emission of $Au_2(dcpe)_3^{2+}$ low temperature (77 K) absorption and emission spectra were measured. The d_{xy}, $d_{x^2-y^2} \rightarrow p_z$ transition assigned to the absorption band involves removing an electron from the Au-P σ^* orbital and placing it into the non-bonding p_z orbital; therefore, the excited state should have stronger Au-P bonds and a narrower potential well. Cooling the sample reduces the number of thermally accessible vibrational levels in the ground state and in the case of a more

Figure 2.17. Absorption spectrum of $Au(dipe)_2$ (PF_6), 67 μM.

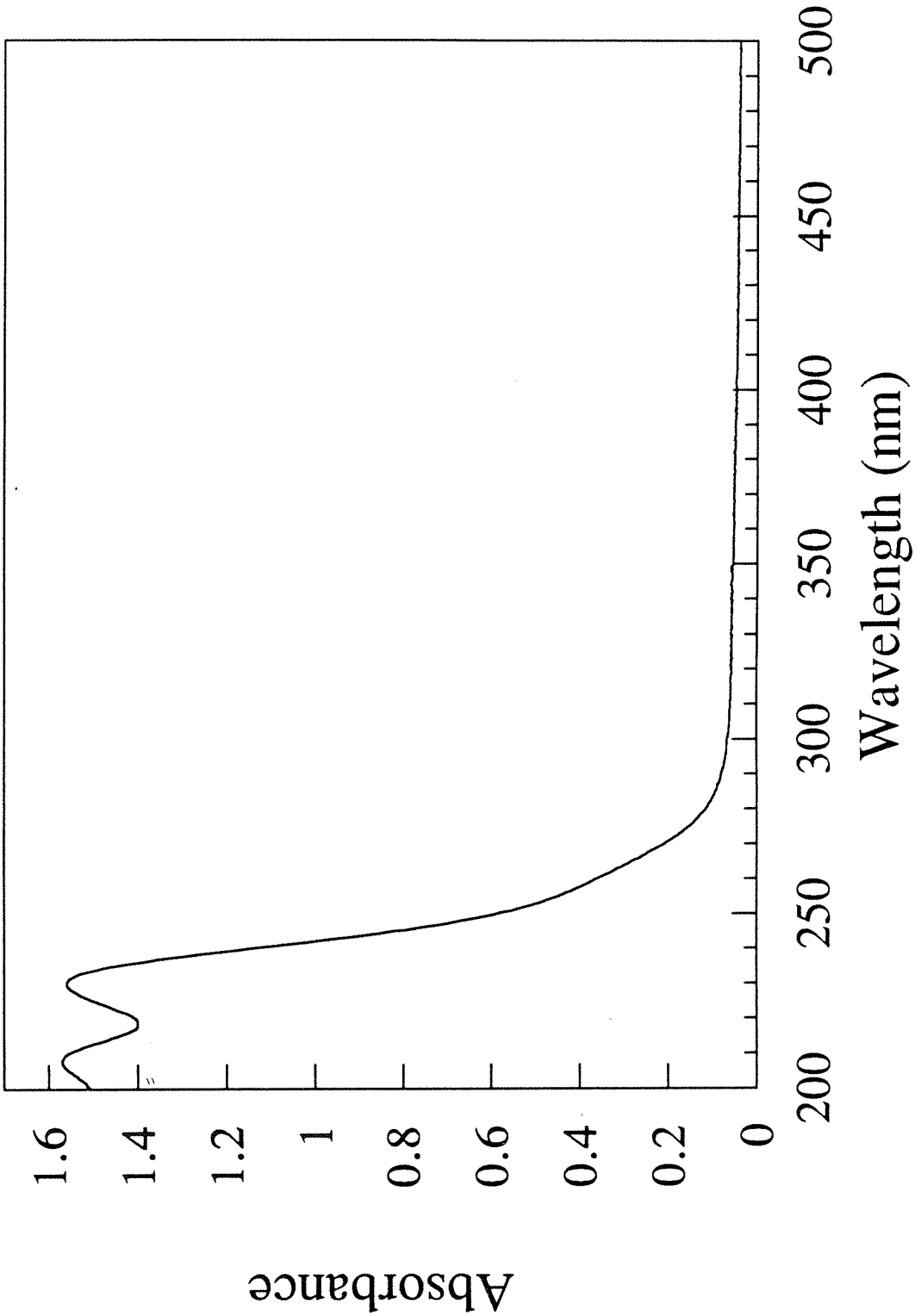

Absorbance
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.18. Absorption spectrum of $Au_2(dipe)_2 (PF_6)_2$, 85 μM.

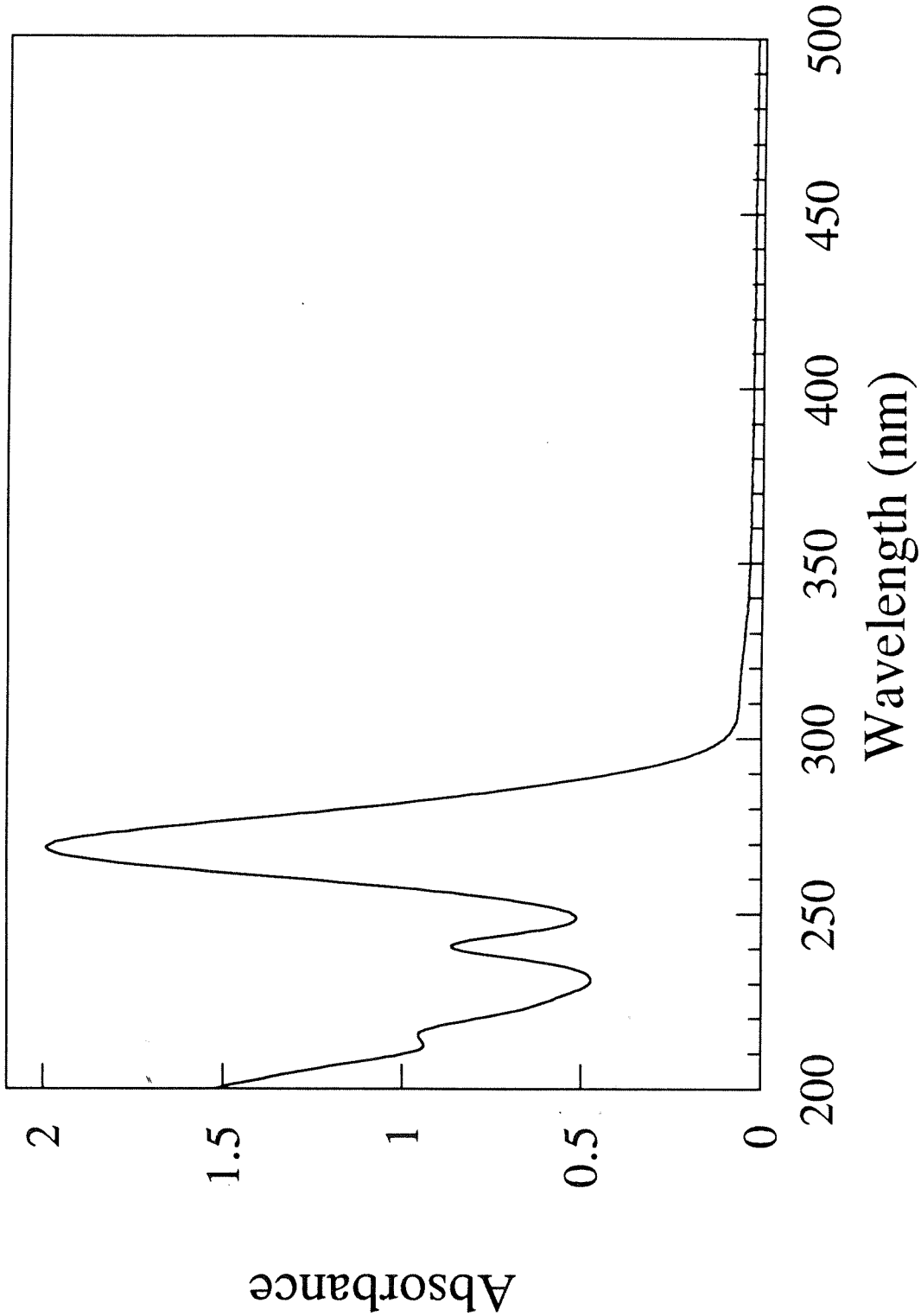

Absorbance
2
1.5
1
0.5
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.19. Absorption spectrum of $Au_2(dipe)_3 (PF_6)_2$, 8 and 800 μM.

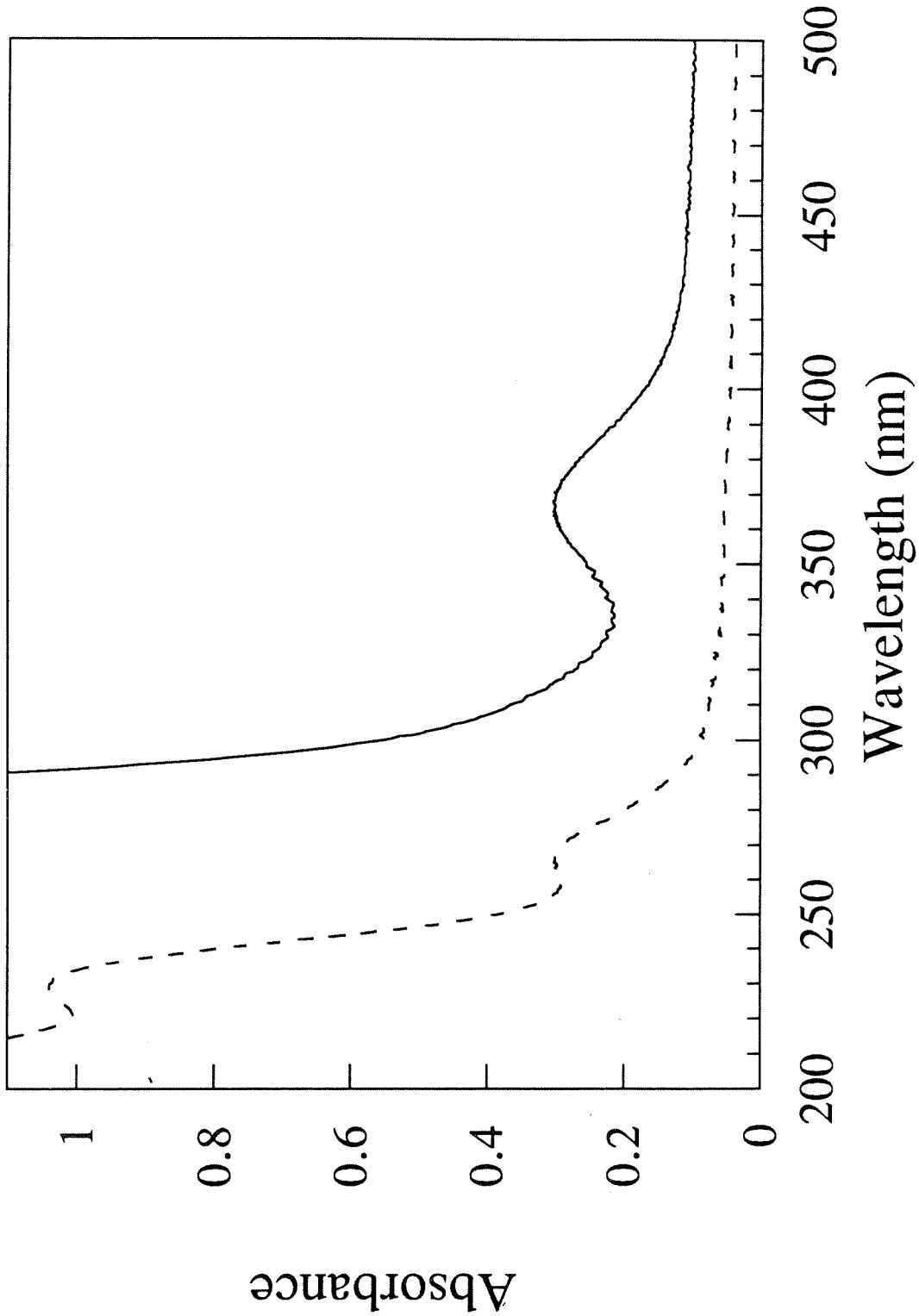

Absorbance
1
0.8
0.6
0.4
0.2
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.20. Solid-state emission spectrum of $Au_2(dipe)_2$ $(PF_6)_2$ at room temperature, 313 nm excitation.

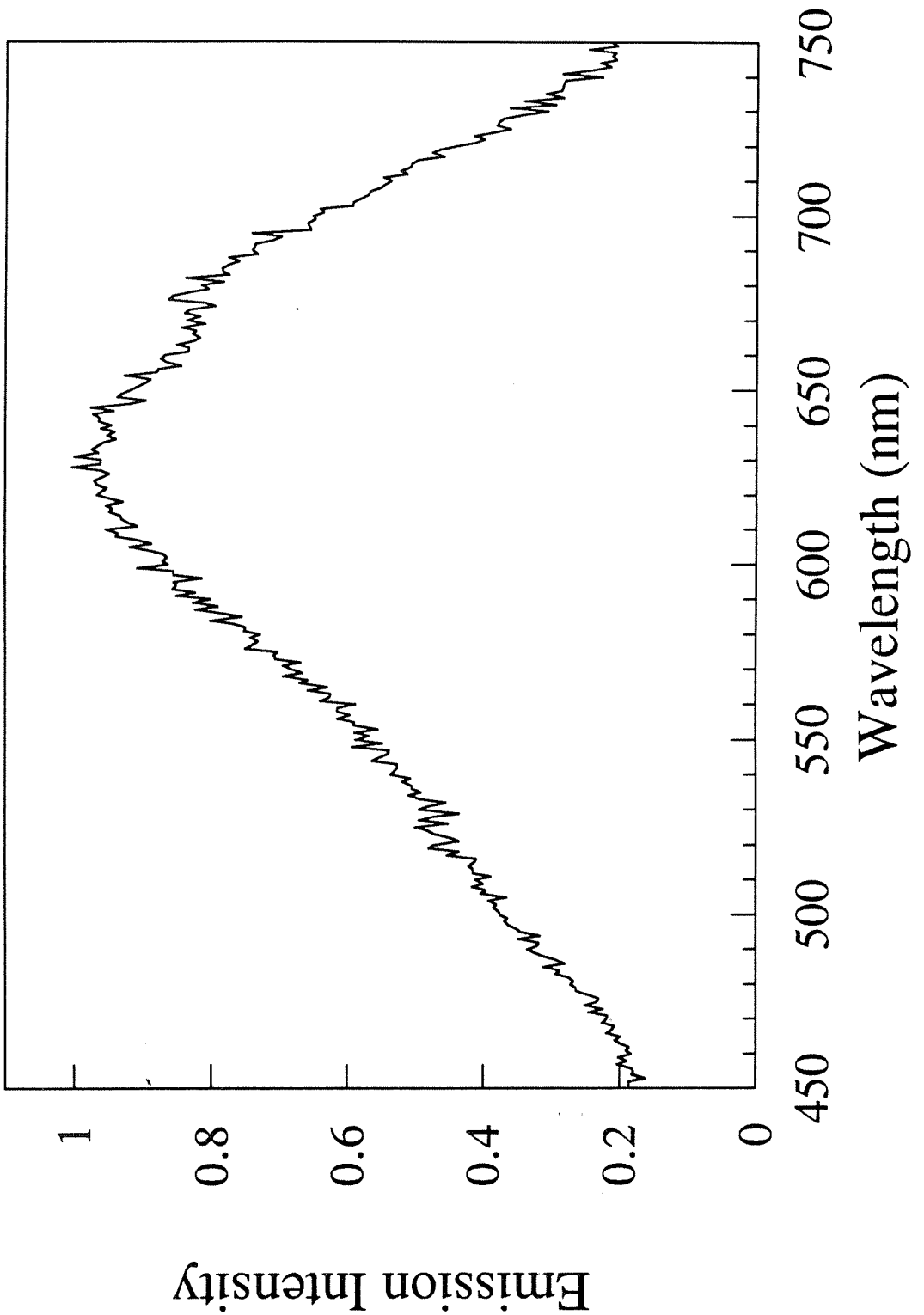

Emission Intensity
1
0.8
0.6
0.4
0.2
0
450
500
550
600
650
700
750
Wavelength (nm)

Figure 2.21. Emission spectrum of $Au_2(dipe)_3 (PF_6)_2$ in acetonitrile solution at room temperature, 366 nm excitation, 10 μM.

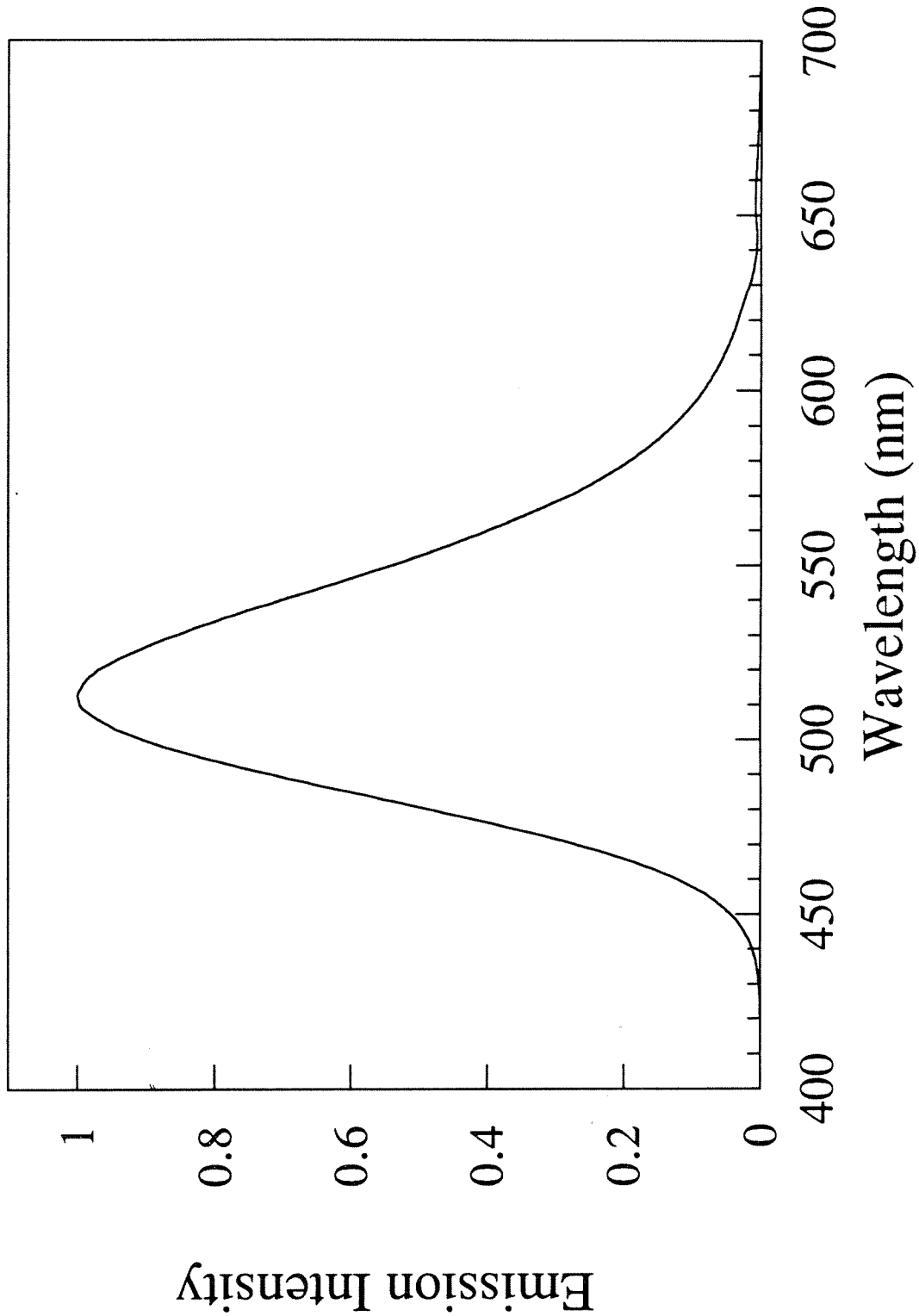

Emission Intensity
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
700
Wavelength (nm)

Figure 2.22. Excitation spectrum of $Au_2(dipe)_3 (PF_6)_2$ in acetonitrile solution at room temperature, 366 nm excitation, 10 μM.

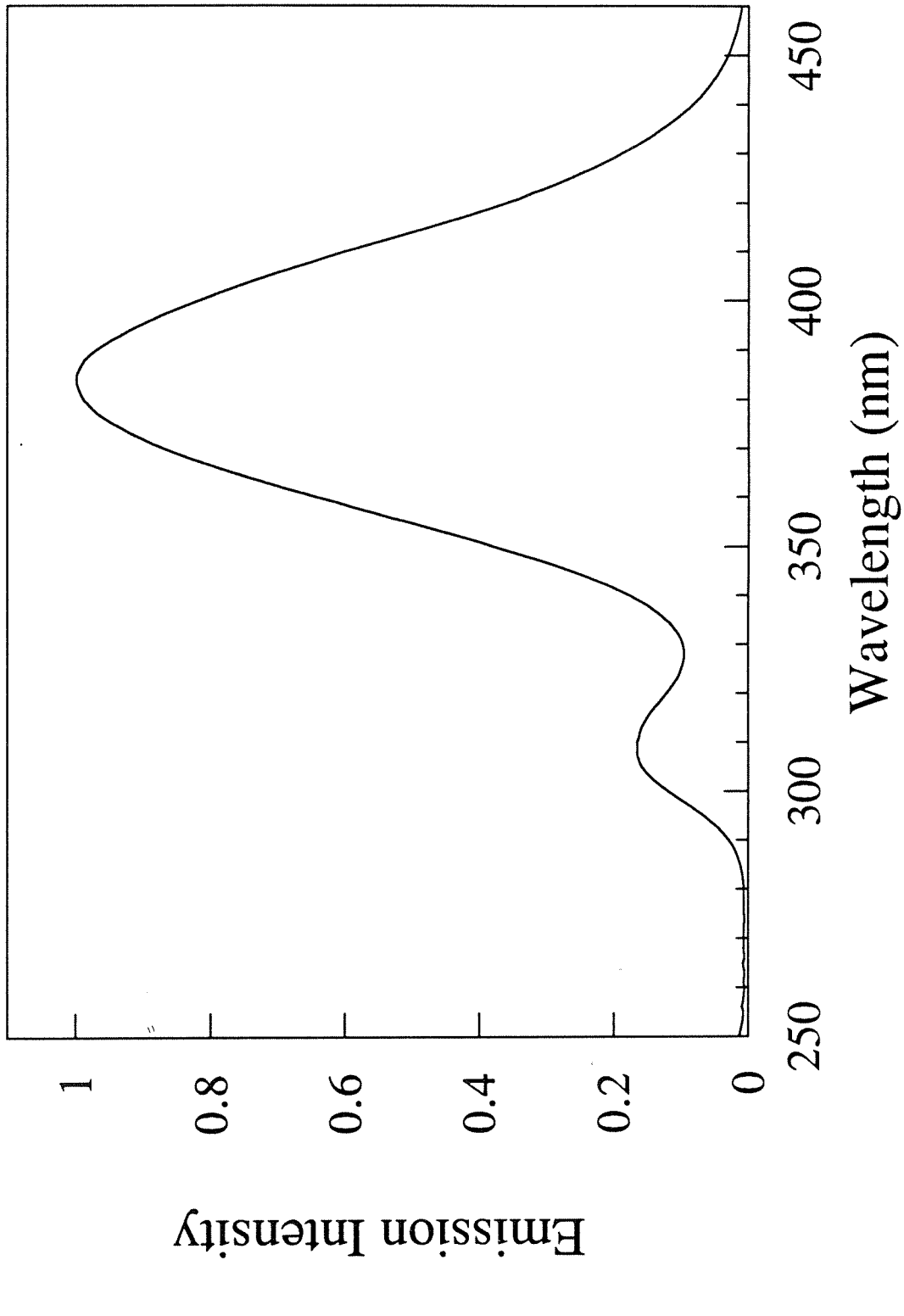

Emission Intensity
1
0.8
0.6
0.4
0.2
0
250
300
350
400
450
Wavelength (nm)

Figure 2.23. Absorption spectrum of $Au_2(dppb)_3 (PF_6)_2$ in ethanol, 3 μM.

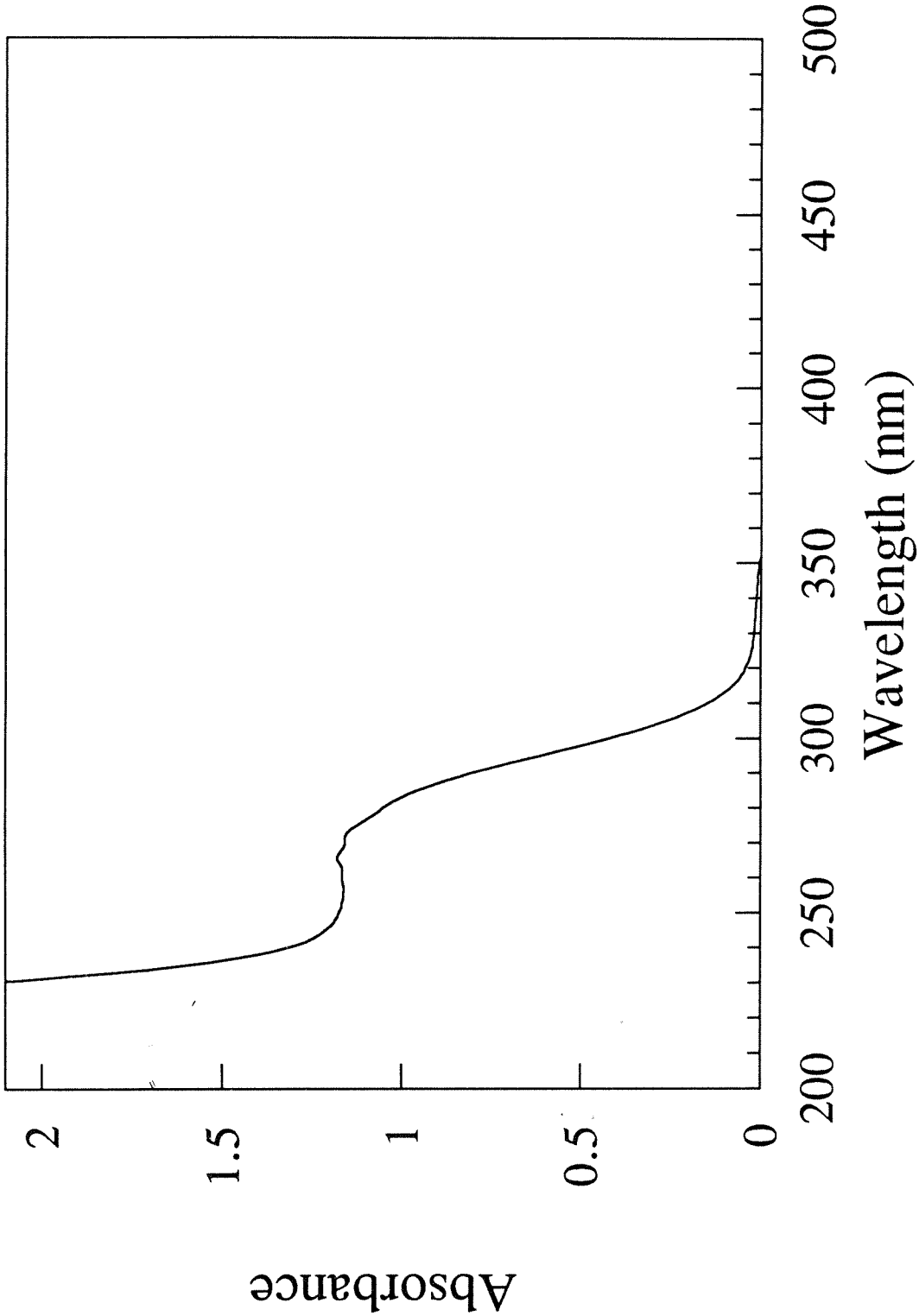

Absorbance
2
1.5
1
0.5
0
200
250
300
350
400
450
500
Wavelength (nm)

Figure 2.24. Emission spectrum of $Au_2(dppb)_3$ $(PF_6)_2$ in ethanol solution at room temperature, 366 nm excitation, 2 μM.

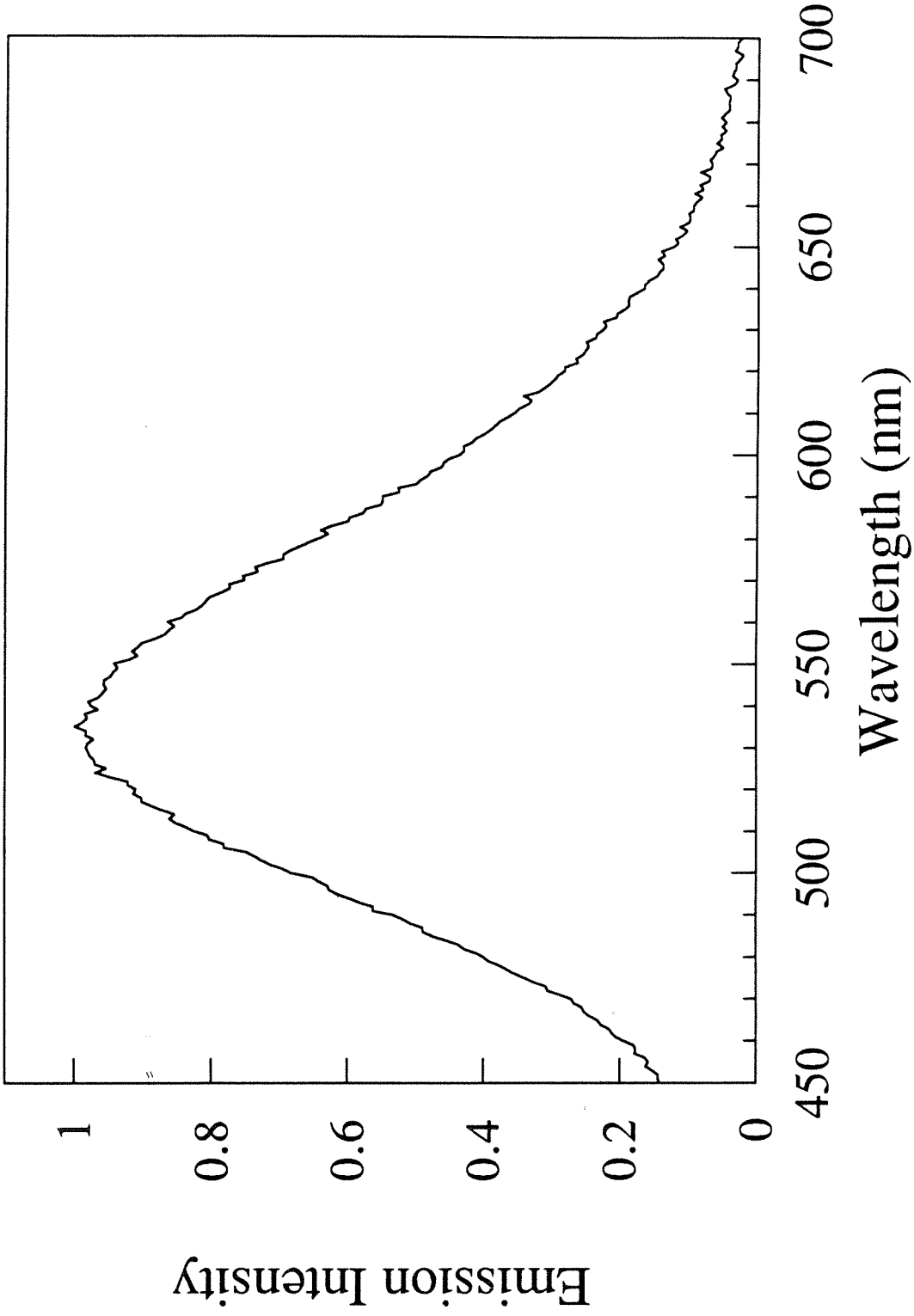
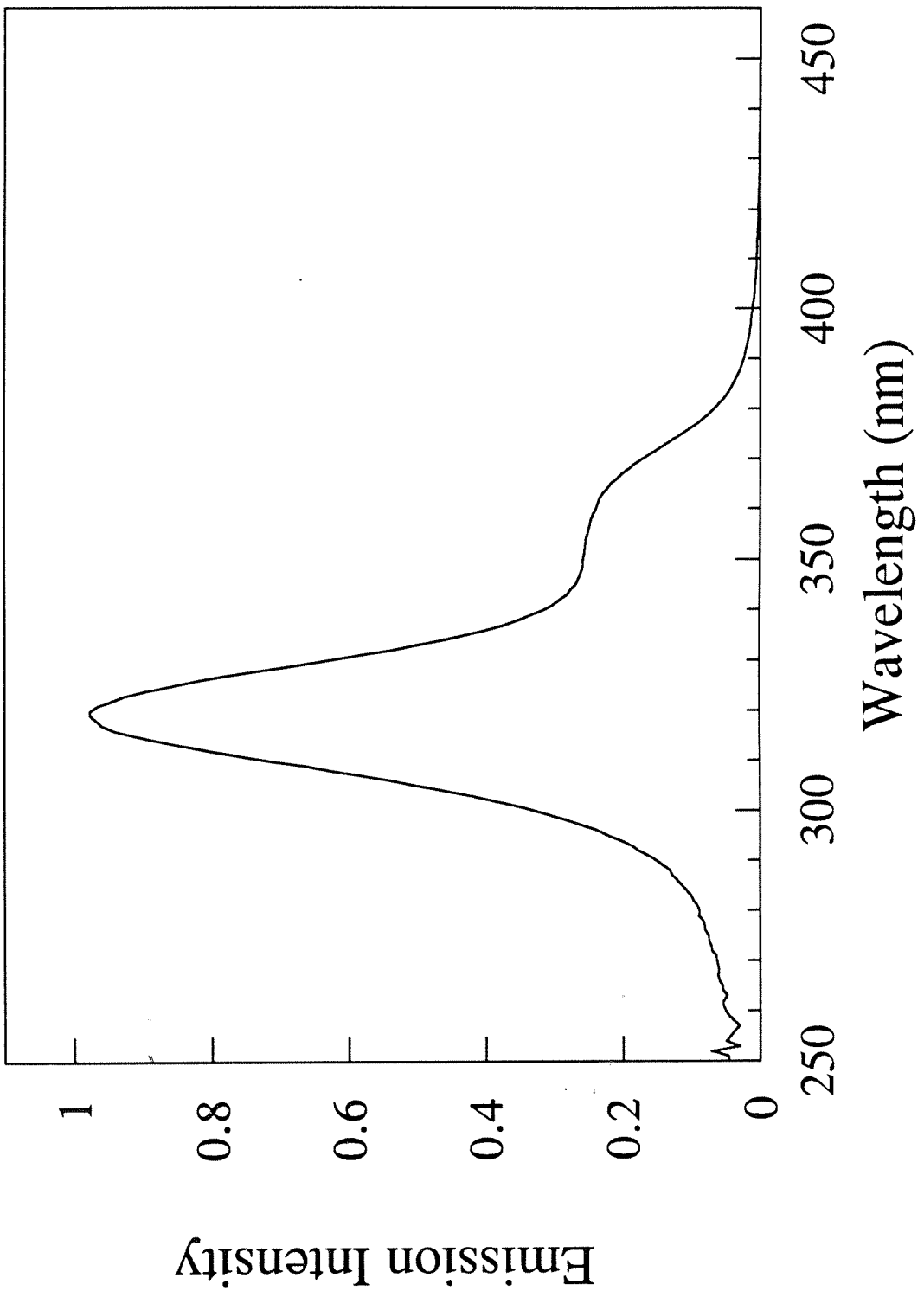

Emission Intensity
1
0.8
0.6
0.4
0.2
0
450
500
550
600
650
700
Wavelength (nm)

Figure 2.25. Excitation spectrum of $Au_2(dppb)_3 (PF_6)_2$ in ethanol solution at room temperature, 366 nm excitation, 2 μM.


Emission Intensity
1
0.8
0.6
0.4
0.2
0
250
300
350
400
450
Wavelength (nm)

strongly bound excited state will lead to a narrowing of the absorption band concomitant with a red shift of the maximum. Figure 2.26 depicts an idealized situation with the excited state directly above the ground state. At temperature T_1, v_0 and v_1 vibrational levels are occupied in the ground state. The allowed vertical Frank-Condon transitions are $v_0 \rightarrow v_0$, $v_1 \rightarrow v_1$, and $v_1 \rightarrow v_2$. As the material is cooled only the v_0 level is occupied in the ground state and the only allowed transition is $v_0 \rightarrow v_0$. Losing the higher energy $v_1 \rightarrow v_2$ transition causes the absorption band to narrow and red shift. Most excited states involve occupation of σ^* orbitals as opposed to bonding or non-bonding orbitals, in which case the bond strength of the excited state is lower than the ground state and a blue shift in the maximum of the absorption band would be expected on cooling. The 7 nm red shift in the absorption band (Figure 2.27) and a 3 nm blue shift of the emission observed for $Au_2(dcpe)_3^{2+}$ demonstrate that the excited state is more strongly bound than the ground state.

Titration with Triphenylphosphine The compound $ClAu(PPh_3)$ was placed into a solution of acetonitrile and degassed. The emission of the solution was then monitored as PPh_3 was added to the solution. The resulting titration (Figure 2.28) shows that the solution begins to emit (λ_{max} = 520 nm) as soon as half an equivalent of PPh_3 is added; emission continues to increase even up to the addition of nine equivalents. This emission is assigned as a $^1A_1' \leftarrow E'(^3E'')$ transition, analogous to that observed for $Au_2(dcpe)_3^{2+}$. The emission is believed to originate from a three coordinate $Au(PPh_3)_3^+$ complex which is in equilibrium with $Au(PPh_3)_2^+$, $Au(PPh_3)_4^+$and free PPh_3. The broad ^{31}P NMR signal at room temperature supports the suggestion of an equilibrium between different species.

Photochemistry The emissive complex $Au_2(dcpe)_3^{2+}$ is a potent photo-reductant capable of reducing a variety of haloalkanes and aryl halides. Emission of $Au_2(dcpe)_3^+$ is completely quenched by 1,2-dibromoethane, bromobenzene, carbontetrachloride, and chloroform (control experiments in the dark showed no change

Figure 2.26. Energy surface diagram: a,b, and c represent the allowed vertical Frank-Condon transitions of ν_o-ν_o, ν_1-ν_1 andν_1-ν_2.

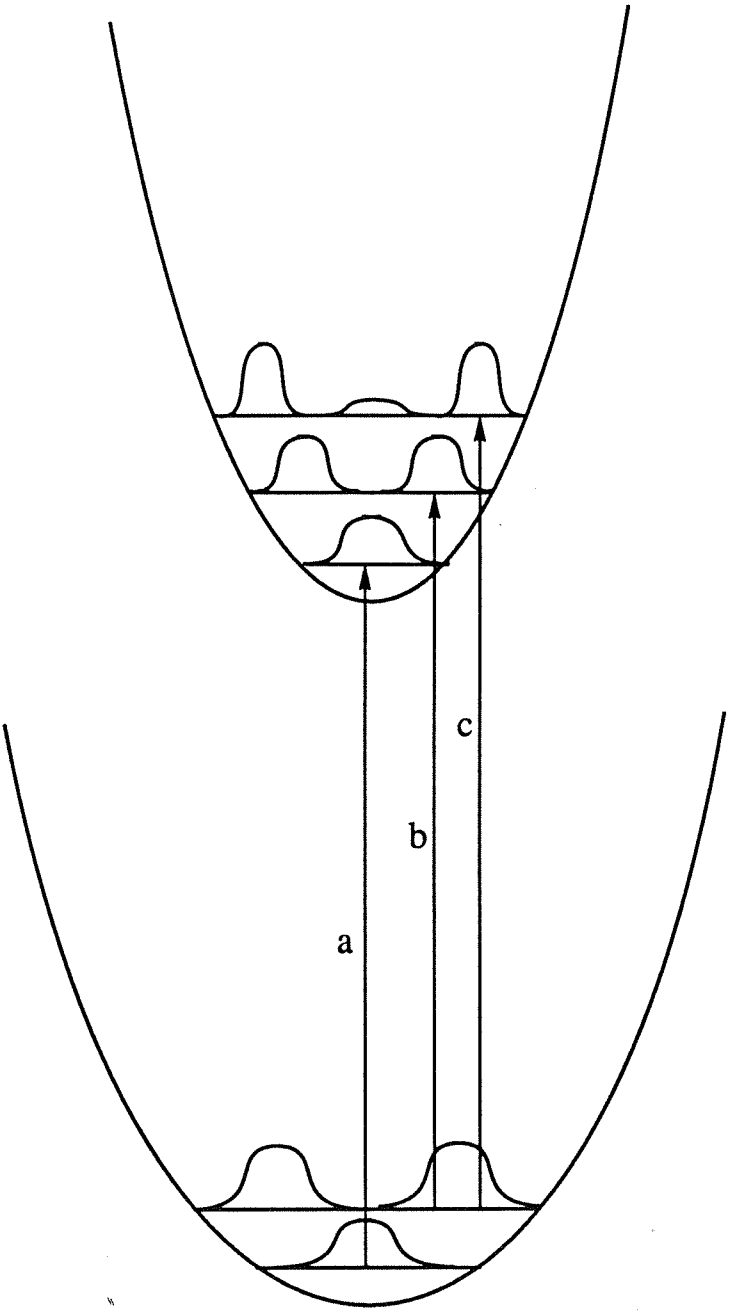

c
b
a

Figure 2.27. Absorption spectra of $[Au_2(dcpe)_3]$ $(PF_6)_2$ at 298 K (lower trace) and 77 K (upper trace).

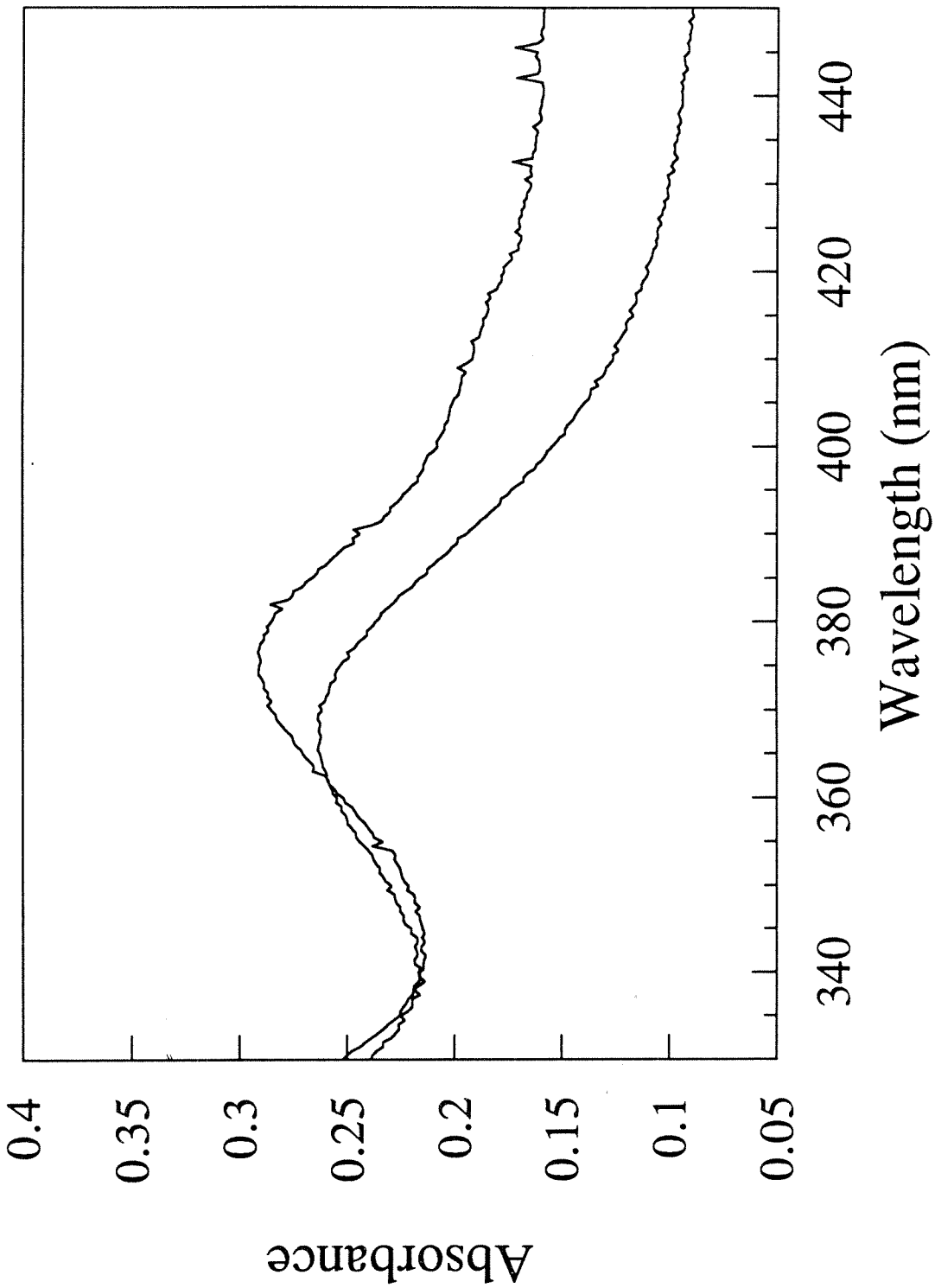
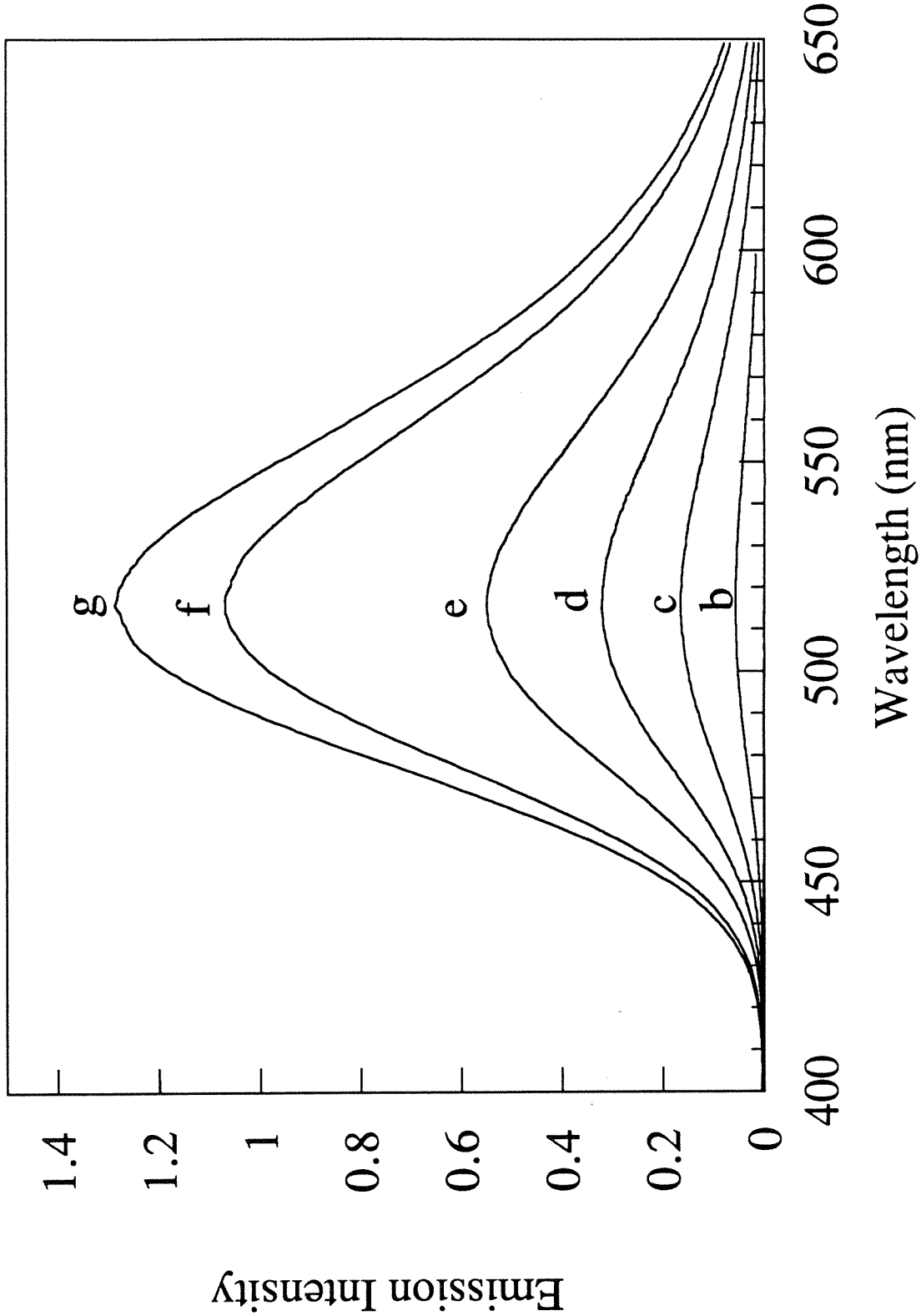

Absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
340
360
380
400
420
440
Wavelength (nm)

Figure 2.28. Emission spectra of $ClAu(PPh_3)$ with a, 0 (coincides with the baseline); b, 0.5; c, 1.0; d, 1.5; e, 2.0; f, 5.0; g, 9.0 equivalents of PPh_3 added.


Emission Intensity
1.4
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
Wavelength (nm)
g
f
e
d
c
b

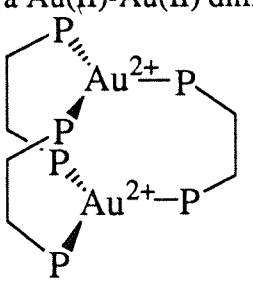
in the electronic absorption spectrum of $Au_3(dcpe)_3^{2+}$ in the presence of the halogenated compounds). No quenching of the emission was observed in the presence of chlorobenzene. The photoreactions with 1,2-dibromobenzene, bromo-benzene and chloroform have been followed by ^{31}P NMR; after photolysis for 15 minutes with a 366 nm Hg hand held lamp, the $Au_2(dcpe)_3^{2+}$ phosphorous signal diminished completely and was replaced by a singlet (1,2-dibromobenzene, 61.1 ppm; bromobenzene, 61.1 ppm; chloroform, 60.7 ppm). Quenching rates were obtained by monitoring the luminescence as a function of the concentration of the quencher as described in chapter 3 (Table 2.3).. In general reduction of haloaromatic compounds is an irreversible two electron process[19] in which the halocarbon is reduced by one electron, dissociates X^-, and the remaining aromatic radical is quickly reduced to Ar^-. The reaction with $Au_2(dcpe)_3^{2+}$ is irreversible and most likely proceeds in this manner with the

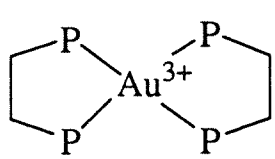
$$ArX + e^- \rightarrow ArX^{\cdot -} \quad \text{slow}$$

$$ArX^{\cdot -} \rightarrow Ar^{\cdot} + X^- \quad \text{fast}$$

$$Ar^{\cdot} + e^- \rightarrow Ar^- \quad \text{fast} \qquad \text{R1}$$

formation of Au(II) as the Cl^- transfers to the gold center; the Au(II) may then disproportionate or transfer a second electron to form Au(III). The nature of the Au product is intriguing. The appearance of a lone singlet shows that there is only one phosphorous product and that all of the phosphorous atoms in the product are equivalent. The signals observed near 60 ppm do not correspond to either the free dcpe ligand (3.0 ppm) or the oxide of the ligand (51.4 ppm). Since all phosphorous atoms must be equivalent there are only a few choices for possible gold complexes. Two possible complexes are a Au(II)-Au(II) dimer similar to the complex reported by Fackler,[20] and a





four coordinate Au(III) complex with two chelating dcpe units. Crystals that diffract have been grown, but lost solvent and cracked before the structure was solved.

Excited State Potential The potential of the excited state can be estimated from the $\nu_0 \rightarrow \nu_0$ energy and the oxidation potential of the metal center. The $\nu_0 \rightarrow \nu_0$ energy of $Au(dcpe)_3^{2+}$ was approximated at 1% of the maximum intensity assuming a Gaussian absorption band (Equation 1).[21] As a check the same procedure was employed with the

$$\nu_{1\%} = \nu_{max} \pm 1.29\ (\Delta\nu_{1/2}) \qquad 1.$$

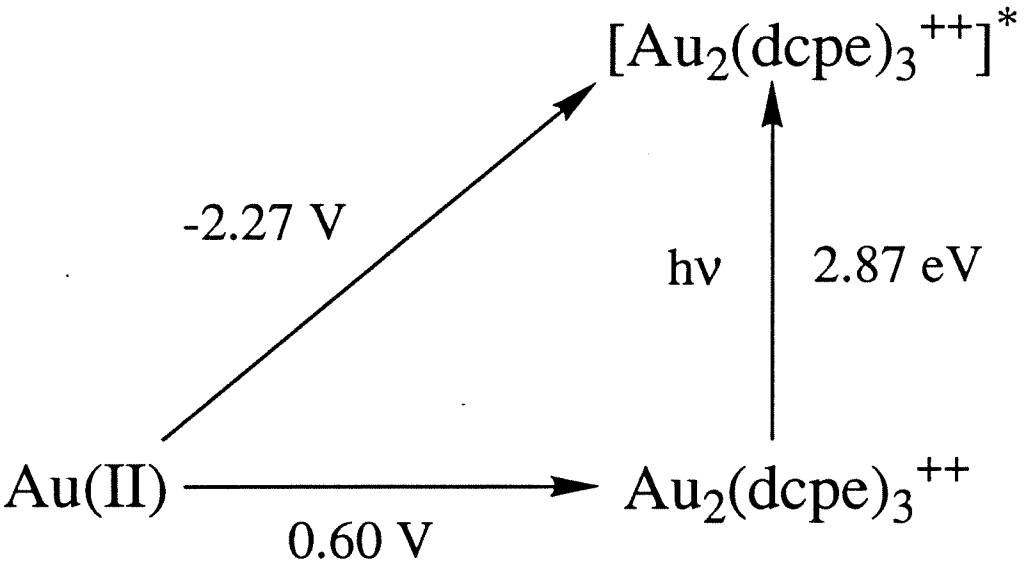
emission band, which gave a value of 23,420 cm^{-1} compared to 22,850 cm^{-1} from the absorption band. The average value of 23,130 cm^{-1} (432 nm) corresponds to 2.9 eV. The ground state electrochemistry shows that the oxidation of the Au(I) center is completely irreversible with E_{pc} at 0.6 V. Using the E_{pc} as a maximum limit on $E_{1/2}$, the $\nu_0 \rightarrow \nu_0$ energy gives an excited state potential of 2.3 V vs SSCE (Figure 2.29). The value 2.3 eV for the ΔG of excited state oxidation fits in well with the observed rate of atom abstraction from bromobenzene. Saveant has studied the reduction of bromobenzene with a series of strong reducing agents and made an experimental plot of the rate of electron transfer vs. the potential of the catalyst.[19] The rate of $8.68 \times 10^7\ M^{-1}s^{-1}$ for reduction by the excited $Au(dcpe)_3^{2+}$ (see chapter 3) corresponds to a potential of 2.5 V vs. SCE.

General Synthesis of Three Coordinate Gold Complexes Several attempts were made to design a general synthetic procedure for three coordinate gold(I) complexes. The first strategy was to make a gold complex with one monodentate phosphine and then add one equivalent of a bidentate chelating phosphine. The $ClAuPR_3$ are readily prepared and isolated by adding one equivalent of PR_3 to compound 3 in acetonitrile. After four hours of stirring, the product precipitates as a white powder. Addition of the bidentate phosphine dcpe lead to a mixture of products which included $Au_2(dcpe)_2^{2+}$. There was no evidence for the desired three coordinate complex $PR_3Au(dcpe)^+$ in the ^{31}P NMR.

Table 2.3 Excited state quenching rates of $[Au_2(dcpe)_3]$ $(PF_6)_2$ with aryl and alkyl halides; the quenching rate with C_6H_5Cl was too slow to measure.

Quencher	$k_q(M^{-1}s^{-1})$	$E_{1/2}$ (V *vs* SCE)
CCl_4	1.8×10^9	
$CHCl_3$	4.7×10^8	
$BrCH_2CH_2Br$	4.7×10^8	
C_6H_5Br	8.8×10^7	-2.44
C_6H_5Cl	$< 1 \times 10^5$	-2.78

Figure 2.29 Modified Latimer diagram for $[Au_2(dcpe)_3]$ $(PF_6)_2$.


[Au2(dcpe)3++]*
-2.27 V
hν
2.87 eV
Au(II)
Au2(dcpe)3++
0.60 V

Attempts to synthesize three coordinate complexes of the type CNAu(dcpe) from AuCN and dcpe were unsuccessful due to the formation of $Au(CN)_2^-$. Most recently, the complex ClAu(dcpp) has been isolated in an effort to take advantage of the poor bridging capabilities of the dcpp bidentate ligand. The propyl bridge between the phosphines adopts a chelating conformation much more readily than a bridging conformation, so that unwanted products such as $Au_2(dcpp)_2^{2+}$ may be avoided. The next step will be to add one equivalent of PR_3 and determine if the compounds $PR_3Au(dcpp)^+$ are stable on the NMR time scale (products should give one doublet and one triplet signal in the ^{31}P NMR spectra).

Conclusions

A series of three coordinate gold complexes which luminesce in solution at room temperature has been synthesized. The novel emission transition in these complexes is a metal centered d ← p transition. The lifetime (τ = 21.1 μs) in solution is long enough for the gold moiety to interact with other compounds and act as a potent photo-reductant with a ($Au(I)^*/Au(II)$) potential of 2.4 V. The excited gold complex is capable of reducing halo aromatics such as bromobenzene. Photo-reactions with haloaromatics and haloalkanes results in halo abstraction of X^- and a total transfer of two electrons to the substrate.

The only complexes which display the long-lived luminescence in solution are $Au_2(dcpe)_3^{2+}$, $Au_2(dipe)_3)^{2+}$, $Au(PPh_3)_3^+$, and $Au_2(dppb)_3^{2+}$. In all four of these cases the emission is ascribed to a $^1A_1$← E' ($^3E''$) emission. The corresponding absorption transition has also been identified as the lowest energy absorption band in $Au_2(dcpe)_3^{2+}$, and $Au_2(dipe)_3^{2+}$. It is clear that the Au-Au interaction is not crucial for solution emission as suggested by previous literature since none of solution emissive complexes have a significant Au-Au interaction.

The crucial aspect for emission from an isolated Au(I) monomer unit is the coordination environment of the metal center. Three coordinate complexes are the only

type of monomers observed to emit. In comparison to the two and four coordinate complexes, the three coordinate species have the greatest electron density on the Au(I) atom while still preserving a non-bonding p orbital as the LUMO. Two coordinate complexes have no low energy d $\rightarrow$ p transitions, because the reduced electron density on the Au(I) center stabilizes the d_{xy}, $d_x2_{-y}2$ orbitals relative to the p_z orbital. Four coordinate compounds have more electron density on the Au(I) center, but the LUMO is a high energy σ^* p orbital so the d $\rightarrow$ p transitions are high in energy.

The three coordinate environment also leads to solution emission not observed for the two coordinate gold dimers. Emission is observed for the two coordinate dimers $Au_2(dcpe)_2^{2+}$ and $Au_2(dipe)_2^{2+}$ in methanol:ethanol glass at 77 K, with an $E_{\nu_0-\nu_0}$ of 404 nm for the $^1A_g \rightarrow {}^3B_{1u}$ ($d\sigma^* \rightarrow p\sigma$) transition. The $E_{\nu_0-\nu_0}$ of 418 nm is similar to the $E_{\nu_0-\nu_0}$ of 432 nm for the $^1A_1 \rightarrow E'$ ($^3E''$) transition of the three coordinate complexes, yet only the three coordinate complexes emit in solution. The sterics of the three coordinate environment reduce the non-radiative decay rate by protecting the metal center from solvent collisions. The two coordinate dimers have open areas for solvent interactions, which may deactivate the excited state by energy transfer.

There is a great deal of distortion in the excited state of the three coordinate gold complexes as evidenced by the large Stokes shift of 7,800 cm^{-1} for $Au_2(dcpe)_3^{2+}$. The corresponding reorganization energy of the excited state, λ_{ex}, is 11 kcal/mol.[22] This energy reflects the increase in bonding to the phosphines due to the removal of an electron from a d M-L σ^* orbital. The Stokes shift for the two coordinate dimers observed in the 77 K glass is nearly twice as large (14,700 cm^{-1}), with λ_{ex} = 21 kcal/mol. The increase in the excited state reorganization energy evinces the large increase in the strength of the Au-Au bond due to the removal of an electron from the d σ^* orbital and occupation of the p σ orbital.

The compounds $Au_2(dcpe)_3^{2+}$ and $Au_2(dipe)_3^{2+}$ are the only compounds to my knowledge that have isolated AuP_3 units which are stable in solution. The other three

coordinate gold complexes reported are solids which undergo equilibria in solution (such as $Au(PPh_3)_3^+$ mentioned earlier) to form two coordinate and four coordinate complexes. The equilibria are evident by broad ^{31}P NMR signals which split into multiple signals upon cooling. Both $Au_2(dcpe)_3^{2+}$ and $Au_2(dipe)_3^{2+}$ show one distinct triplet signal for the bridging phosphines and one distinct doublet signal for the chelating phosphines with the appropriate 1:2 integration ratio. These patterns would be severely broadened if ligands were labile on the NMR time scale. Solution equilibria may be responsible for some of the emission observed in previous literature. For example, $Au_2(dmpm)_3^{2+}$ displays the same strong emission as $Au_2(dcpe)_3^{2+}$, so trace amounts of $Au_2(dmpm)_3^{2+}$ in a solution of $Au_2(dmpm)_2^{2+}$ will lead to emission. These stable three coordinate complexes offer a unique opportunity for studying the potential photochemistry of gold(I) complexes.

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Chapter 3

Electron Transfer at High Driving Forces

Background.

The semi-classical Marcus expression (Equation 1) predicts that ET rates, k_{ET}, are governed by three factors: the matrix coupling element, H_{ab}, the driving force,$-\Delta G^o$,

$$k_{ET} = \left\{ \frac{2(H_{ab}^2)}{h} \sqrt{\frac{\pi^3}{\lambda RT}} \right\} e^{-\left(\frac{(\Delta G^o + \lambda)^2}{4RT(\lambda)} \right)} \qquad 1.$$

and the reorganization energy, λ.[1] The Marcus expression is derived from transition state theory, with the barrier to ET defined as the difference in energy between the minimum of the reactant potential surface and the point where the reactant potential surface crosses the product potential surface. All of the parameters in the Marcus equation can be readily identified by looking at a plot of the potential surfaces for the reactants and the products: the free energy change for the reaction, $-\Delta G^o$, is the difference between the minima of the reactant and product potential wells; λ is the vertical energy difference between the reactant and product surfaces at the reactant surface minimum when $-\Delta G^o = 0$; H_{ab} is represented by one half of the separation between the potential surfaces at the crossing avoidance point (Figure 3.1).

Marcus theory predicts that for a given H_{ab} and λ, k_{ET} will increase as the driving force ($-\Delta G^o$) increases until a maximum rate is reached at $-\Delta G^o = \lambda$; the domain where $-\Delta G^o < \lambda$ is known as the "normal region." When $-\Delta G^o = \lambda$ there is no barrier to electron transfer, because the product potential surface intersects the minimum of the reactant potential surface (Figure 3.2). At higher driving forces ($-\Delta G^o > \lambda$) a new barrier to ET arises as the reactant and product potential surfaces become nested (Figure 3.3). The new barrier to ET causes k_{ET} rates to decrease as the driving force increases; the domain where $-\Delta G^o > \lambda$ is referred to as the "inverted region." A plot of $\ln(k_{ET})$ vs. $-\Delta G^o$ results in a parabola with a maximum rate at $-\Delta G^o = \lambda$ (Figure 3.4). The matrix coupling element, H_{ab}, is a function of the electronic coupling between the donor and the acceptor. Since H_{ab} only appears in the pre-exponential term, a change in H_{ab} simply moves the entire parabola vertically (Figure 3.5); as the

Figure 3.1. Reactant and product energy surfaces for $\Delta G^o = 0$ (self exchange ET)

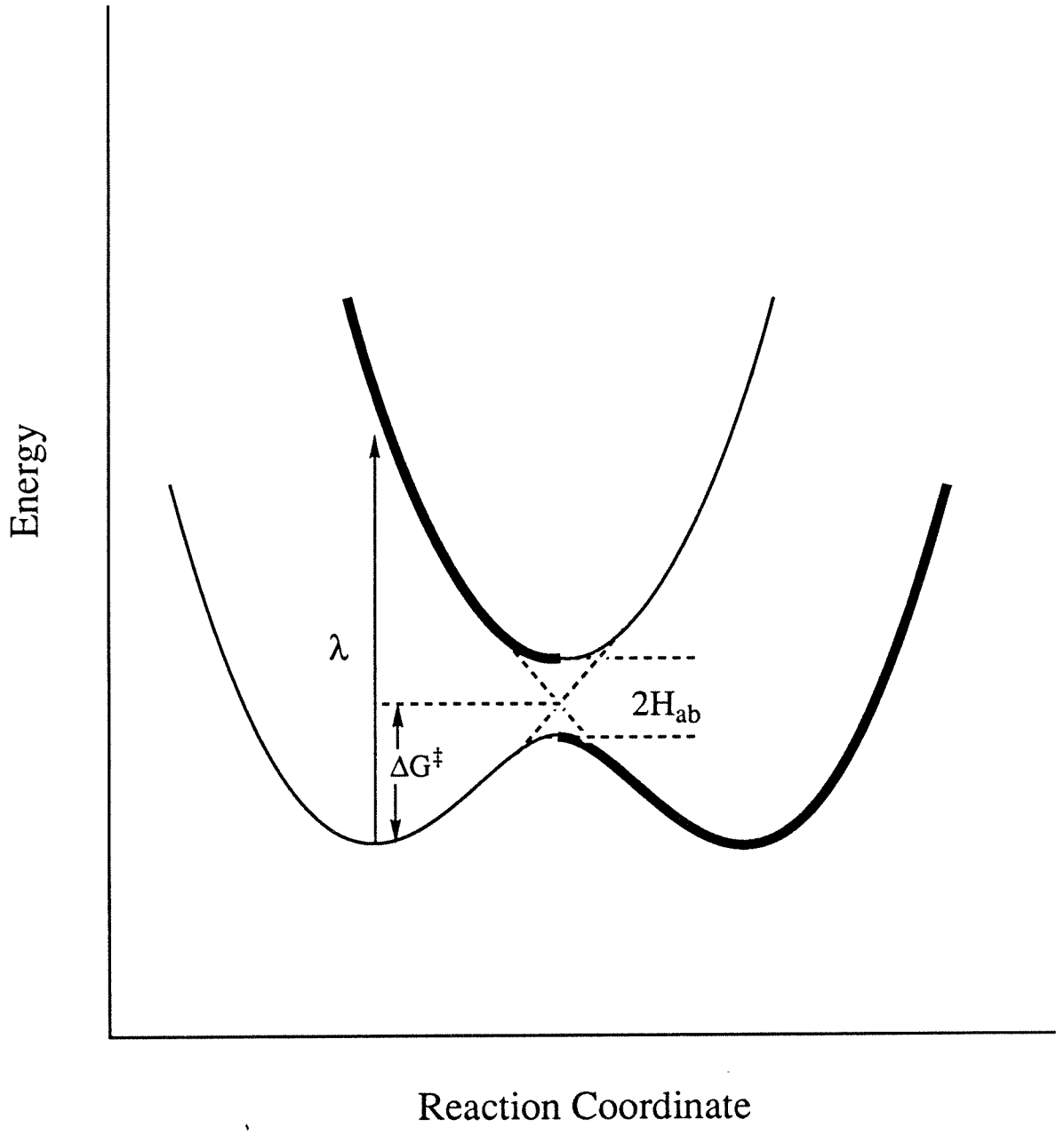

Energy
λ
2H$_{ab}$
ΔG‡
Reaction Coordinate

Figure 3.2. Reactant and product energy surfaces for $\Delta G^o \approx \lambda$.

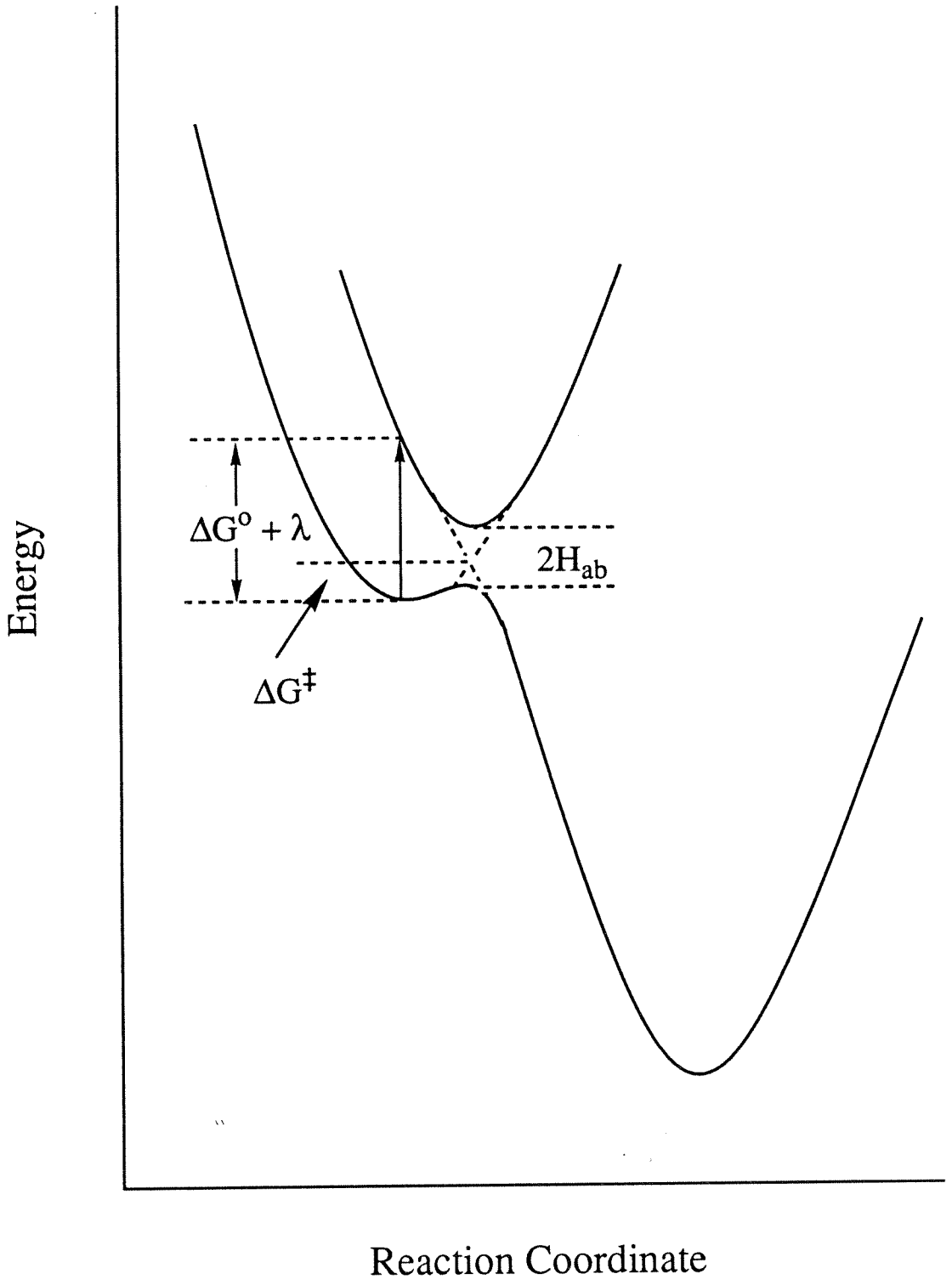

Energy
$\Delta G^o + \lambda$
$2H_{ab}$
$\Delta G^‡$
Reaction Coordinate

Figure 3.3. Reactant and product energy surfaces for $\Delta G^{o} > \lambda$.

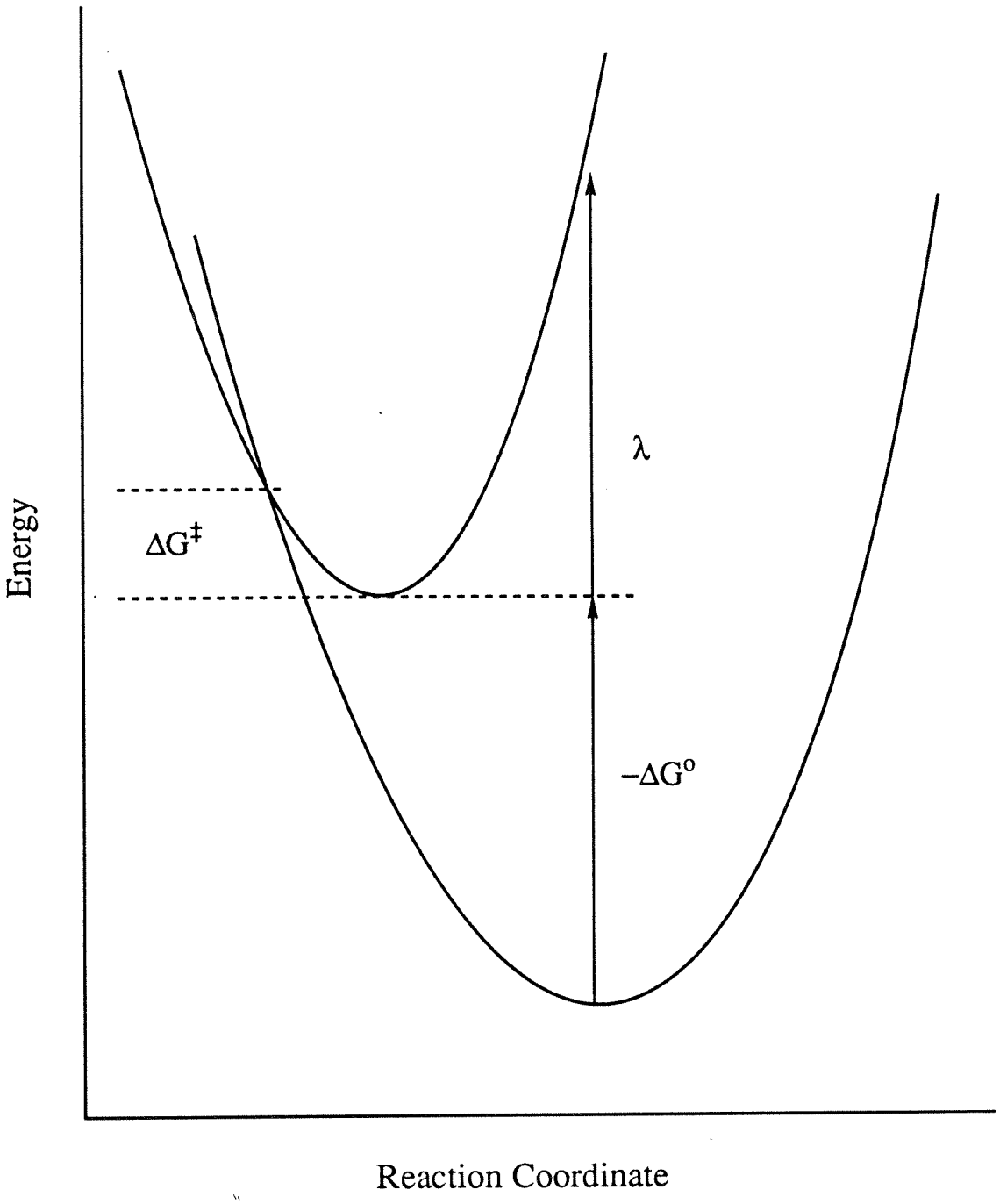

Energy
ΔG‡
λ
−ΔG°
Reaction Coordinate

Figure 3.4 Theoretical Marcus plot of $\ln(k_{ET})$ *vs* $-\Delta G^{o}$.

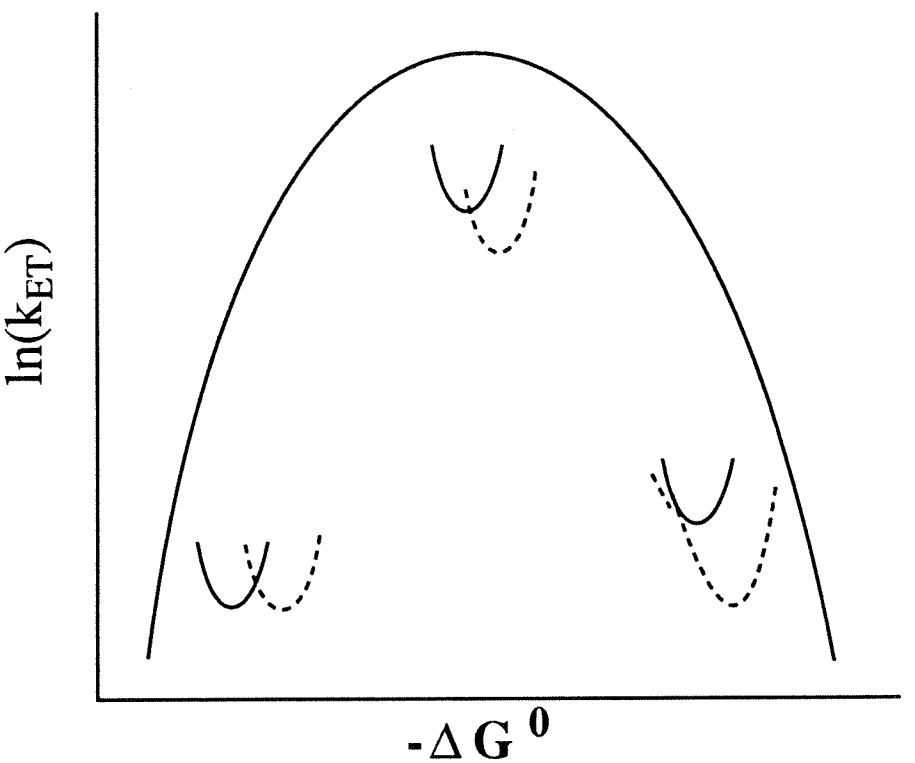

ln(k_ET)
-ΔG 0

Figure 3.5. Coupling effects on the theoretical Marcus curve; $H_{ab}(a) > H_{ab}(b)$.

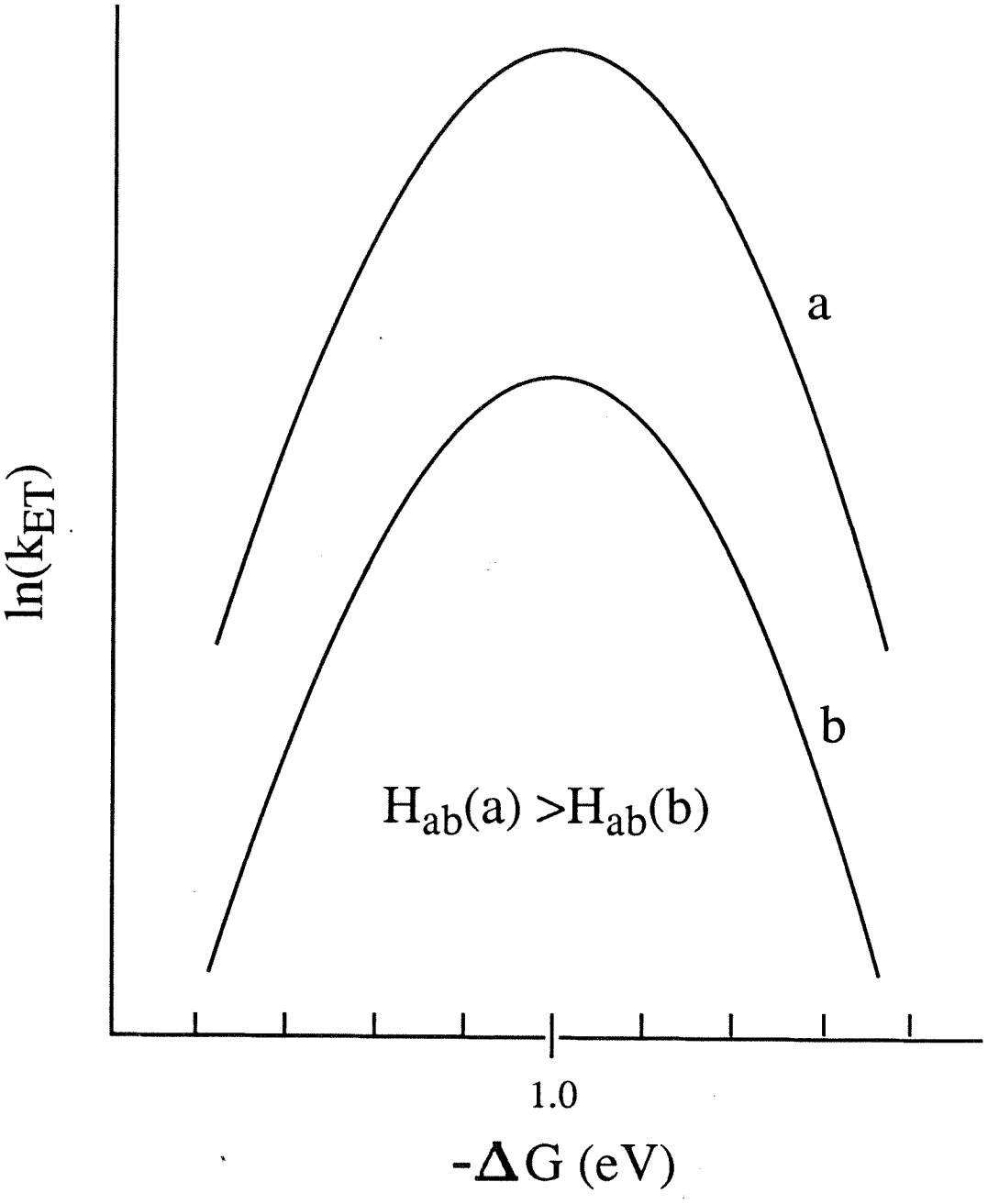
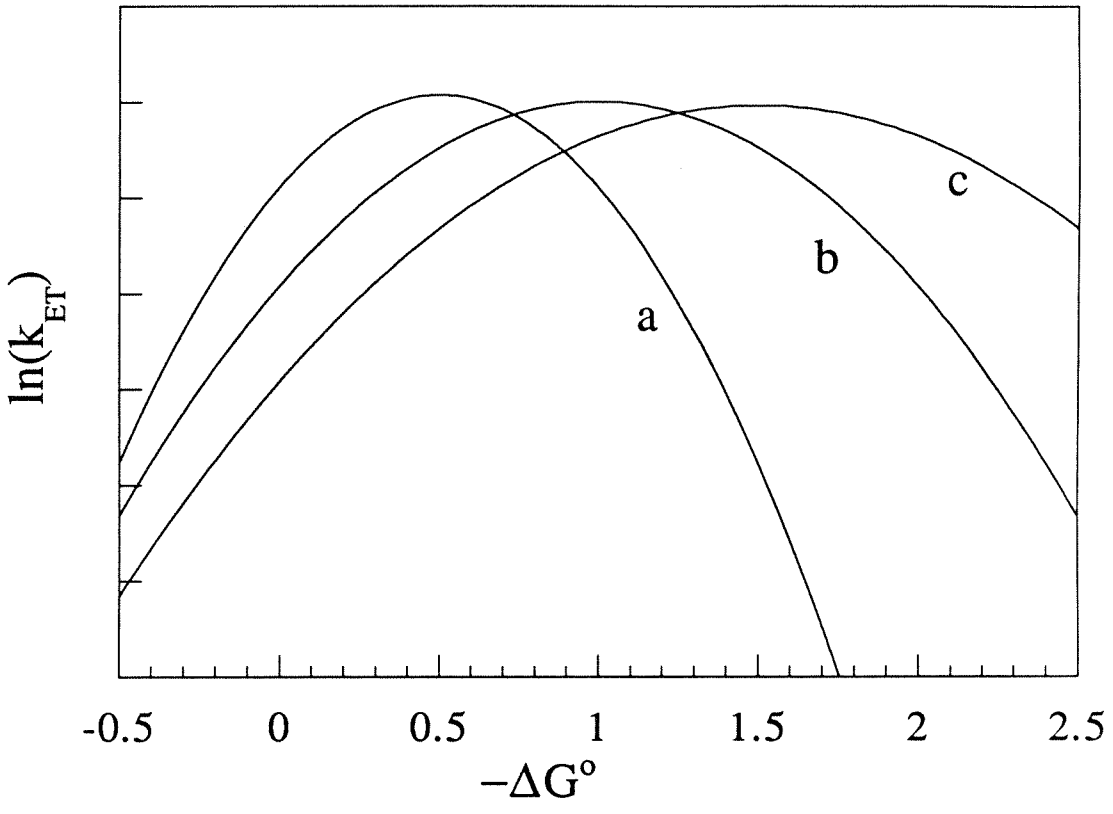
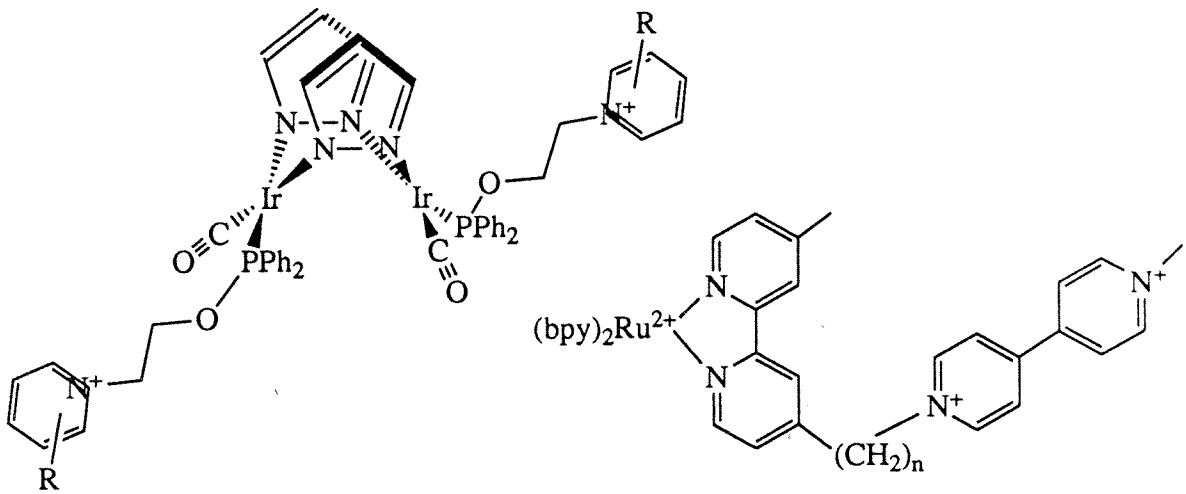

ln(k_ET)
a
b
H_ab(a) >H_ab(b)
1.0
-ΔG (eV)

Figure 3.6. Reorganization energy effects on the theoretical Marcus curve; $\lambda(a) = 0.5$ eV, $\lambda(b) = 1.0$ eV, $\lambda(c) = 1.5$ eV.


ln(k_ET)
a
b
c
-0.5
0
0.5
1
1.5
2
2.5
−ΔG°

coupling increases all of the ET rates increase. The reorganization energy, λ, represents a combination of the energy required for the solvent dipoles to reorient, λ_s, and the energy required for any bond length or bond angle changes within the molecule, λ_i, during the ET reaction. Changing λ affects both the position of the maximum and the shape of the curve; as λ increases the maximum rate occurs at a higher driving force and the parabola becomes broader (Figure 3.6). It has been suggested that the back ET rate in the initial charge separation step of photosynthesis is slow because the driving force for the recombination reaction, $-\Delta G_b$, is much greater than λ so the rate is in the "inverted region" of the parabola, while the forward photo-induced ET reaction has a driving force, $-\Delta G_f$, near λ to give an ET rate close to the maximum of the Marcus curve.

There is a plethora of experimental evidence that supports Marcus theory at low driving forces ($-\Delta G^o < \lambda$), and in the last several years there have also been many reports of recombination ET rates that are inverted at high driving forces ($-\Delta G^o > \lambda$).[2a-h] One of the earliest reports of the inverted region came from the pulse radiolysis experiments of Closs and Miller, who reported inverted behavior for an intramolecular charge shift reaction.[2a] Mallouk et al. have recently attached a methyl viologen acceptor to the



Intramolecular Donor - Acceptor Complexes

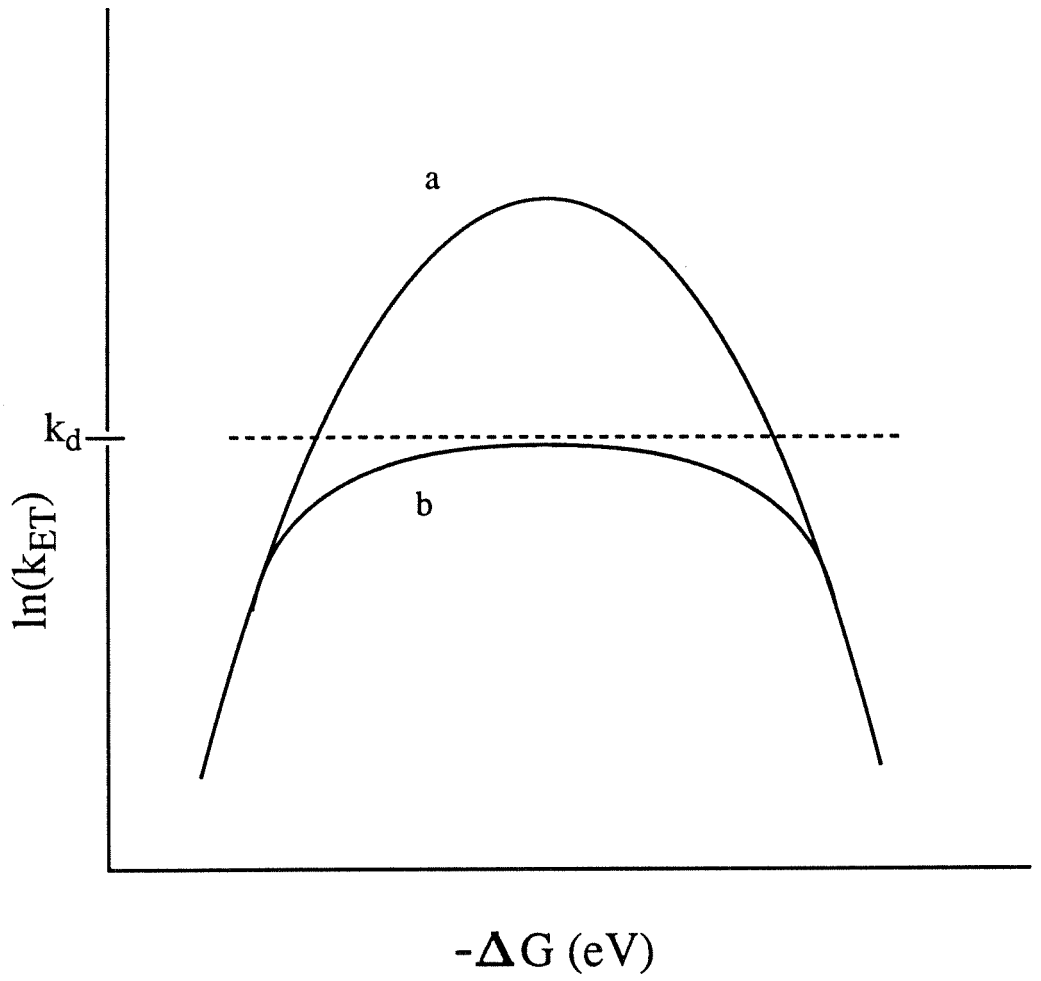
4' position of a bipyridine (bpy) ligand of $Ru(bpy)_3^{2+}$ and studied the photo-induced ET rates as a function of the driving force.[2h] Forward rates from the ruthenium excited state to the methyl viologen acceptor reach a maximum value of 1.4×10^{11} s^{-1}, while the recombination rates show inverted behavior with driving forces greater than 1 eV. Inverted behavior has also been observed by Gray et al. with a series of pyridinium phosphinites attached to an iridium dimer, where it is possible to distinguish forward ET rates from the singlet and triplet excited states of the iridium center independently.[2g] They observed forward ET rates from the singlet excited state as fast as 1×10^{11} s^{-1}, and inverted recombination rates when $-\Delta G_b >$ 1.0 eV. One of the iridium complexes has a fairly long-lived charge separated state with a forward ET rate of 2.7×10^{10} s^{-1} and a slower (inverted) back ET rate of 6.7×10^{7} s^{-1}.

Although there have been several reports of inverted behavior for recombination and charge shift reactions in intramolecular systems, there have been no observations of inverted behavior for a bimolecular system. Rhem and Weller reported bimolecular ET rates with a series of organic complexes for driving forces ranging from -0.25 eV to 2.65 eV. Their observed rates reached the diffusion limit at 0.25 eV and remained pegged at the diffusion limit all the way out to 2.65 eV, with no sign of inverted behavior.[3]

Introduction.

All of the reported "inverted" rates have involved the charge shift or recombination ET reactions of intramolecular systems. The lack of any experimental inverted rates for the bimolecular systems is curious, especially in the case of Rhem and Weller who monitored ET rates for driving forces up to 2.65 eV. Inverted behavior may be more difficult to observe in bimolecular systems because ET rates faster than the diffusion rate in the solution cannot be measured. This diffusion limit caps the top of any Marcus curve which exceeds the diffusion rate (Figure 3.7); a strongly coupled system will have ET rates at the diffusion limit over a wide driving force range. However, the ET rates observed by Rhem and Weller cover such

Figure 3.7. Marcus plots for bimolecular ET; (a) shows the theoretical first order k_{ET}, and (b) shows the theoretical curve corrected for the diffusion limiting rate k_d.


a
b
k_d
$\ln(k_{ET})$
$-\Delta G$ (eV)

a vast range that it is difficult to believe the diffusion limit alone can account for the lack of inverted behavior.

High driving force ET rates were investigated in two different bimolecular systems. First, ET from the excited state donor, $Au_2(dcpe)_3^{2+*}$, to a series of pyridinium acceptors (py^+) was examined. The $E_{v_0-v_0}$ of 2.3 eV for the emissive state makes it possible to study forward ET rates with high driving forces. High driving force recombination ET rates from pyridinyl radicals (py·) to the iridium dimer $[Ir(cod)(pz)]_2^+$ (Ir_2^+) were also examined (cod = cyclooctadiene, pz = pyrazole). Forward ET rates from $[Ir(cod)(pz)]_2$ (Ir_2) to py^+ acceptors have been shown to increase as the driving force increases until they reach the diffusion limit and then remain diffusion limited out to a driving force of 1.03 eV.[4] No inverted behavior was observed for these forward rates.

The recombination ET rates for the bimolecular system were investigated, because inverted behavior was reported for intramolecular recombination rates in a system with a similar donor and acceptor.[2g] The donor for the bimolecular recombination rates is the pyridinyl radical and the acceptor is Ir_2^+. In the intramolecular system the cod ligand is replaced by a CO and a phosphinite; the pyridium is linked to the iridium dimer center via the phosphinite. Electron-transfer rates of the intramolecular system show classical Marcus behavior, in which the forward ET rates fall in the normal region and the recombination ET rates are in the inverted region. The best fit Marcus curve has a λ of 0.85 eV, and an H_{ab} of 35 cm^{-1}. The bimolecular system should have a smaller value for H_{ab}, since the donor and acceptor are not covalently linked to one another. The Ir_2 donor and py^+ acceptor undergo identical charge changes during ET for both systems, so the reorganization energy should be close to 0.85 eV for the bimolecular system. Recombination rates for the bimolecular system have driving forces as high as 1.82 eV, so they should be deeply inverted.

Experimental Section.

Materials. The iridium(III) chloride was a loan from the Johnson Mathey heavy metals program. All other chemicals were reagent grade or better and purchased from the

Aldrich Chemical Company. The synthesis of $Au_2(dcpe)_3^{2+}$ has been described in chapter two.

Lifetime and Transient Absorption Measurements. The basic layout of the time resolved emission and absorption experiments is as follows: the excitation source was either the second (λ_{max} = 532 nm; used for Ir_2) or third (λ_{max} = 355 nm; used for $Au_2(dcpe)_3^{2+}$) harmonic of a Quanta-Ray Nd-YAG laser with 20 ns pulse width ; a PTi arc lamp supplied the white light source, a DH 10 SA Inc. monochrometer was placed before the detector; a R955 Hamamatsu PMT functioned as the detector; a RTD 710A digitizer digitized the analog signal; a 386 PC was used to work up the data (Figure 3.8). The arc lamp power was 68 W, and in the case of weak signals the arc lamp was pulsed at 6 Hz. The laser power was < 10 mJ at the sample to avoid multiphoton reactions. The focusing mirrors (labeled c in Figure 3.8) are designed with a 1 cm radius hole for the laser pulse to pass through. For time bases less than 1 ms the signal was amplified with a fast amplifier designed at Brookhaven National Laboratories, and for time bases greater than 1 ms the signal was amplified with a commercial slow amplifier. All solutions for ET studies with $Au_2(dcpe)_3^{2+}$ were 0.1 M in TBA PF_6 to ensure that the ionic strength remained constant.

Spectroelectrochemistry. The thin layer cell used for the spectroelectro-chemistry has been described previously.[5] For determining the spectrum of the reduced methyl viologen radical $MeV^{+\cdot}$ in acetonitrile, a new cell was constructed out of Ultem, which does not degrade in organic solvents. A Princeton 174A polarographic analyzer was used to apply a constant potential and a Varian Cary 219 spectrophotometer was used to record the spectrum. A sample of $[MeV](PF_6)_2$ was weighed out in a dry box with a nitrogen atmosphere and diluted to a concentration of 375 μM. The solution was placed into the thin layer cell and both the reference and auxiliary electrodes were put in place prior to removal from the dry box. A constant potential of -550 mV *vs* NHE was applied and the absorbance at 395 nm was monitored as a function of time. Absorbance increased dramatically as the radical was formed and then plateaued once the bulk electrolysis reached completion. When

Figure 3.8. Laser arrangement for time resolved emission and absorption; (a) indicates a laser mirror, (b) is a 50% reflecting mirror for the 308 nm fundamental line of the excimer laser, (c) and (d) indicate a broad band focussing mirror with a focal length of 50 cm, (e) indicates a broad band mirror.

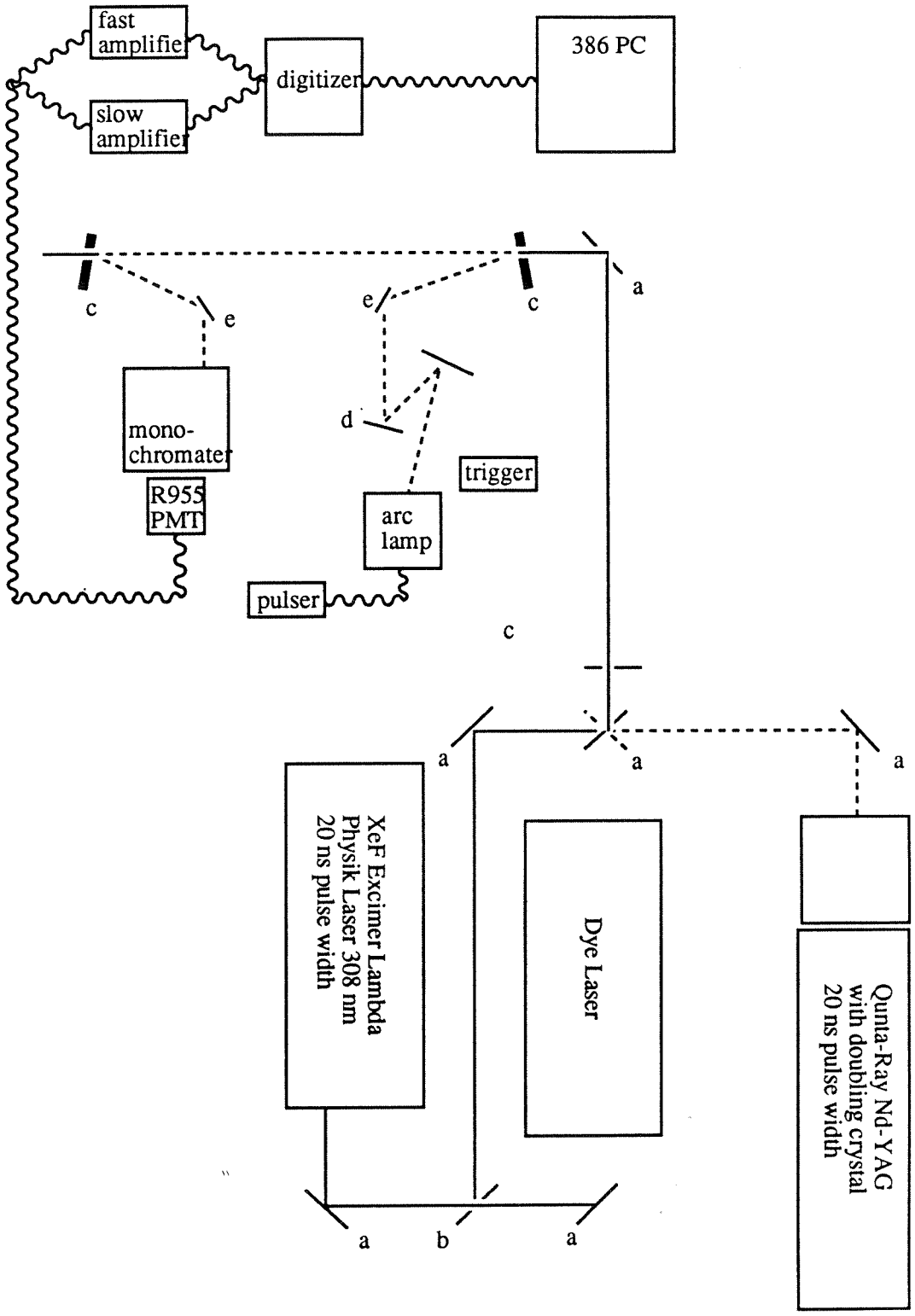

fast amplifier
slow amplifier
digitizer
386 PC
c
e
mono-chromater
R955 PMT
pulser
d
arc lamp
trigger
e
c
a
c
a
a
a
XeF Excimer Lambda Physik Laser 308 nm 20 ns pulse width
Dye Laser
Qunta-Ray Nd-YAG with doubling crystal 20 ns pulse width
a
b
a

Figure 3.9. Absorption spectrum of MeV·.

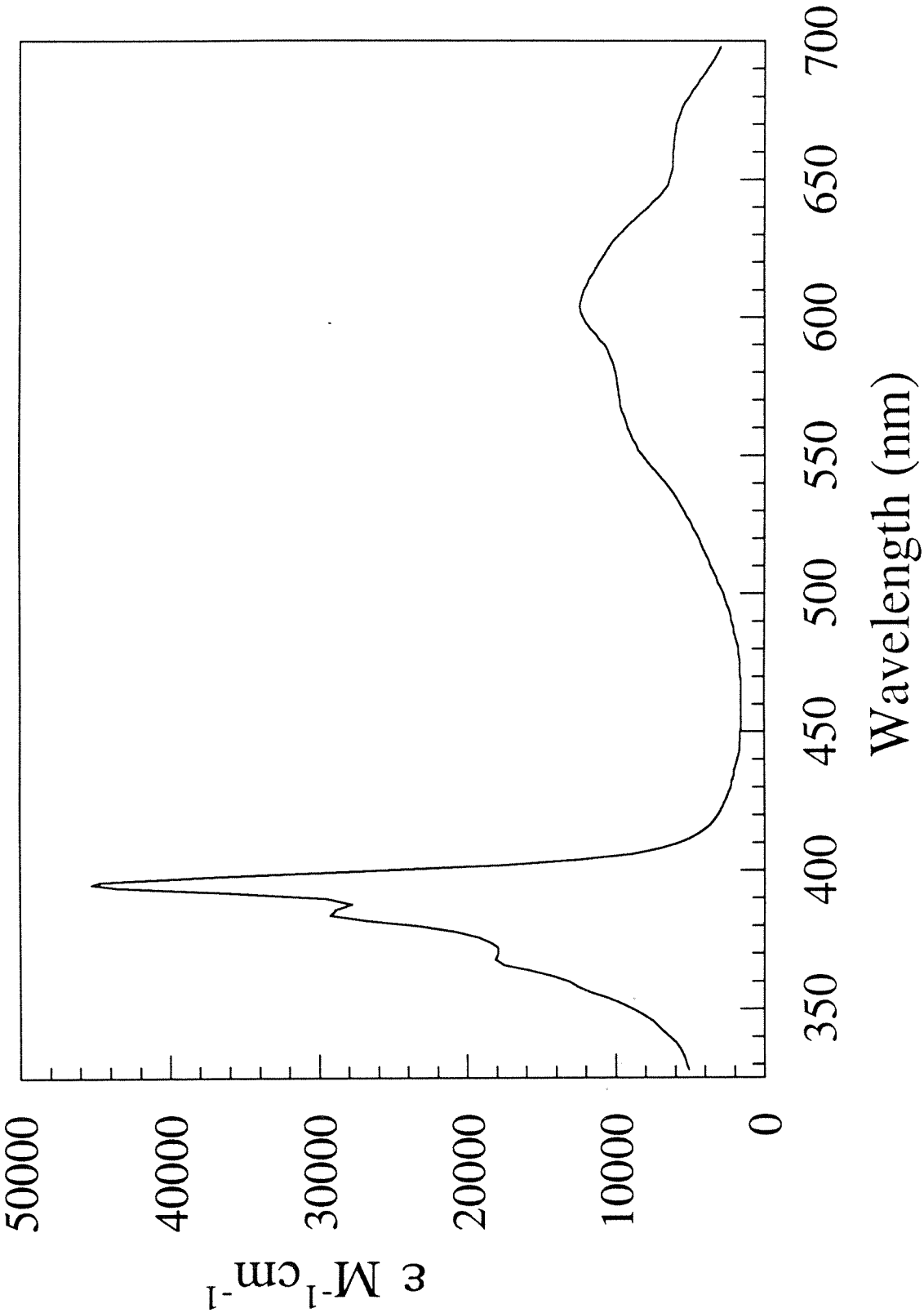

50000
40000
30000
20000
10000
0
ε M-1cm-1
350
400
450
500
550
600
650
700
Wavelength (nm)

Figure 3.10. Transient absorption spectrum of a solution containing MeV^{2+} (380 μM) and Ir_2 (160 μM) at 390 nm, excitation at 532 nm.

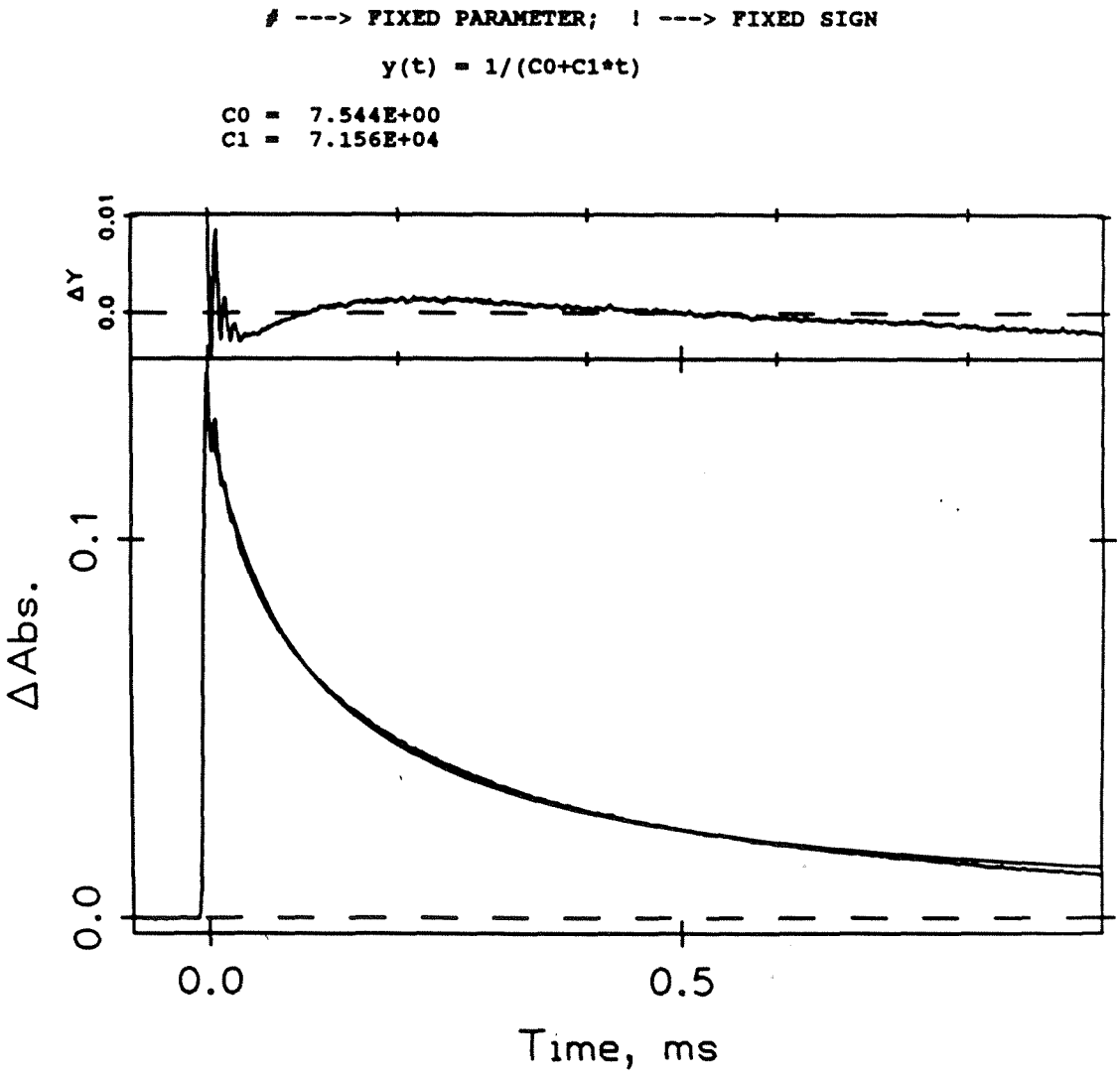
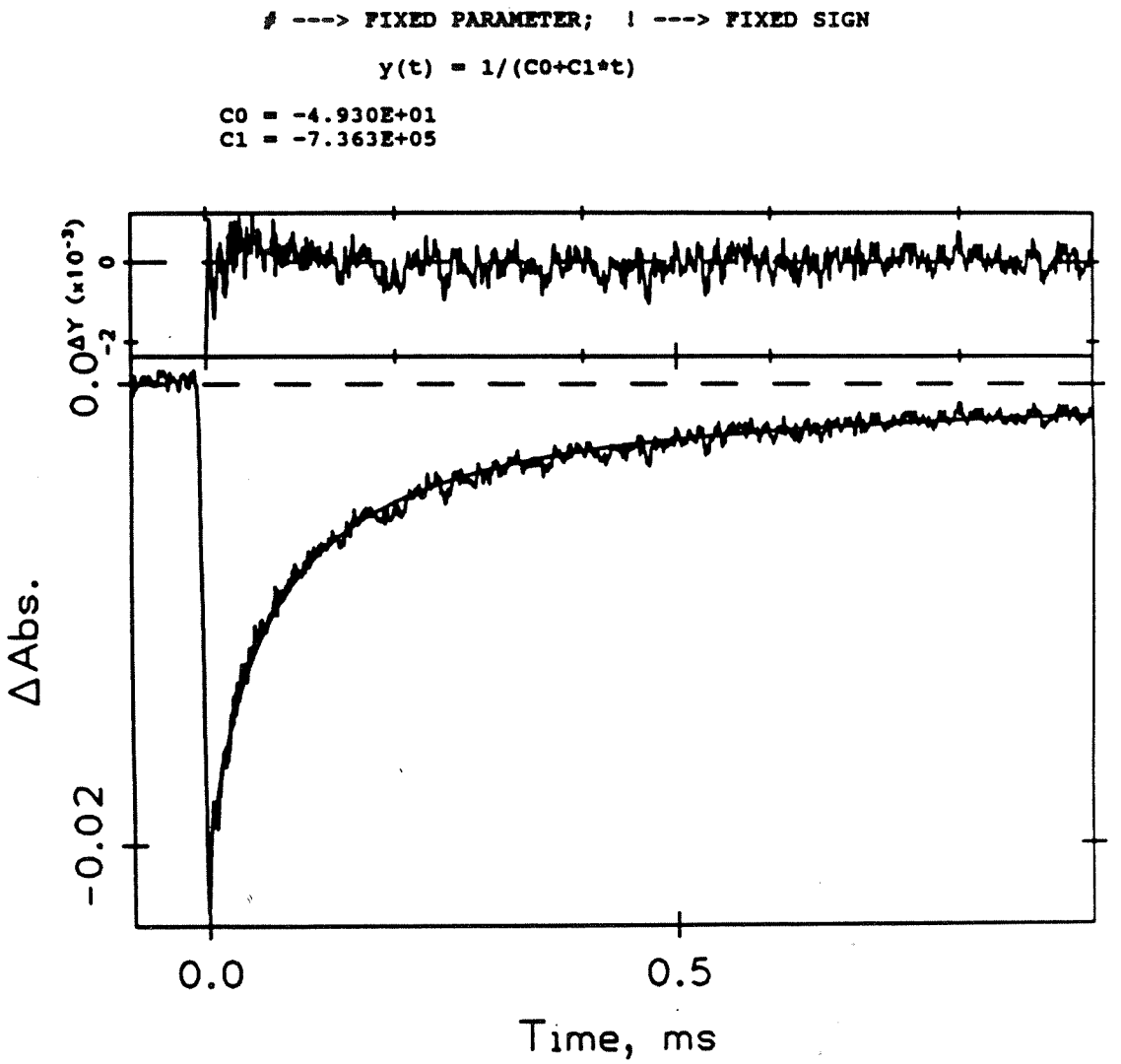

# ---> FIXED PARAMETER; ! ---> FIXED SIGN
y(t) = 1/(C0+C1*t)
C0 = 7.544E+00
C1 = 7.156E+04
ΔY
0.01
0.0
0.1
0.0
ΔAbs.
0.0
0.5
Time, ms

Figure 3.11. Transient absorption spectrum of a solution containing MeV^{2+} and Ir_2 at 500 nm, excitation at 532 nm.


# ---> FIXED PARAMETER; ! ---> FIXED SIGN
y(t) = 1/(C0+C1*t)
C0 = -4.930E+01
C1 = -7.363E+05
0.0
ΔY (x10⁻³)
0
-2
ΔAbs.
-0.02
0.0
0.5
Time, ms

the absorbance remained unchanged for one minute, a spectrum of the $MeV^{+\cdot}$ was taken from 700 nm to 250 nm (Figure 3.9). The potential was then changed to -350 mV vs. NHE to regenerate MeV^{2+}. Absorbance at 390 nm was monitored as a function of time and when the absorbance remained unchanged for one minute a spectrum of MeV^{2+} was taken from 700 nm to 250 nm. The spectrum of MeV^{2+} was taken to ensure no degradation had occurred which could affect the $MeV^{+\cdot}$ spectrum. The ε for $MeV^{+\cdot}$ at 605 nm agreed well with the published value.[6]

Determination of $\Delta\varepsilon$. The $\Delta\varepsilon$ at 500 nm between Ir_2 and Ir_2^+ was necessary to convert the measured Δ OD values in the transient absorption spectra to concentrations. The ε for Ir_2 was easily determined by measuring the absorption spectrum. Unfortunately, the electrochemistry of Ir_2 is not completely reversible, so the ε for Ir_2^+ could not easily be determined by spectroelectrochemistry. Instead, the ε of Ir_2^+ was determined from transient absorption spectra taken in the presence of 380 μM MeV^{2+}. The MeV^{2+} quenches the excited state of Ir_2 by ET, leading to the formation of Ir_2^+ and $MeV^{+\cdot}$. The spectra of MeV^{2+}, $MeV^{+\cdot}$, and Ir_2 are all known, and the $MeV^{+\cdot}$ radical is the only one of the three species which absorbs appreciably at 390 nm. A transient absorbance trace of Ir_2 with N-methylpyridinium was taken at 390 nm to verify that Ir_2^+ has no absorbance at 390 nm (the transient absorbance trace showed no ΔOD). For the solution of Ir_2 and MeV^{2+} the ΔOD at 390 nm depends solely on the concentration of $MeV^{+\cdot}$ (Equation 2).

$$\Delta OD_{390}(t) = \Delta\varepsilon_{390}(MeV^{+\cdot}) * b * [MeV^{+\cdot}]_t \qquad 2.$$

A transient absorbance trace at 390 nm can be used to determine the concentration of $MeV^{+\cdot}$ at any time ($[MeV^{+\cdot}]_t$; Figure 3.10). The ET reaction which leads to the formation of $MeV^{+\cdot}$ must also produce an equal amount of Ir_2^+. Since the back ET reaction has a one to one stoichiometry for $MeV^{+\cdot}$ and Ir_2^+, the concentration of the two species will be equal at all times and the ΔOD at any wavelength (ΔOD_n) can simply be expressed according to

$$\Delta OD_n(t) = \{\Delta\varepsilon_n(MeV^{2+}/MeV^{+\cdot}) + \Delta\varepsilon_n(Ir_2/Ir_2^+)\} * b * [MeV^{+\cdot}]_t \qquad 3.$$

Equation 3. The $\Delta\varepsilon_n$ ($MeV^{2+}/MeV^{+\cdot}$) is known for all wavelengths and $[MeV^{+\cdot}]_t$ can be determined from the transient absorbance trace at 390 nm, so that $\Delta\varepsilon_n$ (Ir_2/Ir_2^+) is readily

$$\frac{\Delta OD_n(t)}{\Delta OD_{390}(t)} = \frac{\Delta\varepsilon_n(MeV^{2+}/MeV^{+\cdot}) + \Delta\varepsilon_n(Ir_2/Ir_2^+)}{\Delta\varepsilon_{390}(MeV^{2+}/MeV^{+\cdot})} \qquad 4.$$

obtained from a transient absorbance trace at the appropriate wavelength using Equation 4. The transient absorbance trace at 500 nm shows a sharp bleach as Ir_2^+ is produced by the forward ET and then a slow decay back to zero as the recombinant ET occurs (Figure 3.11).[7] The $\Delta\varepsilon_{500}$ (Ir_2/Ir_2^+) was determined to be 7,000 $cm^{-1}M^{-1}$.[8]

[Ir(cod)(pz)]$_2$ The synthesis of the iridium dimer was adapted from the procedure described by Marshall.[4,9] An excess of cod (12.0 mL) was added to a stirring solution of $IrCl_3 \cdot 3H_2O$ (5.0 g) and 100 mL of a 2:1 ethanol:water mixture in a 250 round-bottom Schlenk flask. The flask was equipped with a condenser and a bubbler, and then heated to reflux. After refluxing for 48 hours, a red product had precipitated. The solution was cooled to room temperature and the product, $[Ir(cod)(Cl)_2]_2$, was collected by vacuum filtration. If too much cod is used, or the ethanol:water ration is not quite right the cod will separate out and the product will remain dissolved in the cod layer. In this event the product can be precipitated by adding just enough isopropanol to solubilize the cod layer. The isolated red product was then added to 50 mL of freshly distilled, Ar purged THF in a 100 mL round-bottom Schlenk flask. The solution was stirred under Ar as a solution of pyrazole and excess triethylamine in 10 mL of THF was added dropwise. The solvent was removed from the resulting deep red solution under vacuum. The residue was chromatographed on a Florisil column under an Ar atmosphere with benzene as the eluant. Evaporation of the benzene produced deep red crystals which were dried under vacuum. The solid product is air stable and need not be stored under Ar, but solutions of the iridium dimer are air sensitive and must be prepared using degassed or Ar purged solvents. Analysis Calculated: C: 35.95; H: 4.11; N: 7.62. Found C: 36.13; H: 4.06; N: 7.32.

N-methyl pyridinium hexafluorophosphate[4] The following method was used to prepare all of the hexafluoro phosphate salts. A three fold excess of the alkylating agent (iodomethane) was added to a solution of the pyridine or substituted pyridine (4 g) and 100 mL of a 1:1 acetone:ethanol mixture. The solution was refluxed for 24 hours. If the iodide salt precipitated upon cooling then it was collected by vacuum filtration, otherwise the solvent was removed by rotary evaporation under reduced pressure. The solid iodide salt, or the residue remaining after evaporation was dissolved in a minimum of water. Addition of a slight excess of ammonium hexafluorophosphate in 2 mL of water resulted in the precipitation of the hexafluorophosphate salt as a white powder. The white powder was collected by vacuum filtration, recrystallized from a 2:1:1 water:acetone:ethanol solution and dried under vacuum.

N-methyl 3,4-dicyanopyridinium tetrafluoroborate[10] One equivalent of trimethyloxonium tetrafluoroborate was added to a stirring mixture of 3,4-dicyanopyridine and 40 mL of acetonitrile under nitrogen at room temperature. After stirring for four hours the solvent was removed by rotary evaporation. The residue was recrystallized from methanol/ether to give clear plates of the desired product. Analysis calculated for $C_8H_6N_3BF_4$: C, 41.60; H, 2.62; N, 18.19. Found: C, 41.91; H, 2.98; H, 18.45.

Results and Discussion.

ET Rates with $Au_2(dcpe)_3^{2+*}$. The rate of ET can be measured by monitoring the lifetime of a luminescent species as a function of the concentration of quencher; the quencher in the ET studies discussed here is a pyridinium or substituted pyridinium (py^+). In the absence of a quencher, there are two intramolecular processes the excited molecule can undergo. The excited state may radiate light to go back to the ground state, k_r, or it may decay to the ground state by some non-radiative process, k_{nr}. The lifetime of the excited state with no acceptor present, τ_o, is given by Equation 5.

$$\tau_o = (k_r + k_{nr})^{-1} \qquad 5.$$

Adding a quencher provides another possible route for decay to the ground state. The new non-radiative, bimolecular process shortens the lifetime , τ, according to Equation 6.

$$\tau = (k_r + k_{nr} + k_q [Q])^{-1} \qquad 6.$$

The Stern-Volmer equation can be derived from Equations 5 and 6 (Equation 7). A plot

$$\tau_o/\tau = 1 + \tau_o[Q]k_q \qquad 7.$$

of τ_o/τ vs. [quencher] will yield a straight line with a slope of $\tau_o(k_q)$.[11]

The luminescent complex $Au_2(dcpe)_3^{2+*}$ acts as the electron donor and py^+ performs the role of the acceptor. Electron-transfer rates were studied as a function of the driving force for the reaction by monitoring the quenching with a series of different pyridiniums. Altering the substituents on the pyridinium changes $E_{1/2}$ for the acceptor which in turn changes the driving force according to Equation 8 (W_r is the work required to bring the reactants together and W_p is the work required to bring the products together).[12] The

$$-\Delta G^o = [\, E_{1/2}\,(py^+/py\cdot) - E_p^a(Au_2(dcpe)_3^{2+}) + E_{v_o\text{-}v_o} + W_r - W_p] \qquad 8.$$

work terms were derived from the electrostatic equation W (eV) = $(0.395*Z_aZ_b/d)$ $[1/(1+0.48d*\mu^{1/2})]$; Z_a and Z_b are the charges on the donor and acceptor; d is the center to center distance when ET occurs; μ is the ionic strength (since one of the products is neutral $W_p = 0$).. The values for $E_p^a(Au_2(dcpe)_3^{2+})$ and the $E_{v_o\text{-}v_o}$ of the emissive transition were reported in chapter two

All luminescence decays for the quenching studies fit well to single exponential functions. A sample of the transient decay of the excited state is given in Figure 3.12. A representative example of a Stern-Volmer plot is shown in Figure 3.13. All of the Stern Volmer plots yielded lines with correlation factors > 0.99. A summary of the data for the rates obtained with the gold complex and the pyridiniums is provided in Table 3.1.

The quenching rates with the entire series of pyridiniums are then used to generate a Marcus plot of $\log(k_q)$ vs. driving force (see Figure 3.14). The rates increase as the driving force increases until they reach the diffusion limit of 1×10^{10} in acetonitrile. The rates continue to remain at the diffusion limit as the driving force increases from 1.2 eV to 1.9 eV.

In order to fit the data to the Marcus expression it is necessary to note that the measured quenching rates are bimolecular rates and the ET rates predicted by the Marcus expression are unimolecular rates. The true kinetic scheme for the bimolecular electron transfer involves the formation of a donor-acceptor contact pair followed by unimolecular ET and diffusion away of the oxidized donor and the reduced substrate (see Figure 3.15). The k_{23} in this scheme is now the same unimolecular ET rate predicted by Marcus theory. By assuming a steady-state approximation for $[D^*A]$, and $[D^+A^-]$ one can derive an expression for the

$$k_q = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}}\left(1 + \frac{k_{32}}{k_{30}}\right)} \qquad 9.$$

quenching rate k_q (Equation 3.9). As long as the association and dissociation rates for the D^*A contact pair are both equal to the diffusion rate ($k_{12} = k_{21} = k_d$), and the rate of back electron transfer to regenerate the excited state, $[D^*A]$, is negligible compared to the combined rates of dissociation to $[D^+]$ and $[A^-]$ and back electron transfer to the ground state [DA] ($k_{32} <<< (k_{30} + k_{34})$), k_q can be related to the electron transfer rate, k_{ET} ($k_{ET} = k_{23}$), and the diffusion rate, k_d, as seen in Equation 3.10.[11]

$$1/k_q = 1/k_d + 1/k_{ET} \qquad 10.$$

Equation 3.10 was used along with the Marcus expression to obtain theoretical values for k_q. Figure 3. 14 shows the data and the best theoretical fit. The results give a value of 10.5 cm^{-1} for H_{ab} and 1.66 eV for λ. The large value for λ can be divided into two components: λ_i refers to reorganization within the molecule such as bond length and bond angle changes, and λ_o refers to the reorganization energy of the solvent as the solvent dipoles align to the new charge distribution. Based on the bimolecular electron transfer study with Ir_2 and the same pyridiniums performed in acetonitrile, the solvent contribution can be estimated as $\approx$ 0.75 eV. The resulting λ_i of 0.91 eV(21 kcal/mol), indicates that a large amount of reorganization is involved during the first electron transfer to make Au(II). This result is not entirely surprising in light of the large Stokes shift associated with the emission

Figure 3.12. Luminescence decay of $Au_2(dcpe)_3^{2+}$, excitation 355 nm.

---> FIXED PARAMETER; ! ---> FIXED SIGN

y(t) = C0 + C1exp(-k1*t)

#C0 = 0.000E+00
!C1 = 3.959E-02 !k1 = 5.131E+04 s\-1

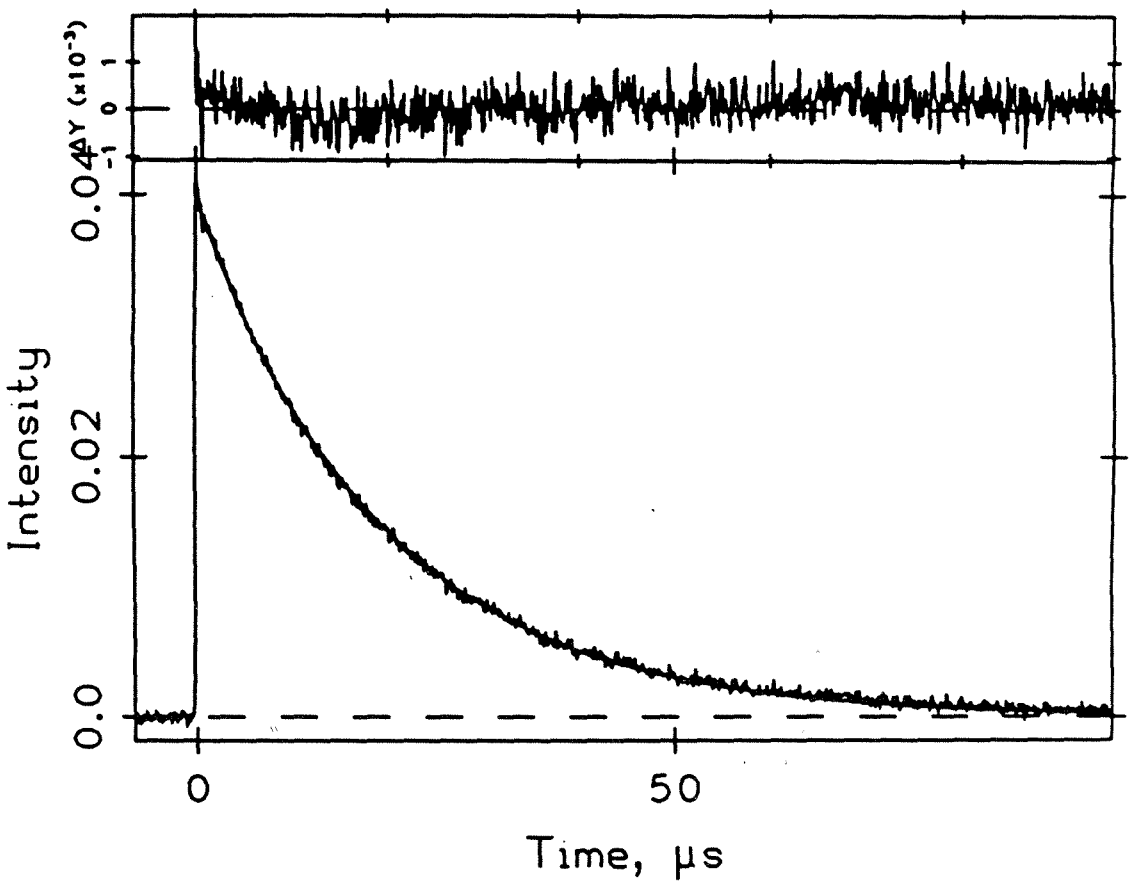


Figure 3.13. Sample Stern Volmer plot with 3,4-dicyanopyridinium as the quencher.

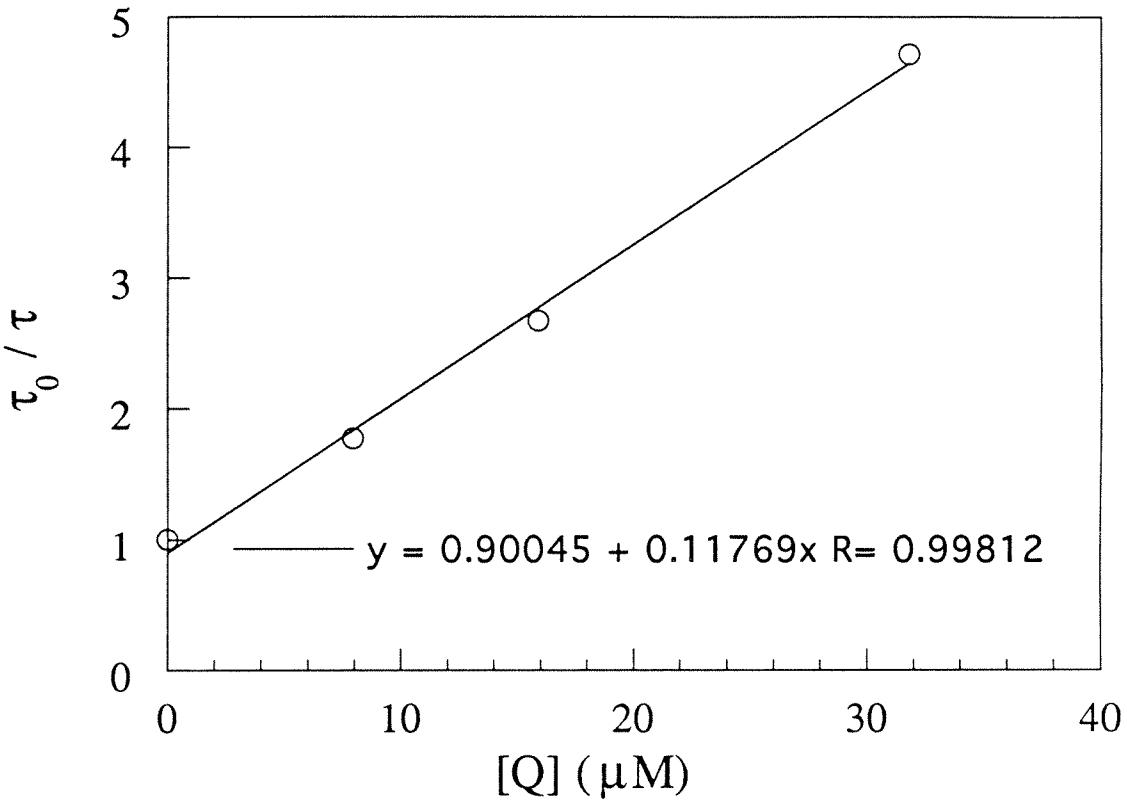

5
4
3
2
1
0
τ_0 / τ
y = 0.90045 + 0.11769x R= 0.99812
0
10
20
30
40
[Q] (μM)

Figure 3.14. Marcus plot for the forward ET reactions between $Au_2(dcpe)_3^{2+}$ and a series of substituted pyridiniums; each point represents a quenching rate with a different pyridinium. The solid line represents a the theoretical best fit curve.

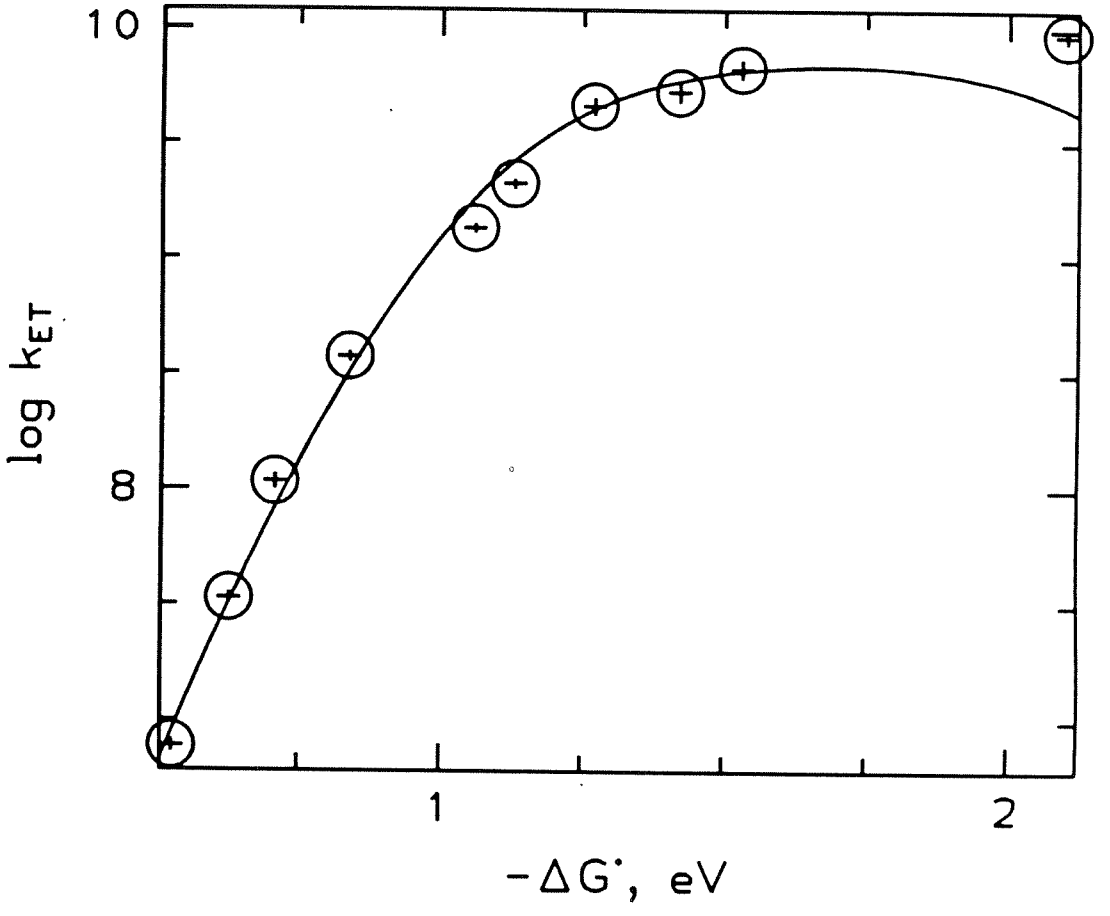

10
8
log k_{ET}
1
2
$-\Delta G^{\circ}$, eV

Table 3.1. Quenching rates and driving forces for the forward ET reactions between $Au_2(dcpe)_3^{2+}$ and a series of substituted pyridiniums.

R	R'	$E_{1/2}$ (V *vs* SCE)	$-\Delta G^o$ (eV)	k_q ($M^{-1}s^{-1}$)
CH_3	3,4-CN	-0.10	2.10	9.46×10^9
CH_3	4-CN	-0.67	1.53	6.72×10^9
CH_3	4-CO_2NH_3	-0.78	1.42	5.10×10^9
C_2H_5	4-$CONH_2$	-0.93	1.27	4.59×10^9
$C_6H_5CH_2$	3-$CONH_2$	-1.07	1.13	2.10×10^9
CH_3	3-$CONH_2$	-1.14	1.06	1.35×10^9
CH_2CH_5		-1.36	0.84	3.75×10^8
CH_3	2-OCH_3	-1.48	0.72	1.08×10^8
CH_3	2,3,6-CH_3	-1.57	0.63	3.38×10^7
CH_3	2,4,6-CH_3	-1.67	0.53	7.74×10^6

Figure 3.15. Kinetic scheme for bimolecular ET.

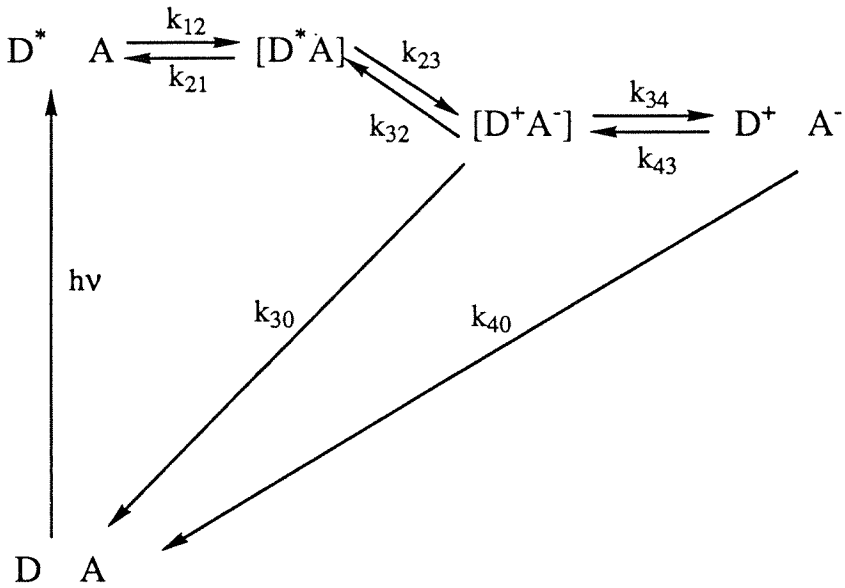
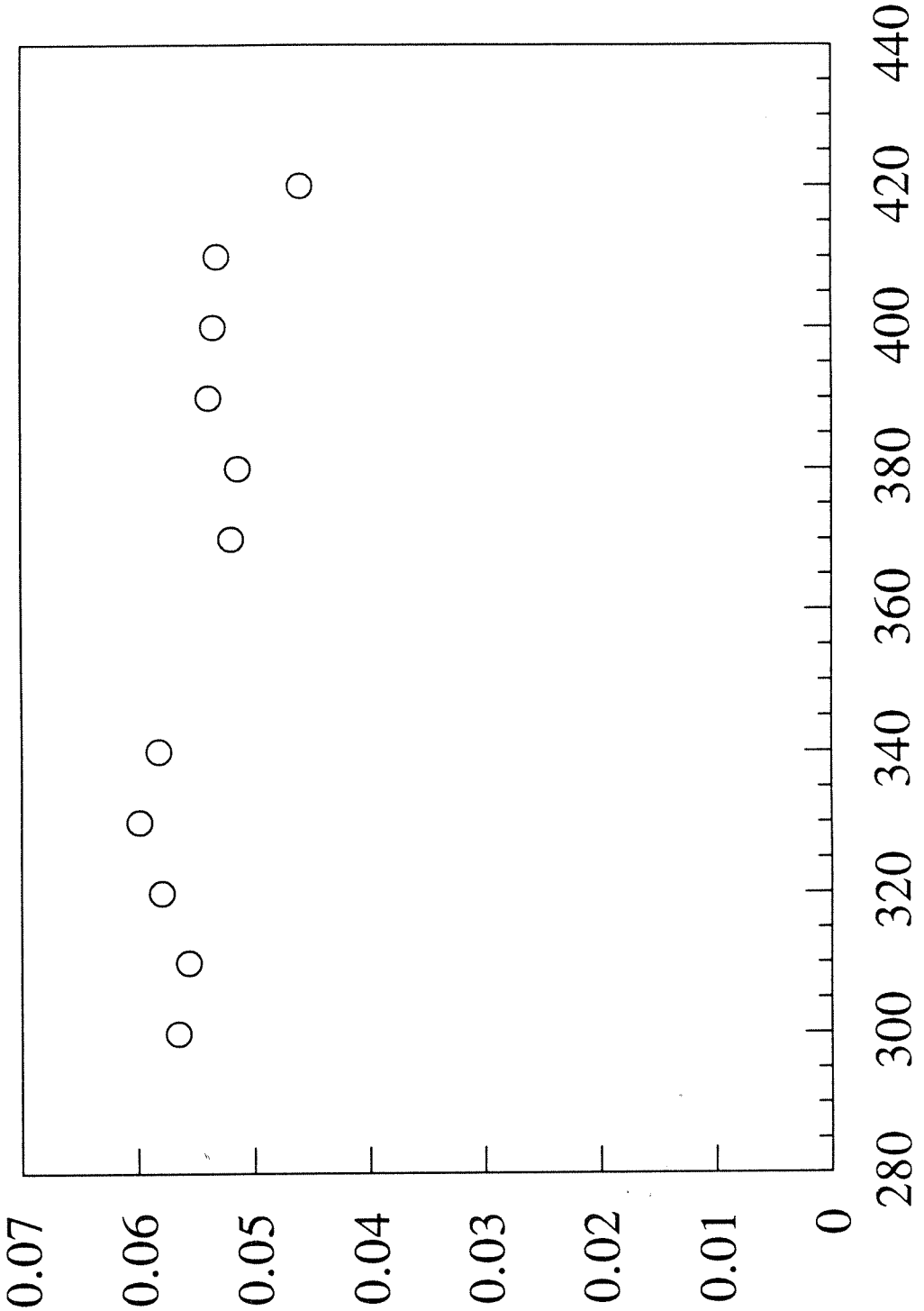

D*
A
k12
k21
[D*A]
k23
k32
[D+A-]
k34
k43
D+
A-
hν
k30
k40
D
A

Figure 3.16. Transient absorption spectrum of $Au_2(dcpe)_3^{2+}$.


Δ OD
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
280
300
320
340
360
380
400
420
440
Wavelength (nm)

of $Au_2(dcpe)_3^{2+}$ (7,800 cm^{-1}), which demonstrates a substantial distortion of 11 kcal/mol even in the excited state. In fitting the data to Marcus theory, the diffusion limited high driving force points were discarded based on results with the iridium system (*vide infra*). Recombination rates could not be studied because changes in the absorption spectrum were not intense enough in the visible region. The excited state transient absorption spectrum (Figure 3.16) shows only moderate increase in absorption in the UV area.

Forward ET Rates with $[Ir(cod)(pz)]_2$. The photophysics of the iridium dimer, Ir_2, have been well characterized. The lowest energy absorption band (Figure 3.17) is at 500 nm and has been assigned as a $d\sigma^* \rightarrow p\sigma$ absorption. Emission of the complex at 680 nm (Figure 3.18) has been assigned as the corresponding $d\sigma^* \leftarrow p\sigma$ transition and has a lifetime of 240 ns in acetonitrile at room temperature.[13] Forward electron transfer rates were determined in the same manner as described above for the gold complex. The resulting rates are given in Table 3.2, and correlate well with those measured by Marshall.[4] Driving forces were calculated according to Equation 11 in the same manner as described for the gold

$$-\Delta G^o = E_{1/2}(py^+/py\cdot) - E_{1/2}(Ir_2^+/Ir_2) + E_{v_o\text{-}v_o} + W_r - W_p \qquad 11.$$

system (*vide supra*) Although the driving force for ET has been extended to 1.6 eV, the rates continue to be diffusion limited. To verify that all of the observed quenching was due to electron transfer, quantum yields for the electron transfer were measured by monitoring the absorption spectrum at 500 nm during the lifetime of the excited state with quencher present. The excited state transient absorption spectrum shows a strong bleach at 500 nm.[4] With no quencher present the bleach recovers back to zero with an exponential rate equal to the rate of the luminescence decay. When an ET quencher is present the recovery of the bleach consists of two components: a fast step corresponding to the lifetime of the excited state and proportional to the amount of unquenched excited state, and a second, slower component due to the formation of Ir_2^+ which decays according to the recombination ET rate. Quenching by energy transfer leads to the ground state, Ir_2, directly, as opposed to Ir_2^+, so the bleach will

Figure 3.17. Absorption spectrum of Ir_2.

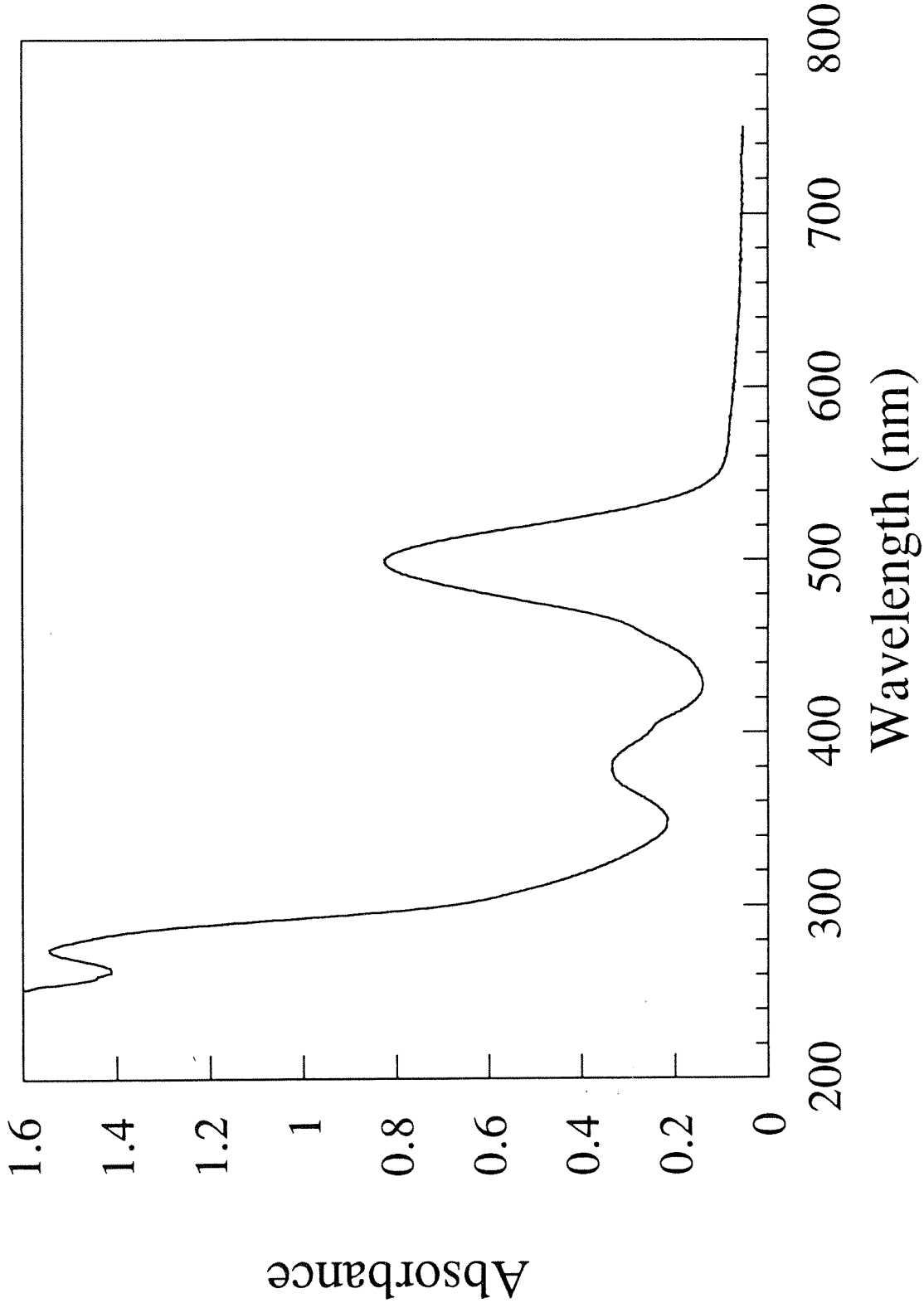

Absorbance
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
700
800
Wavelength (nm)

Figure 3.18. Emission spectrum of Ir_2.

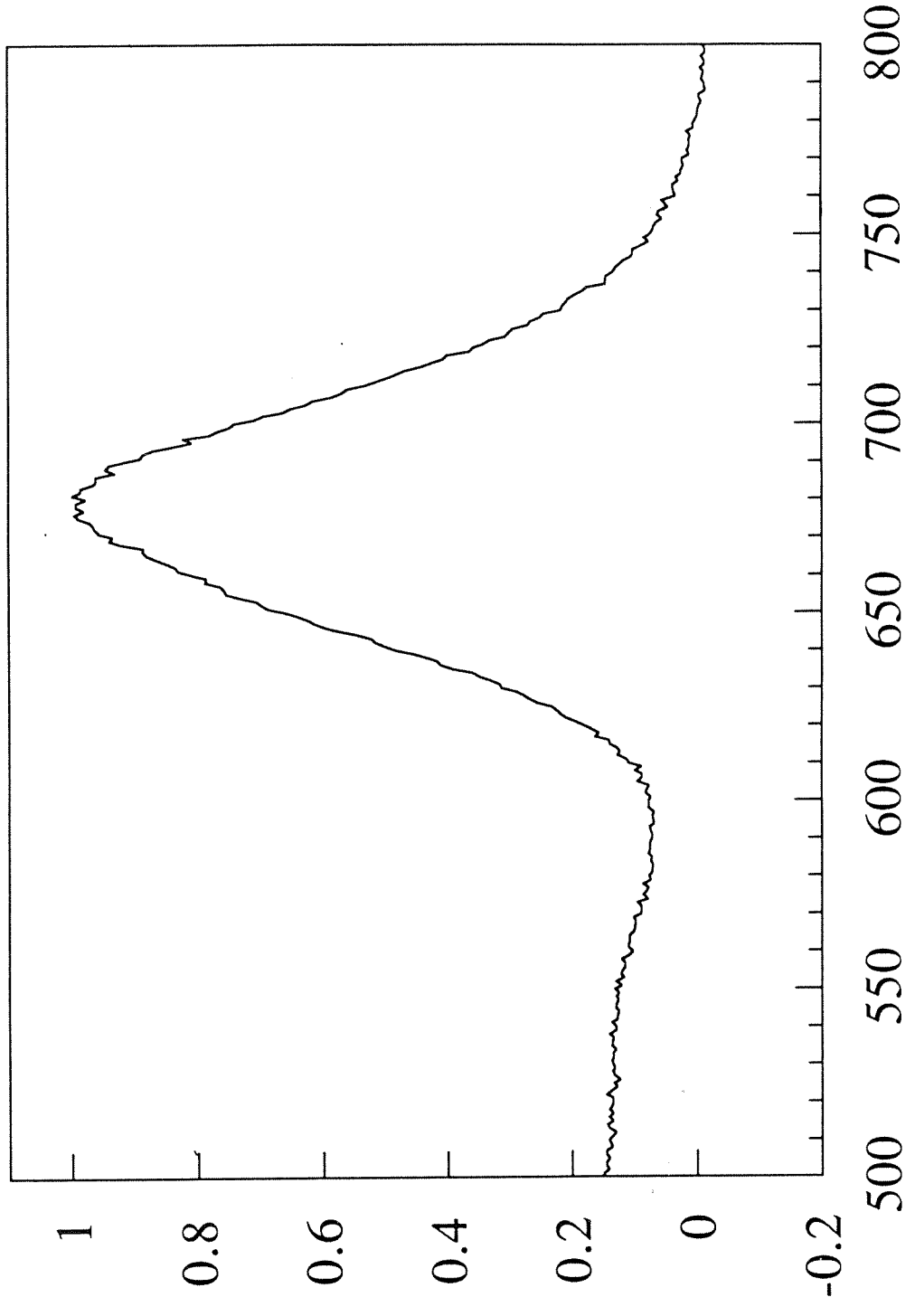

Emission Intensity
1
0.8
0.6
0.4
0.2
0
-0.2
500
550
600
650
700
750
800
Wavelength (nm)

Figure 3.19. Transient absorbance trace used for the quantum yield determination with 3,4-dicyano-N-methylpyridinium.

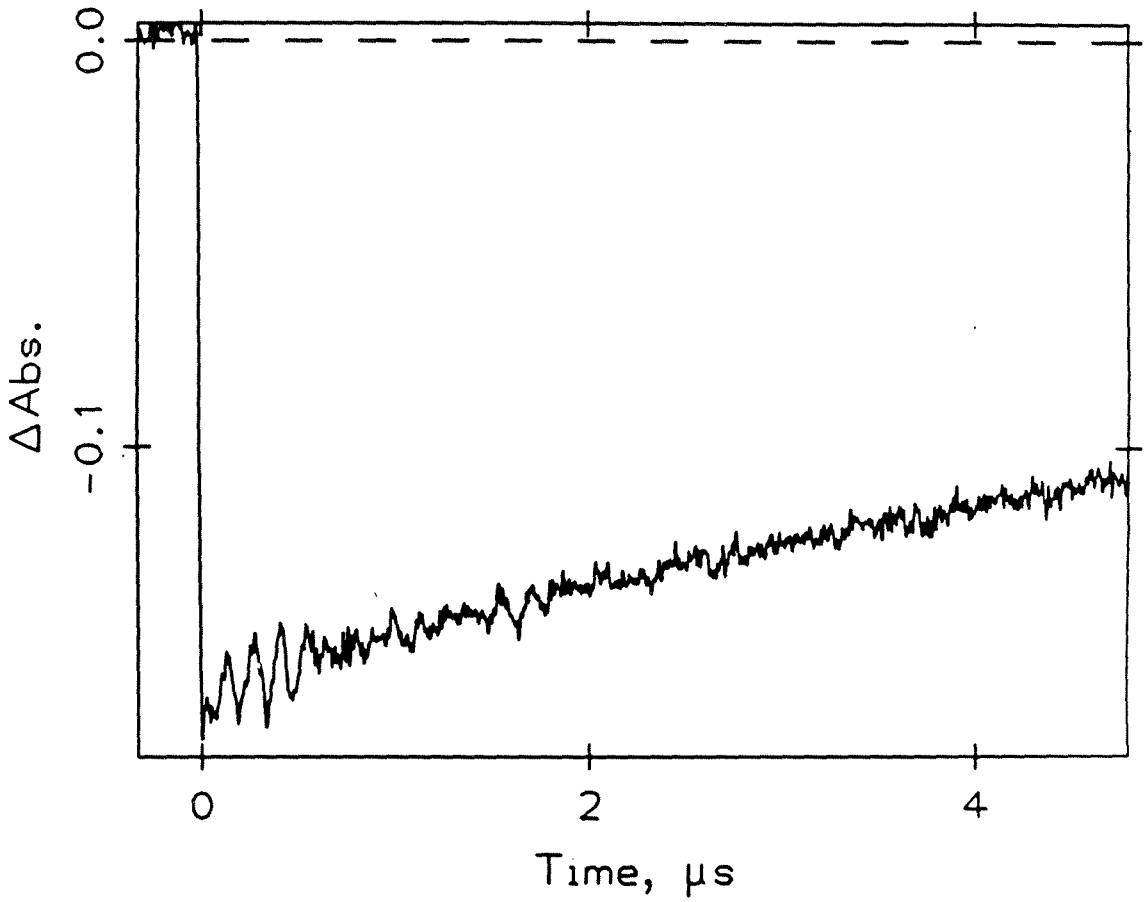

0.0
-0.1
ΔAbs.
0
2
4
Time, μs

Table 3.2. Quenching rates and driving forces for the forward (k_q) ET reactions and the recombination (k_b) reactions between Ir_2 and a series of pyridiniums.

R	R'	$E_{1/2}$ (V *vs* SCE)	$-\Delta G_f^o$ (eV)	k_q ($M^{-1}s^{-1}$)	$-\Delta G_b^o$ (eV)	k_b ($M^{-1}s^{-1}$)	ϕ_{ET}
CH_3	3,4-CN	-0.10	1.60	1.26×10^{10}	0.40	2.52×10^9	1.00
CH_3	4-CN	-0.67	1.03	1.30×10^{10}	0.97	7.77×10^9	0.78
CH_3	4-CO_2NH_3	-0.78	0.92	9.27×10^9	1.08	5.95×10^9	0.69
C_2H_5	4-$CONH_2$	-0.93	0.77	8.81×10^9	1.23	3.36×10^9	0.53
$C_6H_5CH_2$	3-$CONH_2$	-1.07	0.63	6.12×10^9			
C_2H_5		-1.36	0.34	2.47×10^9	1.66	9.52×10^8	0.36
CH_3	2-OCH_3	-1.48	0.22	7.83×10^8	1.78	8.61×10^8	0.19
CH_3	2,6-CH_3	-1.52	0.18	6.27×10^8	1.82	6.86×10^8	
CH_3	2,3,6-CH_3	-1.57	0.13	2.80×10^8			
CH_3	2,4,6-CH_3	-1.67	0.03	2.80×10^7			

recover with a time constant equal to the luminescent decay time constant. The decay trace used in the quantum yield determination for ET to 3,4-bis-dicyanopyridinium is shown in Figure 3.19 and all of the measured quantum yields are listed in Table 3.2. The measured quantum yields increase as the ET rate increases and reach unity for the highest driving force point, confirming the fact that the quenching is solely due to ET.

Recombination Rates with $[Ir(cod)(pz)]_2$. The bleach at 500 nm observed in the transient absorption spectrum provides a means to study the recombination ET rates. In the recombination reaction (R1) an electron is transferred from the py· donor to the Ir_2^+

$$Ir_2^+ + py\cdot \text{ ---> } Ir_2 + py^+ \qquad \text{R1}$$

acceptor resulting in the formation of the original ground states of py^+ and Ir_2. The time traces of the change in absorption at 500 nm show a strong negative ΔOD followed by a recovery back to zero (Figure 3.20). The recovery back to zero indicates that all of the Ir_2^+ goes back to Ir_2. The rate of the reaction is expressed as $\partial[Ir_2^+]/\partial t = -k_b [Ir_2^+] [py\cdot]$. For every molecule of Ir_2^+ produced by the forward ET, one molecule of py· is also produced, so one can make the substitution $[py\cdot] = [Ir_2^+]$ to generate the second-order rate law: $\partial[Ir_2^+]/\partial t = -k_b [Ir_2^+]^2$. The second-order rate constant k_b (analogous to the quenching rate k_q measured for the forward ET rates) was determined by two methods. The traces of ΔOD vs. time were first fit to second-order kinetics, $y = 1/(C_o - kt)$, using a non-linear fitting routine (Figure 3.20).[14] The k_b was then obtained according to: $k_b = k (\Delta\varepsilon)b$ where b is the path length in cm (1 cm) and $\Delta\varepsilon$ for the Ir_2^+ / py· system was determined to be 7000 $M^{-1}cm^{-1}$ as described earlier. Back ET rates were also determined using the relationship $(-\Delta OD)^{-1} = C_o + (k_b /b\Delta\varepsilon)t$. A plot of $(-\Delta OD)^{-1}$ vs. time gives a straight line with a slope of $k_b /b\Delta\varepsilon$ (Figure 3.21). The resulting rates presented in Table 3.2 are the average of applying both rate determination methods to at least two measurements. Driving forces for the recombination rates were calculated according to Equation 12. The recombination ET rates represent the

$$-\Delta G^o = E_{1/2} (Ir_2^+/Ir_2) - E_{1/2}(py^+/py\cdot) - W_p + W_r \qquad 12.$$

first observation of inverted behavior for a bimolecular system. The decrease in the recombination ET rate as the driving force increases can be seen in Figure 3.21, where the slope of the lines decreases dramatically as the pyridinyl radicals become better donors (slope $\alpha\ k'_{ET}$).

Although the recombination rates display inverted behavior, the rates do not decrease as fast as classical Marcus theory predicts. The plot of $\log(k'_{ET})$ vs. driving force (Figure 3.22) depicts both the forward and recombination rates. Most of the literature reports on the inverted region in unimolecular systems also demonstrate this rate enhancement in the inverted region. Incorporating quantum mechanics into the Marcus theory can explain the asymmetry of the experimental results. Addition of quantum mechanics lead to the modified Marcus expression in Equation 13.[15] The pre-exponential term remains unchanged, but the

$$k = \frac{2H^2_{ab}}{h}\sqrt{\frac{\pi^3}{\lambda_s RT}}\ \exp\left\{-S_f - S_c \coth\left(\frac{h\omega_c}{4\pi KT}\right)\right\}$$

$$x \sum_{m_f=0}^{\infty} \sum_{m_c=-\infty}^{\infty} \frac{S_f^{m_f}}{m_f!}\ \exp\left(\frac{m_c\omega_c}{4\pi KT}\right) I_{m_c}\left\{S_c\ \mathrm{csch}\left(\frac{\omega_c}{4\pi KT}\right)\right\}$$

$$x\ \exp\left\{-\frac{(\Delta G^o + m_f h\omega_f/2\pi + m_c h\omega_c/2\pi + \lambda_s)^2}{4\,\lambda_s RT}\right\} \qquad 13.$$

exponential term involves a summation over the vibrational levels of a high frequency vibration, ω_f, and a moderate frequency vibration, w_c; the low frequency vibrational modes, ω_s, (which include the solvent interactions) are treated classically; $S_i = 2\pi\lambda_i / h\omega_i$. In the limit that only low frequency vibrational modes are coupled to the ET, Equation 13 reduces to the classical Marcus expression in Equation 1. Coupling to high energy modes has no effect in the normal region of the Marcus plot, but leads to a substantial increase in the ET rates which lie in the inverted region.

Enhanced tunneling in the inverted region can be best understood by looking at the potential wells of the reactants and products. In the normal region the reactant and product curves are separated below the crossing point, so that there is little or no overlap between v_o

Figure 3.20. Transient absorbance trace at 500 nm with Ir_2 and 3,4-dicyano-N-methylpyridinium, excitation at 532 nm; solid line is the best fit to bimolecular kinetics.

---> FIXED PARAMETER; ! ---> FIXED SIGN

y(t) = 1/(C0+C1*t)

C0 = -3.686E+01
C1 = -4.257E+05

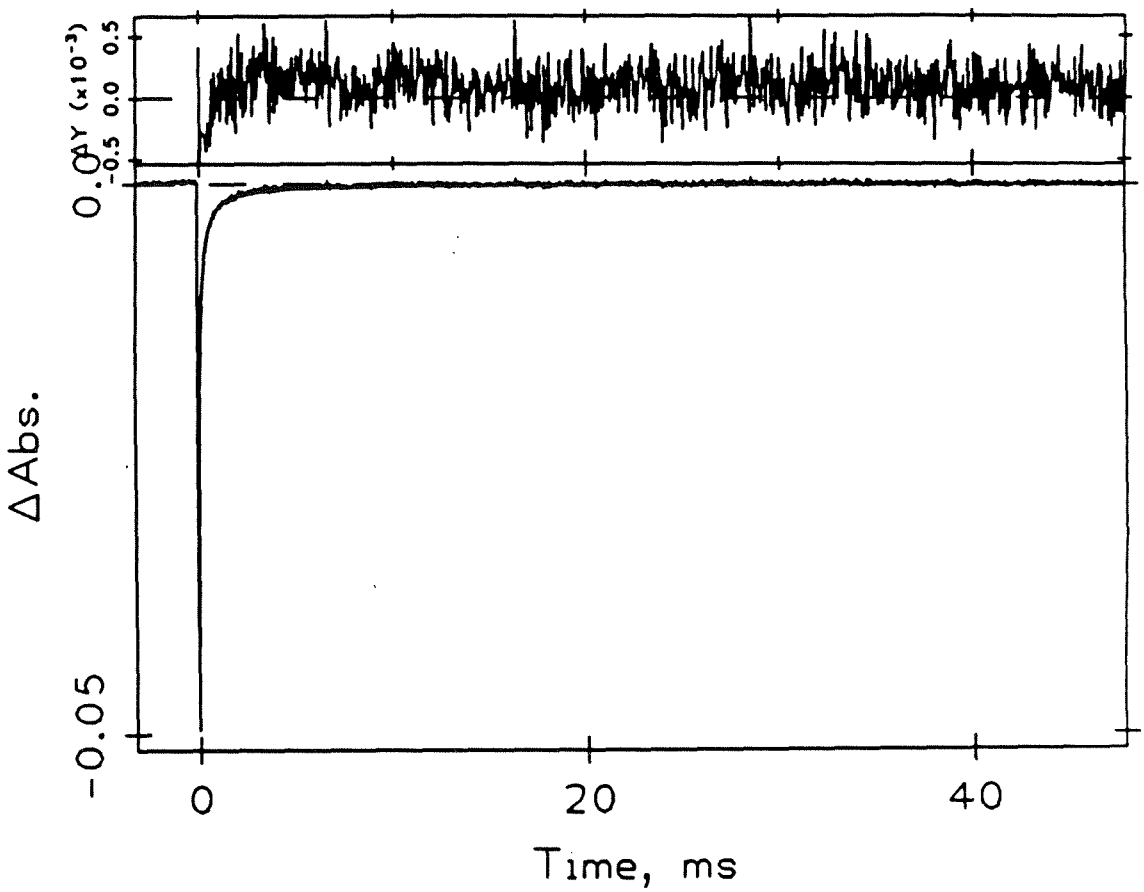


Figure 3.21. Plot of 1/Δabsorbance *vs* time for the recombination reaction with 4-cyano-N-methylpyridinium (squares), N-ethylisonicatinamide (triangles), N-ethylpyridinium (circles), and 2,6-dimethyl-N-methylpyridinium (asterisks).

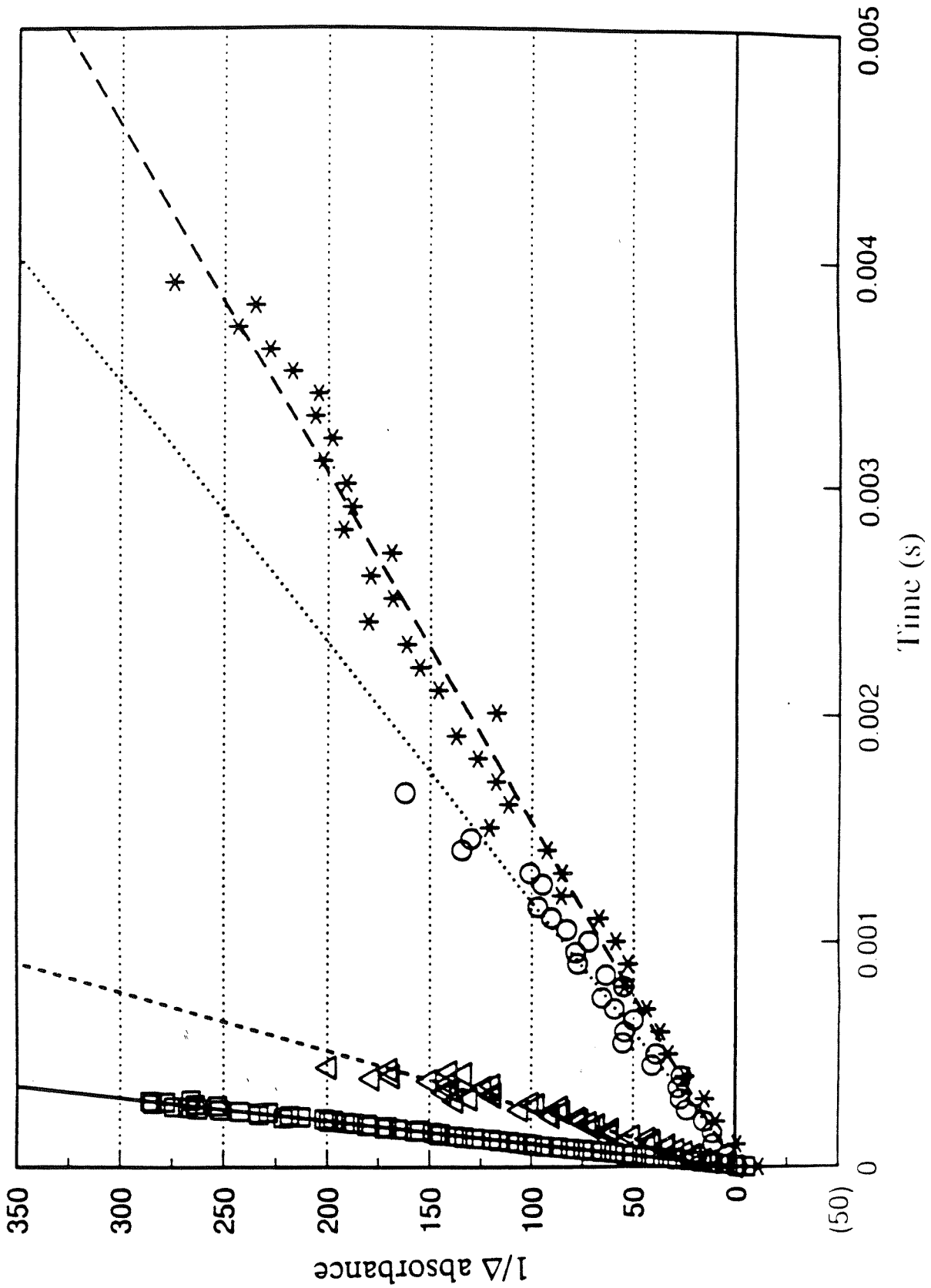
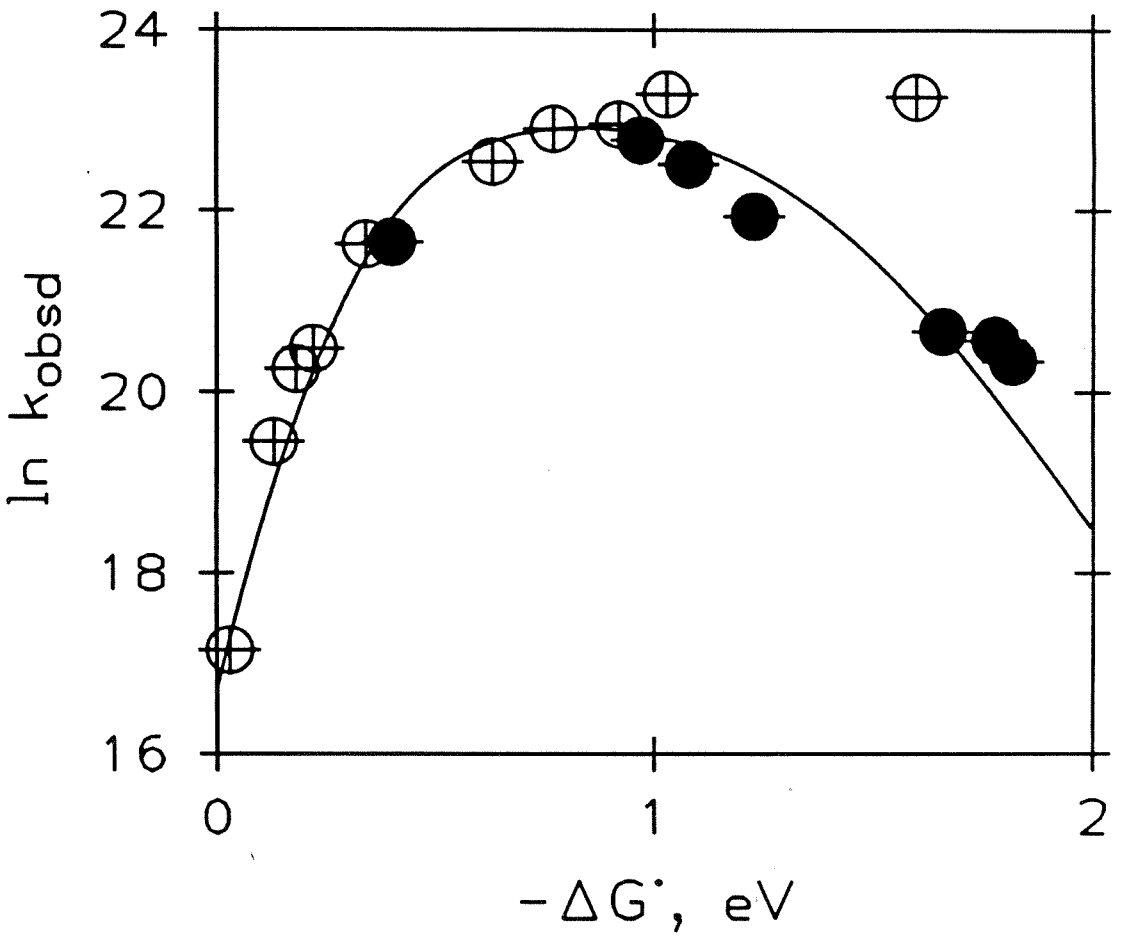

1/Δ absorbance
350
300
250
200
150
100
50
0
(50)
0
0.001
0.002
0.003
0.004
0.005
Time (s)

Figure 3.22. Marcus plot of forward (open circles) and recombination (filled circles) ET rates. The solid line is the best fit theoretical curve excluding the diffusion limited forward rates; $H_{ab} = 10\ cm^{-1}$, $\lambda = 0.85$ eV.


24
22
20
18
16
ln k_{obsd}
0
1
2
$-\Delta G^{\circ}$, eV

wave function of the reactants and any ν_n wave function for the products. The lack of any overlap prohibits tunneling to excited vibrational states of the product. In the inverted region the reactant and product potential wells become nested and it is possible for the reactant wave function to have considerable overlap with one of the vibrationally excited wave functions for the product. In order to have reasonable overlap the product wave function must have the same energy as the reactant wave function. For low energy vibrations the vibrational level where $\Delta E_{\nu_0-\nu_0} = \Delta G^o$ will be large; therefore, the electron density will be primarily at the classical turning points. This situation generates very little overlap with the ν_o wave function of the reactant since the turning points lie outside of the reactant potential well. For high energy vibrations the vibrational level required to match the energy of the reactant ν_o level will be considerably smaller, and the wave function will show more quantum mechanical effects with significant electron density between the turning points. Electron density between the turning points will have a large overlap with the ν_o wave function of the reactant, resulting in a significant amount of tunneling to the excited vibrational state (Figure 3.23). Tunneling through the reaction barrier will enhance the observed ET rates. Rate enhancement will only be significant ET in the inverted region when there is coupling to high frequency vibrations.

The quantum modified Marcus expression provides a very good fit for the bimolecular data with $\lambda = 0.85$ eV and $H_{ab} = 10$ cm^{-1}. The values obtained for λ and H_{ab} are very similar to those reported by Gray et al. for the intramolecular system of iridium phosphinites; however, the intramolecular system shows classical behavior in the inverted region. The discrepancy between the bimolecular and the unimolecular results in the inverted region can be explained if the bimolecular ET is coupled to a high frequency vibration and the unimolecular system is only coupled to low frequency vibrations. It is difficult to imagine why the vibrational coupling would change drastically, since the two systems are so similar chemically.

Part of the discrepancy at high driving forces can be explained by taking into account the fact that bimolecular ET can occur at a variety of distances, where as the donor - acceptor distance is relatively fixed in the unimolecular system. As the donor and acceptor approach one another in a bimolecular system both the coupling and the reorganization energy change as a function of distance. The coupling, H_{ab}, represents the overlap between the donor and acceptor orbitals and falls off exponentially as the distance increases (Equation 14; r is the donor acceptor distance; σ is the sum of the hard sphere radii of the donor and acceptor;

$$H_{ab}^2 = (H_{ab}^o)^2 \exp[-\beta(r-\sigma)] \qquad 14.$$

β is the decay constant). The other distance dependent factor is the reorganization energy of the solvent, λ_s. As the charge separation distance for ET becomes greater more solvent dipoles are affected by the ET and λ_s increases as seen in Equation 15 (a_1 and a_2 are the radii

$$\lambda_s = (\Delta e)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right] \left[\frac{1}{D_{op}} - \frac{1}{D_s}\right] \qquad 15.$$

of the donor and acceptor; D_{op} and D_s are the optical and static dielectric constants).[16]

In the normal region of a bimolecular system, both the increase in H_{ab} and the increase in λ_s as the donor and acceptor approach lead to a greater ET rate at shorter distances; ET will take place almost exclusively at the point of contact between the donor and acceptor for all points in the normal region. As long as the ET occurs at the fixed contact distance (cd) both H_{ab} and λ_s will remain constant at $H_{ab\text{-}cd}$ and $\lambda_{s\text{-}cd}$. A Marcus curve using $H_{ab\text{-}cd}$ and $\lambda_{s\text{-}cd}$ should fit all of the observed rates with $-\Delta G^o < \lambda_{s\text{-}cd}$. In the inverted region, the decrease of H_{ab} with increasing distance still reduces the ET rate, but the increase in λ_s causes the ET rate to increase as the distance increases. Increasing λ_s shifts the maximum of the Marcus curve to a higher driving force so that a point which used to lie in the inverted region for the curve with $H_{ab\text{-}cd}$ and $\lambda_{s\text{-}cd}$ moves closer to the maximum for the new curve with $\lambda_s > \lambda_{s\text{-}cd}$ (Figure 3.24). At large donor acceptor separations the exponential drop in H_{ab} will predominate and the ET rate will decrease. Since the ET rate is no longer a maximum at the contact distance, a significant amount of ET will occur at distances greater

Figure 3.23. Tunneling effects; (a) in the normal region, (b) in the inverted region coupled to a low energy vibration, and (c) in the inverted region coupled to a high energy vibration.

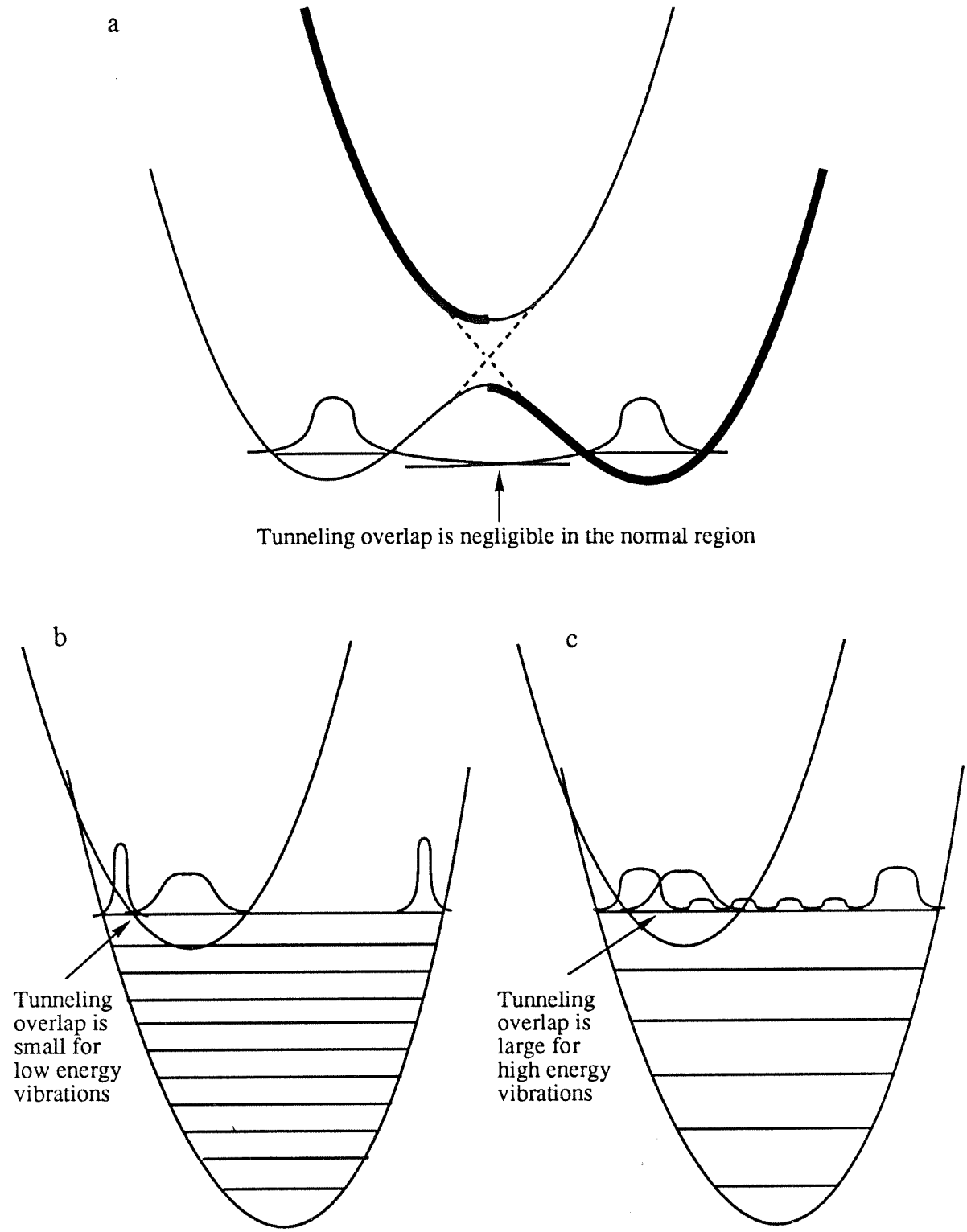

a
Tunneling overlap is negligible in the normal region
b
Tunneling overlap is small for low energy vibrations
c
Tunneling overlap is large for high energy vibrations

Figure 3.24. Distance effect on ET rates in the inverted region; (a) Marcus plot for the λ at the contact distanceand (b) Marcus plot for the slightly larger λ at some distance d (d > the contact distance).

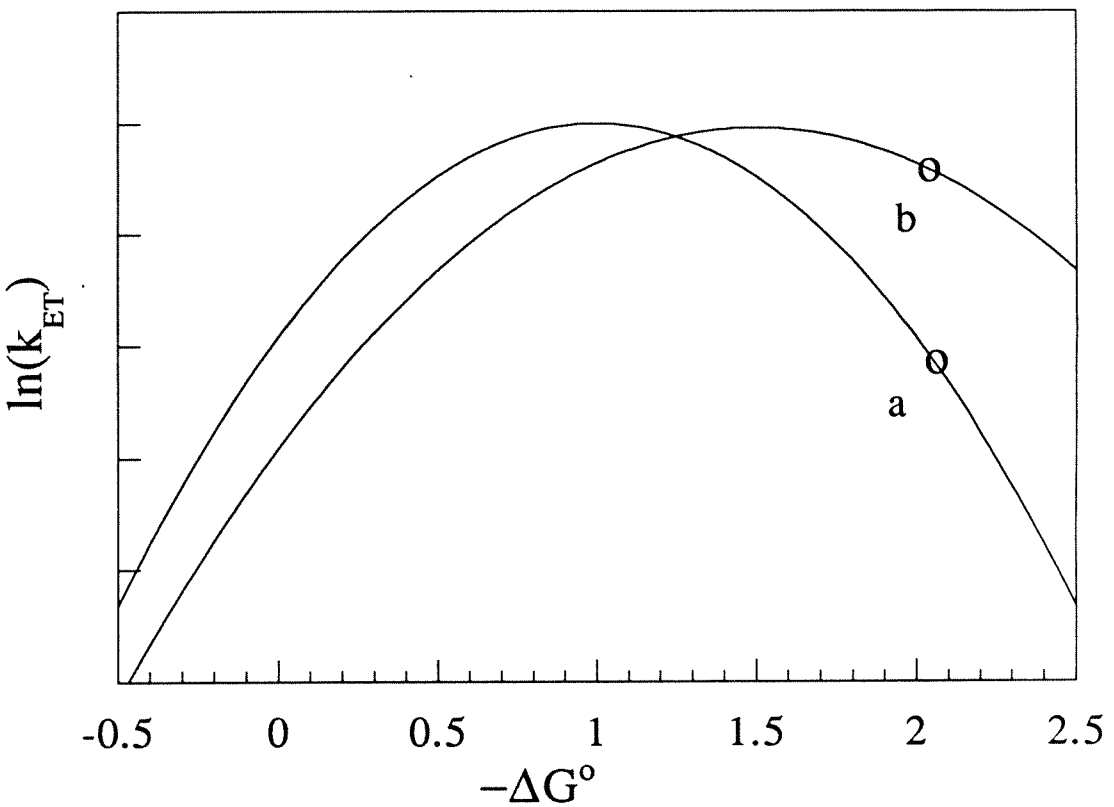
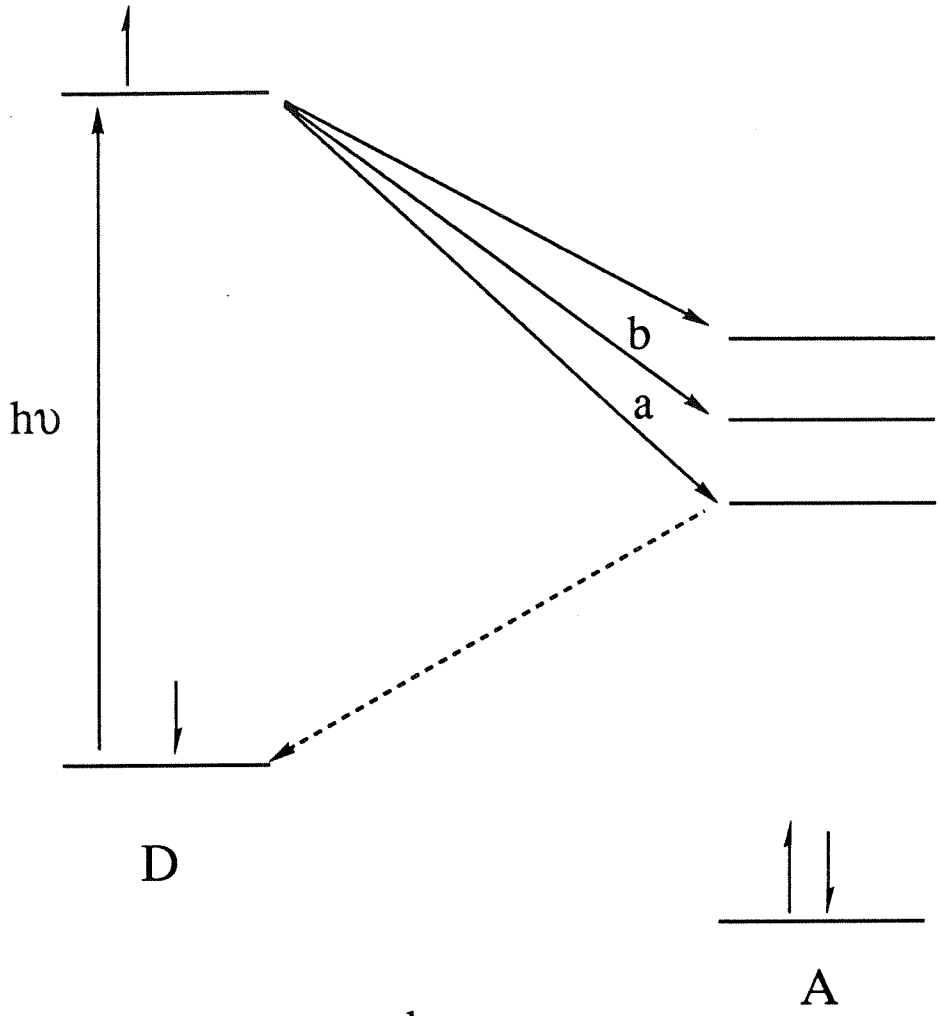
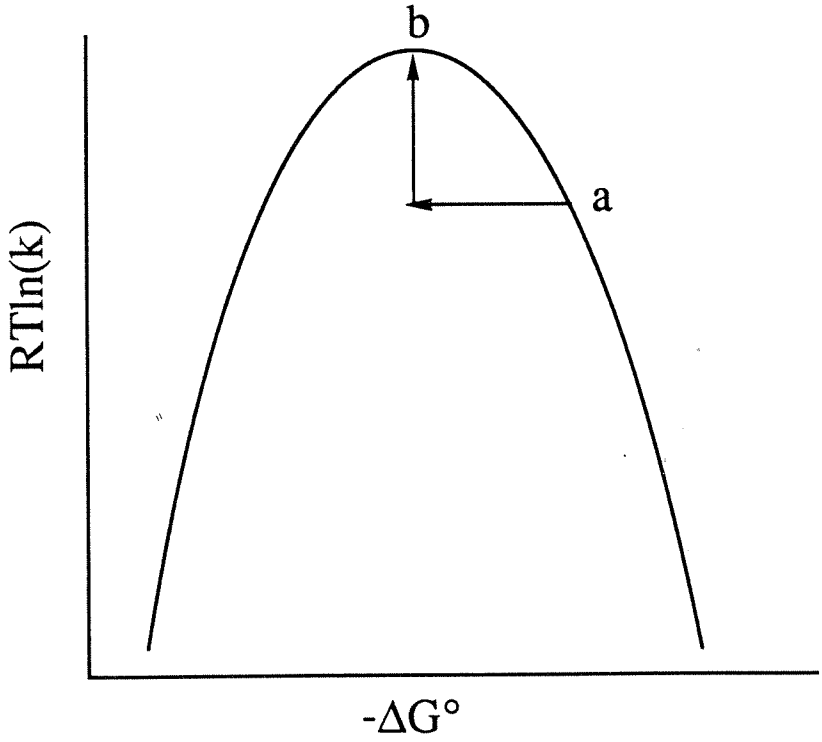

ln(k_ET)
b
a
-0.5
0
0.5
1
1.5
2
2.5
−ΔG°

Figure 3.25. Enhancement of ET rates in the inverted region by low lying excited states; (a) ET to the LUMO on the acceptor, and (b) ET to a low lying excited state. Lower Marcus curves shows the rates for paths (a) and (b).


hυ
b
a
D
A


b
a
RTln(k)
-ΔG°

than the contact distance. The parameters H_{ab} and λ_s will differ from $H_{ab\text{-}cd}$ and $\lambda_{s\text{-}cd}$ for the reactions with $-\Delta G^o > \lambda_{s\text{-}cd}$ so the classical Marcus curve will not fit the experimental data. The faster ET rates at distances slightly greater than the contact distance will lead to faster observed rates than those predicted from theory. Sutin et al. have calculated that the magnitude of this effect for a hypothetical system at a driving force of 2.0 eV can be as large as an order of magnitude. A correction of this type to the observed back ET rates for the bimolecular Ir_2 system would compensate for a large amount of the discrepancy with the unimolecular system, but the correction is not enough to fit completely classical behavior. Some tunneling must be occurring.

Conclusions.

We have made the first observation of inverted behavior for a bimolecular system. The observed rates are extremely interesting, because the high driving force recombination ET rates show clear inverted behavior even in the region where the forward ET rates are diffusion limited (Figure 3.22). This is the first system where both forward photo-induced ET and recombination ET rates have been observed at high driving forces. The difference in behavior between the forward and recombination rates can be explained by postulating that the electron can transfer to low lying excited states in the forward ET reaction which are not accessible for the back ET.

In the photo-induced reaction the electron transfers from the $d\sigma^*$ of the Ir_2^+ to a π^* orbital on the pyridinium. There exists a manifold of π^* orbitals to which the electron can transfer. At low driving forces the electron will transfer exclusively to the lowest lying π^* orbital; ET to higher excited states will be substantially slower since the driving force would be lower. At high driving forces $-\Delta G^o > \lambda$, lowering the driving force will increase the ET rate if the new driving force is closer to λ (Figure 3.25). In order to explain the diffusion limited forward ET rates it is necessary to have excited states available that are within 0.3 eV of the lowest energy ET state. Reports in literature estimate that the pyridinyl radical has excited states 0.5 eV above the ground state.[17] The PES spectrum of the Ir_2 complex shows

that there are also low energy states in Ir_2^+ which are only 0.4 eV above its ground state.[18] Electron transfer to produce either Ir_2^+ or pyridinyl excited states could account for the fast rates observed at high driving forces for the photo-induced ET. The back reaction produces the ground state Ir_2 and pyridinium complexes. From their UV/VIS spectra it is known that the lowest excited state in the Ir_2 complex is 2.5 eV above the ground state and the lowest excited state for the pyridiniums is > 3.0 eV, so that ET to an excited state would be an endoergonic reaction. With the excited states inaccessible the back rates display the expected inverted behavior at high driving force.

The results reported here have intriguing implications for the initial charge separation step of photosynthesis. As mentioned in chapter 1, the photosynthetic center is contained within a membrane. The lack of a mobile solvent leads to a small value for λ, estimated λ to be 0.3 eV.[19] The initial long-lived, charge-separated state in photosynthesis could be explained if the forward ET reaction falls on the top of the Marcus curve and the back reaction at higher driving force falls in the inverted region. One drawback to this hypothesis is that it places a very strict requirement on the driving force for the forward ET, since the small value of λ will cause the ET rates to drop off precipitously as the driving force changes from the optimal value of $\Delta G^o = \lambda$.

The results presented here suggest an alternative possibility. If low lying excited states are accessible on either the donor chlorophyll or the acceptor pheophiton then the forward ET rate would be fast for any driving force greater than λ. The back ET to form the ground state complexes will still remain inverted for driving forces greater than λ because no low lying excited states are accessible.

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(7) The time chosen for the ΔOD values at 395 nm and 500 nm corresponded to when the largest signals were observed.

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Chapter Four:
Gold as a Luminescent Probe for the Coordination Environment of the Active Site in Azurin

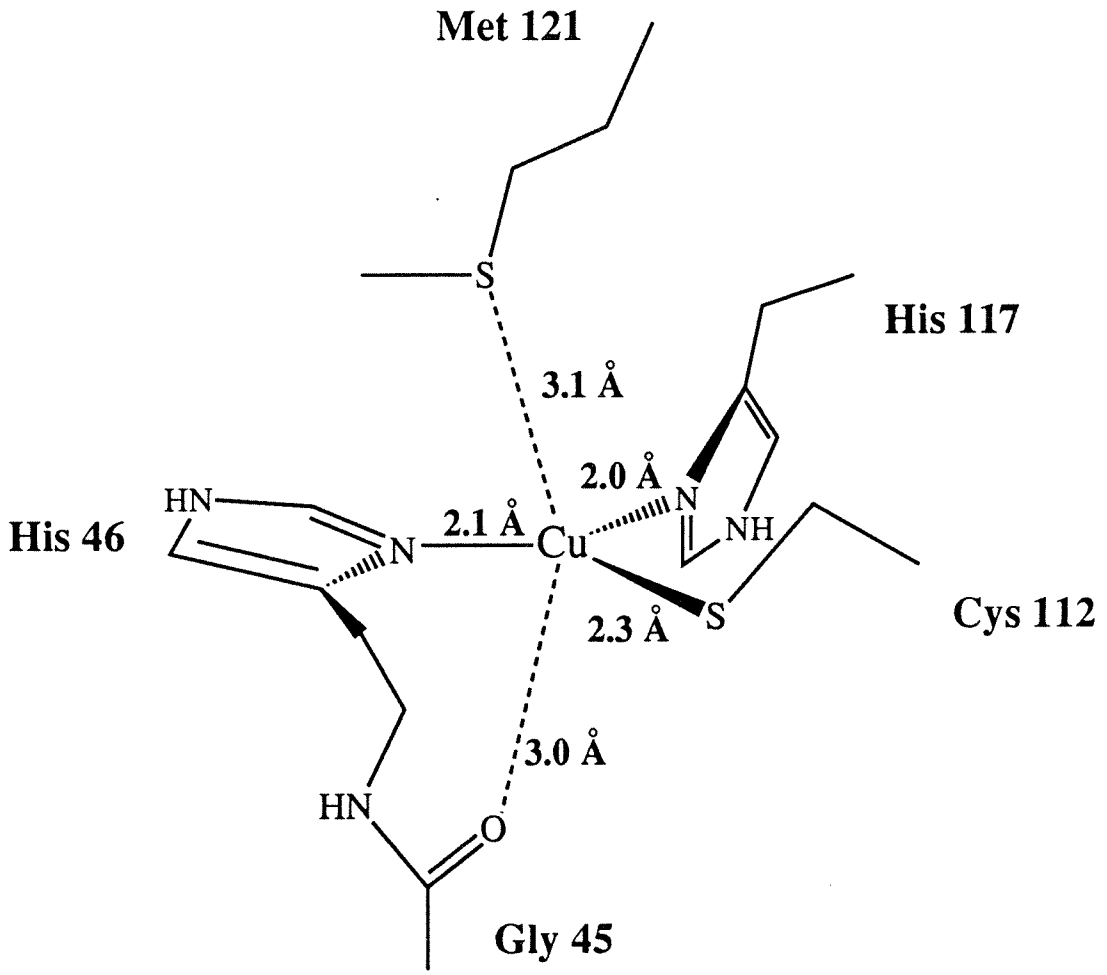
Background

There has been a great deal of discussion in literature concerning the coordination chemistry of the active site in the blue copper protein azurin.[1,2] It is agreed that the site is a type I copper site with three essential features: the Cu(II) is strongly bound to two histidines and a cysteine with an intense band (λ_{max} = 630 nm) due to a ligand to metal charge transfer from the cysteine to the Cu(II); the epr spectrum has a small hyperfine splitting of 58 x 10^{-4} cm^{-1}; the copper reduction potential ($E_{1/2}$ = 288 mV, pH 8.5) is high compared to aqueous Cu(II). The question under discussion is the strength of the interaction between the copper center and the methionine at position 121. The crystal structure of the oxidized form of *Pseudomonas aeruginosa* has been determined, yielding copper-ligand distances of: Cu(II)-His117, 2.0 Å; Cu(II)-His46, 2.1 Å; Cu(II)-Cys112, 2.3 Å; Cu(II)-Met121, 3.1Å (Figure 4.1).[3] The distance of 3.1 Å between the Cu(II) and the methionine is clearly longer than a normal copper thioether bond, but there is still the possibility of some interaction. Solomon et al. have used these crystal coordinates to perform SCF-Xα-SW calculations to determine that a 30 % bond exists between the copper and the methionine.[4] Recent NMR experiments on the Co(II) and Ni(II) substituted azurins have shown paramagnetic shifts of the methyl proton resonances of the methionine is observed; these observations have been interpreted as an indication that the methionine is bound to the copper center.[5]

Introduction

In chapter two it was shown that three-coordinate Au(I) complexes emit, where as four-coordinate Au(I) complexes show no emissive properties. This feature was exploited by using gold as luminescent probe for the coordination geometry of the active site in *Pseudomonas aeruginosa* azurin. The Au(I) center is known to bind thiols strongly, so the cysteine will be a good ligand. The Au(I) is a more appropriate substitution for the Cu(I) center than the Ni(II) and Co(II), since Au(I) is isoelectronic with Cu(I), and is found in similar coordination environments. In terms of the

Figure 4.1 Active site of *Pseudomonas aeruginosa*.


Met 121
S
3.1 Å
His 117
2.0 Å
N
NH
HN
His 46
2.1 Å
N
Cu
S
2.3 Å
Cys 112
3.0 Å
HN
O
Gly 45

methionine interaction, Au(I) is a softer metal than Cu(I), so one would expect any metal-methionine interaction in the reduced wild-type (WT) holo azurin to increase upon Au(I) substitution. If the Au(I) azurin has a significant interaction with the methionine to generate a distorted tetrahedral geometry, then no emission will be observed. No interaction with the methionine would place the Au(I) in a trigonal planar environment, and strong luminescence should be observed from the Au(I) center.

A previous attempt to make Au(I) substituted azurin has been published, using gold thiomalate as the starting material. The initial thiomalate starting material already has a fairly strong gold-thiolate bond, so one would expect surface binding to form a two coordinate gold complex with the gold-thiolate bond remaining intact. The report shows only a portion of the ^1H spectrum, and offers no evidence for whether or not the gold atom is bound to the active site.

A mutant azurin was also prepared, in which the methionine at position 121 (Met 121) is replaced with a leucine residue. The Met121 to Leu121 mutant has been made previously and is known to retain a type I blue copper site.[6] The mutant Au(I) azurin will serve as a good control since it has no possible fourth ligand for the Au(I) center. Luminescence form the gold(I) center should be readily observed in this gold substituted protein. Comparison between the WT-Au(I) and Met121→ Leu121 -Au(I) azurins will show even subtle bonding interactions by a shift in the emission maximum. Any bonding interaction will raise the energy of the p_z orbital and lead to higher energy emission.

Experimental

Materials All enzymes and buffers for DNA manipulations were purchased from New England BioLabs or Mannheim Boehringer Biochemicals unless otherwise specified. Most techniques were standard biological techniques.[7] Sequencing was performed with a Sequenase version 2.0 kit purchased from the United States Biochemical Corp. Oligonucleatides were synthesized at the Caltech microchemical

facility. Electroporation was induced with a Bio-Rad Gene-Pulser set at 2.5 kV and 200 ohms. Cells were centrifuged with a RC2-B Sorvall Superspeed centrifuge. Ultracentrifugation for DNA isolation was carried out with a Beckman L2-75B ultracentrifuge. The Muta-Gene Kit was purchased from Bio-Rad. The QIAX-Gel Extraction kit and the Plasmid Maxi-kit were purchased from Quiagen. The pET System was purchased from Novagen. The FPLC purifications were done with a Pharmecia FPLC System using a Mono Q column. The loading buffer, A, is a solution of 10 mM Diethanolamine (DEA) at pH = 8.8, and the eluant buffer, B, is a solution of 100 mM NaCl, and 10 mM DEA at pH = 8.8. All media was autoclaved for 20 minutes and allowed to cool prior to use.

Protein Preparation *Pseudomonas aeruginosa* azurin was expressed from a synthetic gene in *Escherichia* coli with a frozen cell culture previously prepared.[8] An aliquot (200 μL) of frozen (-70°C) cells which had been transformed with a pET 9-A plasmid containing the azurin gene was suspended in 20 mL of 2xYT media with 50 μg/mL kanamycin and shaken for 14 to 20 hours at 30 °C. The 20 mL of suspended cells were then added to a 6 L flask containing 4 L of 2xYT media with 50 μg/mL kanamycin. The solution was shaken at 30 °C for 5 hours. The absorbance was measured at 1 hour intervals at 550 nm and 650 nm. When the absorbance at 550 nm was greater than 2.0 and the absorbance at 650 nm was greater than 1.5, 3mL of a 20% aqueous solution of IPTG was added, and the cell mixture was shaken for ≈ 5 hours at 30°C. The cell paste was then isolated by centrifugation at 5000 rpm. The cells were then resuspended in 360 mL of a 20% sucrose, 30 mM Tris, and 1mM EDTA at pH = 8.0 by shaking at room temperature. The cell paste was isolated by centrifugation at 8000 rpm and resuspended in 360 mL of a 4 mM NaCl, ice-cold, aqueous solution causing osmotic shock. The azurin produced by the *E.* coli is transported to the periplasm between the inner and outer cell membranes. The mild lysing conditions cause only the outer membrane to lyse so that the contents of the periplasm are released into solution,

but the rest of the cell remains intact. The solution was shaken in a cold room at 4°C overnight. The cell paste was removed by centrifugation at 5000 rpm, and the supernate was stirred gently 4°C. Addition of 36 mL of a 0.5 M aqueous solution of ammonium acetate (pH = 4.1; note initial addition of the solution should be made slowly to avoid fast pH changes) resulted in the precipitation of some unwanted proteins. The precipitate was removed by centrifugation at 7000 rpm, and the supernate was reduced in volume to 35 mL by ultrafiltration at . The buffer system was the exchanged to pH = 8.8 with 10 mM DEA by adding three aliquots of the new buffer and reducing the volume by ultrafiltration between additions. The apo-azurin was further purified by FPLC. The FPLC trace shows two peaks at 15% buffer B; the first peak is due to Zn^{2+}-azurin and the second peak corresponds to apo-azurin.

Site-Directed Mutagenisis The site-directed mutagenisis involves taking an oligonucleotide of ≈ 20 base pairs with the desired mutation and annealing it to a single stranded plasmid containing the WT-azurin gene. The oligonucleotide was synthesized to match with the Met121 area of the azurin gene. The uracil containing plasmid and the oligonuceotide were combined with annealing buffer and water. The solution was then placed in a water bath at 80°C. The water bath was allowed to cool to 30°C, at which point the annealed plasmid was placed on ice. The plasmid was ligated by addition of synthesis buffer, 5 fold diluted polymerase, and T4 ligase. The resulting solution was kept at 37°C for 90 minutes. The ligase was stopped with the addition of 90 μL TE. The plasmid was then transformed into MV1190 cells: 45 μL of frozen MV1190 cells were placed on ice for 30 minutes; 10 μL of the plasmid solution were added; the mixture was shocked with 2.5 KV at 100 ohms; shocked cells were promptly treated with 900 μL SOC. The transformed cells were placed at 37°C for 1 hour and then centrifuged for 1 minute. The supernate was discarded to leave 100 μL of solution. The cells were resuspended and plated out onto LB culture plates containing ampicillin. The plates were incubated at 30°C for 14 hours. One of the resulting cell colonies was placed into 10 mL

of 2xYT media containing 30 μg/mL of ampicillin and shaken overnight at 30°C. The 10 mL of suspended cells was placed into a flask containing 500 mL of 2xYT and shaken for 12 hours at 30°C. The cells were isolated by centrifugation at 5000 rpm and the DNA was isolated using a Quiagen DNA kit. An aliquot of DNA was sequenced by standard procedures. Another aliquot of the DNA was cleaved with Bagel II and NDE I. The DNA was separated on a gel and the resulting small fragment containing the mutant azurin gene was isolated. A kanamyacin resistant pET 9-A plasmid was cleaved with NDE I and BamHI. The DNA from the cleavage reaction was separated on an agar gel. The large fragment was isolated from the gel. The DNA was extracted from the gel according to the procedure for the Quiagen DNA extraction. Next the Pet-9A DNA (3 μL) and the mutant azurin DNA (6 μL) were combined and ligated with T4-ligase (1 μL T4-ligase with 2 μL ligase buffer and 8 μL water). The Pet 9A plasmid was transformed into BL21(DE3) *E.* coli cells by a heat shock procedure: competent BL21(DE3) cells (20 μL) and an aliquot of the Pet-9A plasmid solution (5 μL) were mixed together and placed on ice for 30 minutes; the solution was placed in a 42°C bath for 45 seconds; 80 μL of SOC were added and the solution was iced for 2 minutes and then incubated at 37°C for 1 hour. The cells were plated out onto LB plates containing 30 μg/mL kanamyacin and incubated at 30°C overnight. One colony from the cell culture was placed into 20 mL of 2xYT containing 30 μg/mL kanamycin and shaken for 12 hours at 30°C. The 20 mL of suspended cells were then added to 1 L of 2xYT containing 30 μg/mL kanamyacin and shaken at 30°C for 14 hours. Twenty aliquots of 100 μL were diluted with 100 μL of 50% glucose and frozen for protein preparations and the remaining cells were isolated by centrifugation at 5000 rpm. The DNA was extracted according to the Quiagen procedure and the entire gene was sequenced . The protein was expressed and purified in the same manner as described for WT-azurin except that prior to high pressure ultra filtration the solution was made 1mM EDTA and stirred at room

temperature for 24 hours. The addition of EDTA removes a large percentage of the zinc from the Zn-azurin. The FPLC trace shows two peaks just as the WT-azurin.

Incorporation of Gold(I) The Au(I) starting material, $ClAuS(CH_2CH_2OH)_2$, was prepared by adding a two-fold excess of $S(CH_2CH_2OH)_2$ to a stirring solution of 1g auric acid ($HAuCl_4$) in 50 mL of nanopure water. After stirring for three hours, the water was removed by rotary evaporation under reduced pressure. The resulting oil was dissolved in 15 mL of ethanol followed by the addition of ether to precipitate the product. The $ClAuS(CH_2CH_2OH)_2$ can be stored for months under ether, but will decompose in less than twelve hours if one tries to isolate the solid. A threefold excess of $ClAuS(CH_2CH_2OH)_2$ in 1 mL of water was added to a solution of 10 mg of apo-azurin in 8 mL of 10mM DEA at pH = 8.8 and the solution was allowed to sit for forty-eight hours. Surface bound gold was removed reducing the volume in a centricon and exchanging the buffer with a 100 mM NaCl, 10mM DEA solution at pH = 8.8. After sitting for three hours the buffer was exchanged back to 10 mM DEA at pH = 8.8. The gold substituted protein was purified by FPLC. The FPLC trace shows a major peak for the gold substituted protein followed by a small peak for the apo-protein (Figure 4.2).

Results and Discussion

Electronic Absorption Spectra The Au(I)-WT-azurin has an absorption spectrum similar to that of apo-WT-azurin (Figures 4.3 -4.4). Both proteins have a strong UV absorption band at 260 nm and the characteristic spike, due to the tryptophan residue, at 292 nm. The Au(I) -WT-azurin spectrum differs from that of apo-WT-azurin spectrum with a low energy shoulder at 308 nm and a large increase in the absorbance at 250 nm. The two new features must be due to transitions which involve the metal orbitals. The band at 308 nm is tentatively assigned as the metal centered $^1A_1 \rightarrow E'$ ($^3E''$) transition in analogy with the three coordinate gold complexes discussed in chapter two. The low energy shoulder observed in the Au(I)-WT-azurin spectrum is also observed in the isoelectronic reduced-holo-WT-azurin spectrum. The only difference between the

Figure 4.2. FPLC trace for Au(I)-WT-azurin purification.

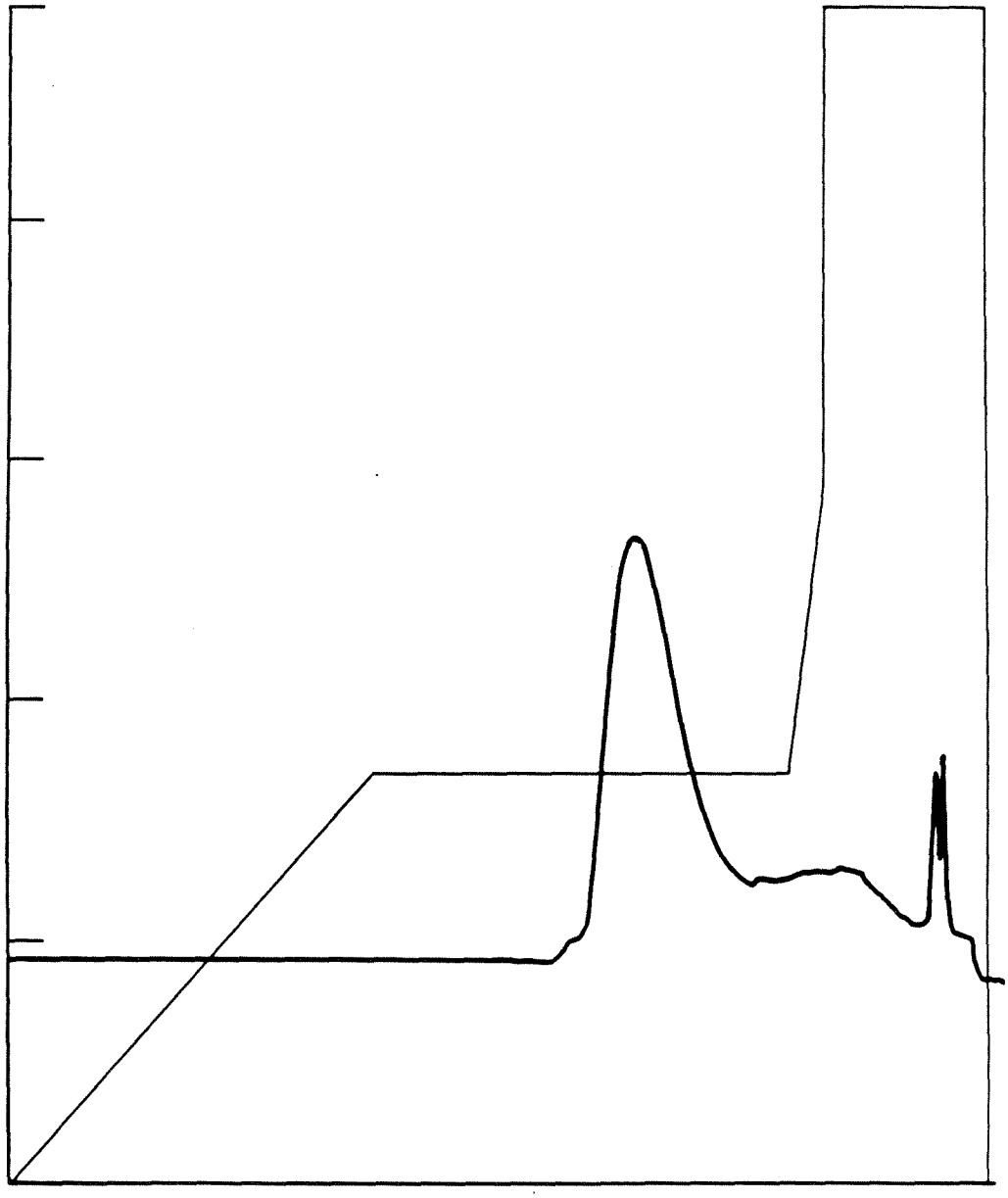


Figure 4.3. Absorption spectrum of apo-WT-azurin.

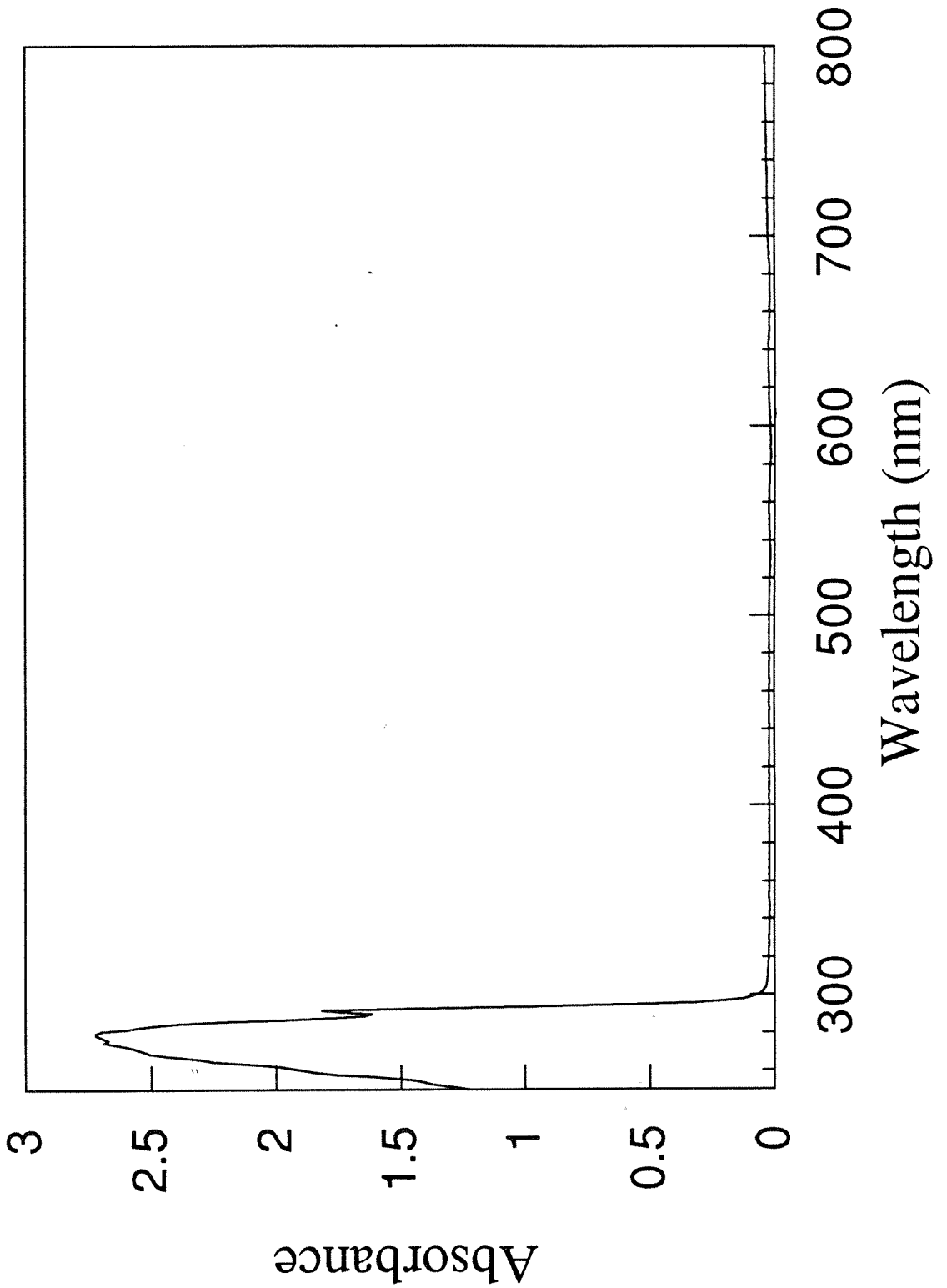

Absorbance
3
2.5
2
1.5
1
0.5
0
300
400
500
600
700
800
Wavelength (nm)

Figure 4.4 Absorption spectrum of Au(I)-WT-azurin.

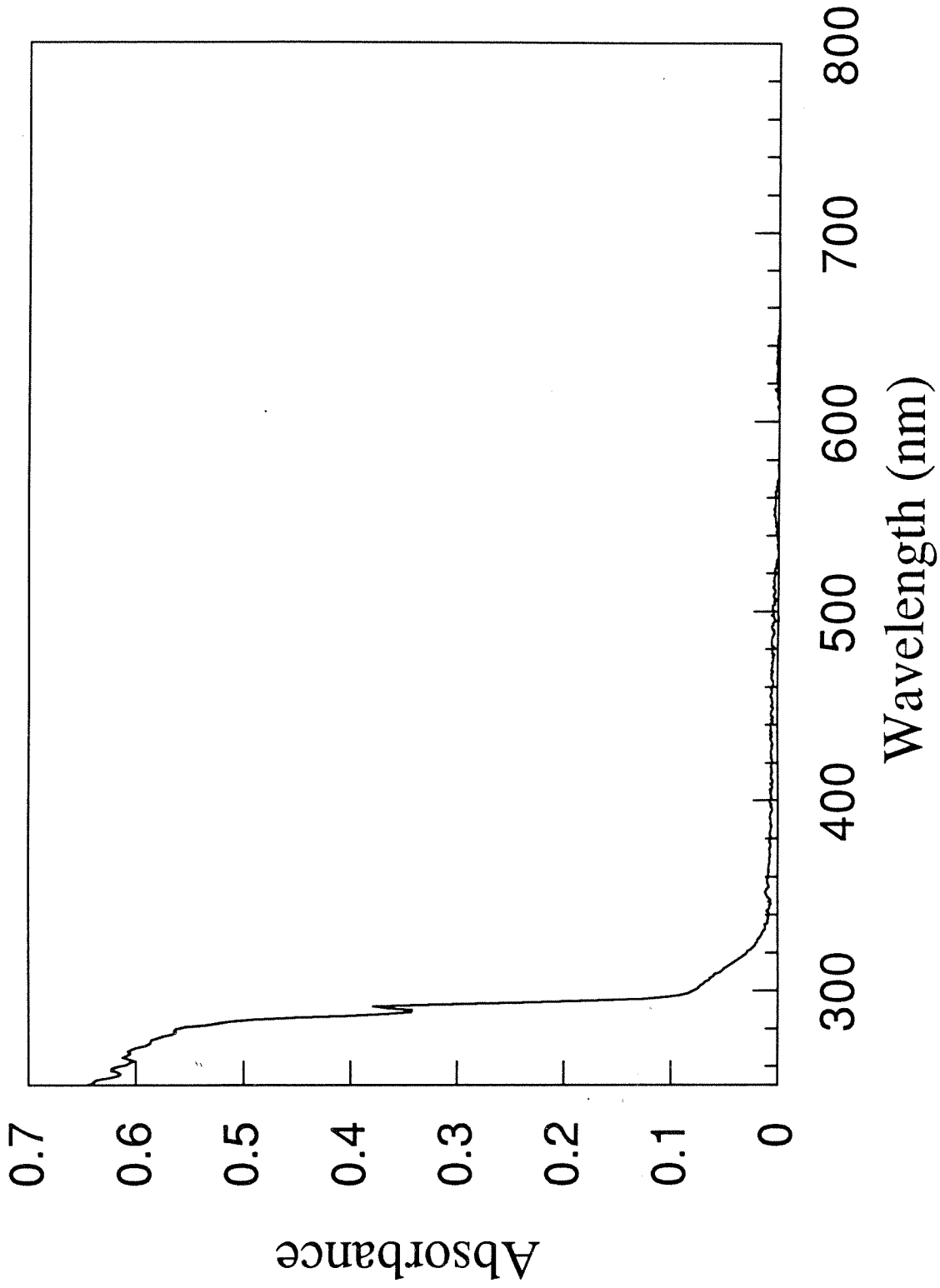

Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
400
500
600
700
800
Wavelength (nm)

Figure 4.5. Emission spectrum of apo-WT-azurin, 77 K glycerol:water glass.

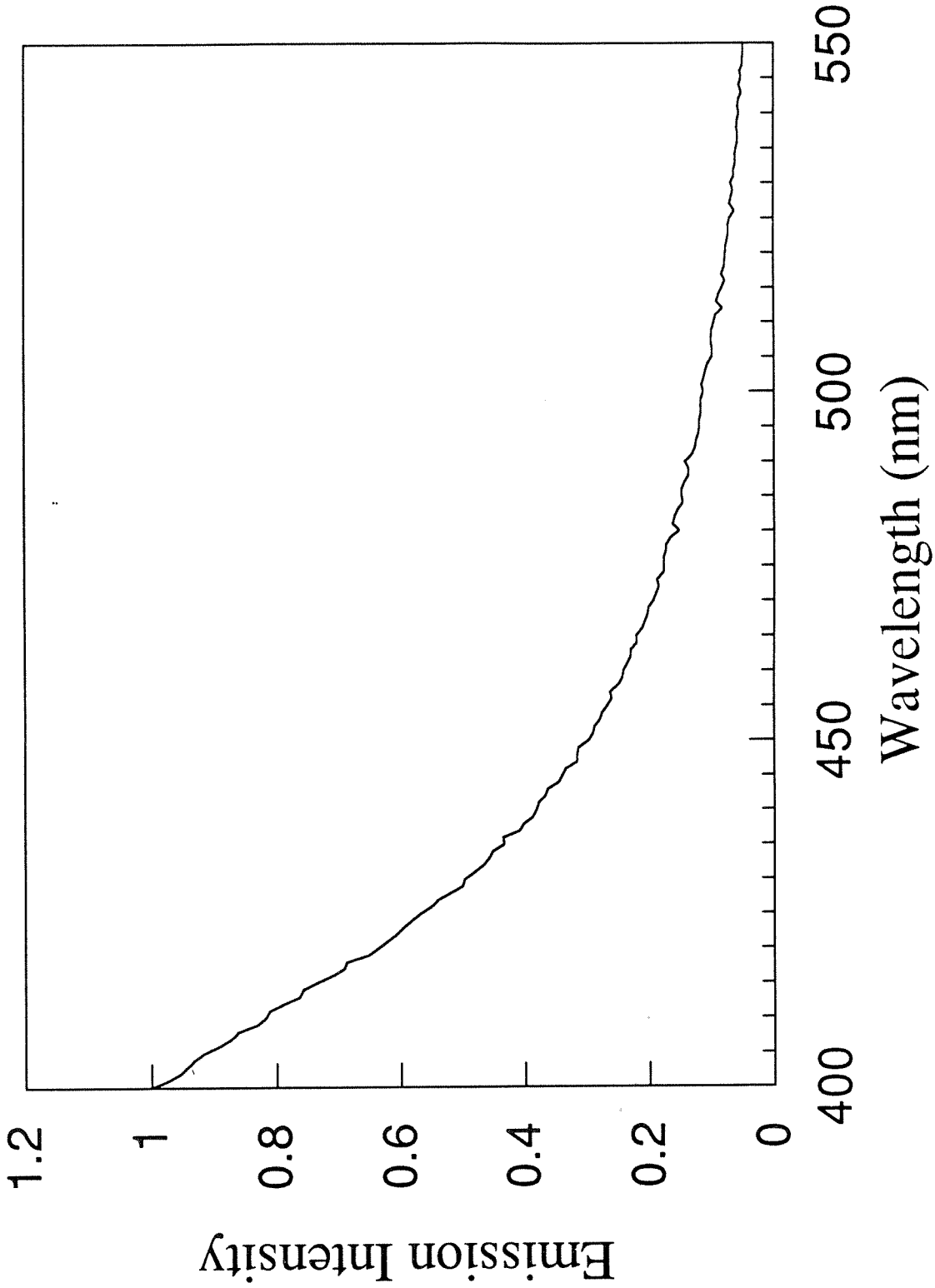

Emission Intensity
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
Wavelength (nm)

Figure 4.6. Emission spectrum of reduced-holo-WT-azurin, 77 K glycerol:water glass.

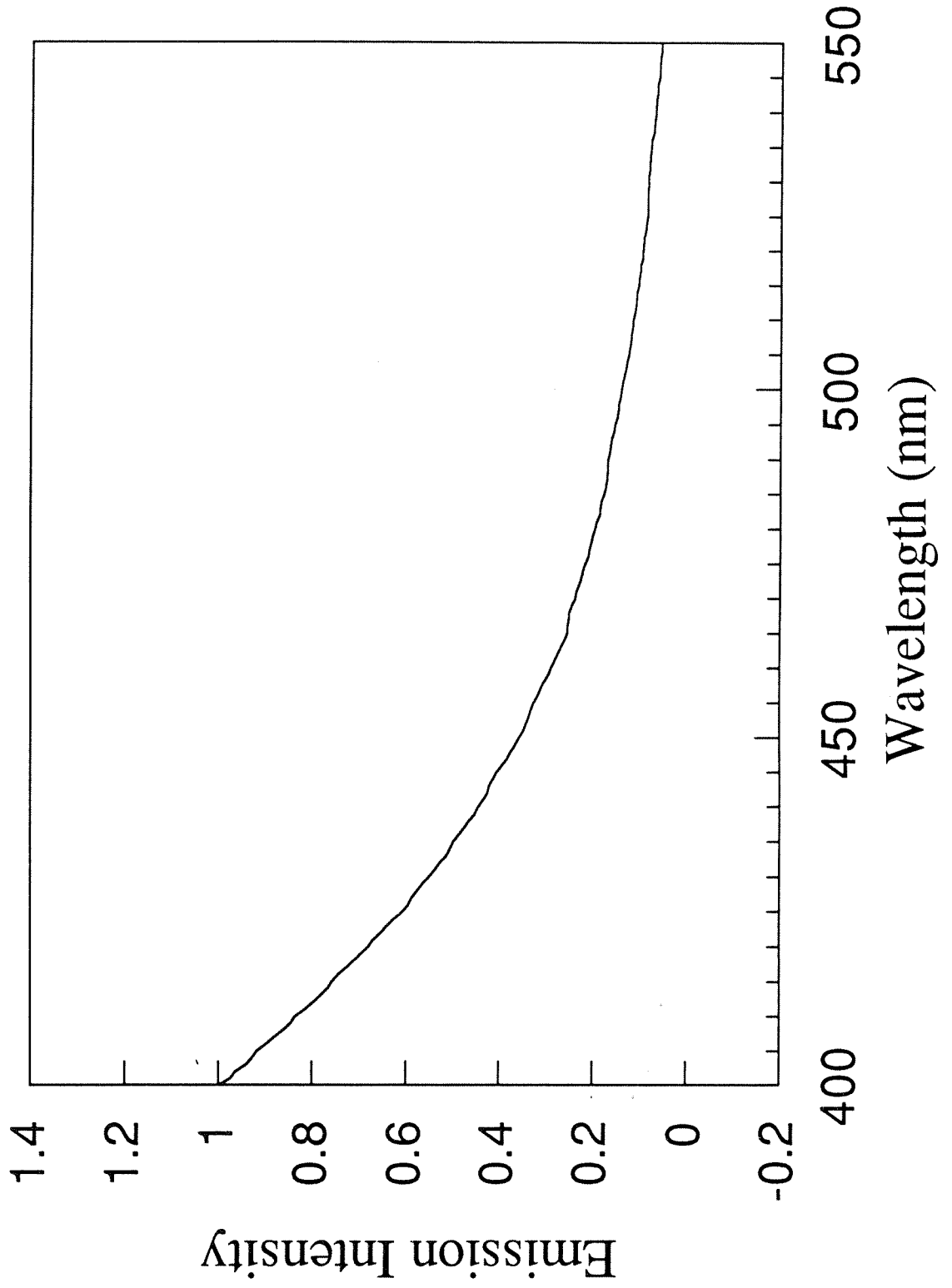

Emission Intensity
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
400
450
500
550
Wavelength (nm)

Figure 4.7. Emission spectrum of holo-WT-azurin, 77 K glycerol:water glass.

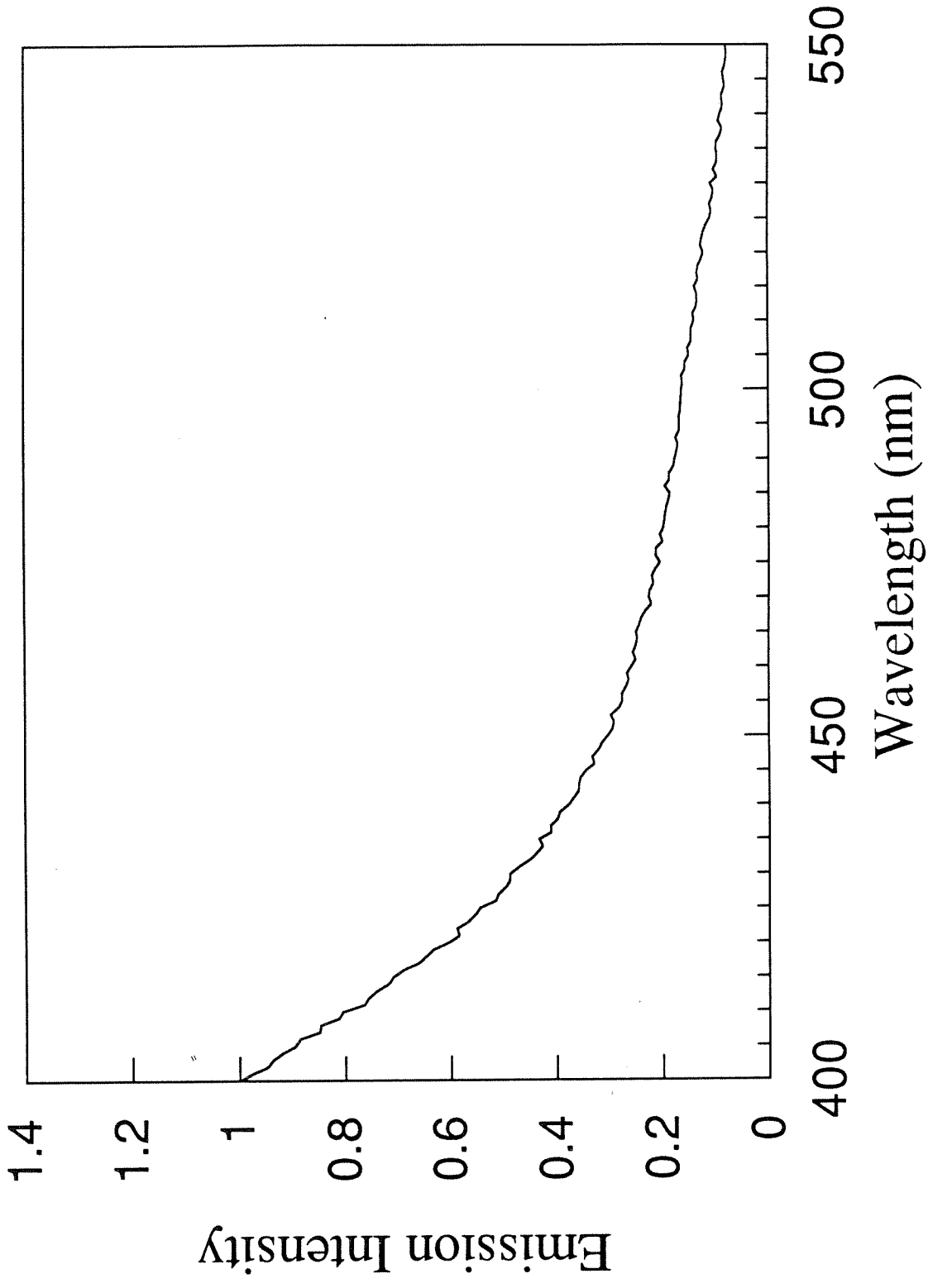

Emission Intensity
1.4
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
Wavelength (nm)

Figure 4.8. Emission spectrum of Au(I)-WT-azurin, 77 K glycerol:water glass.

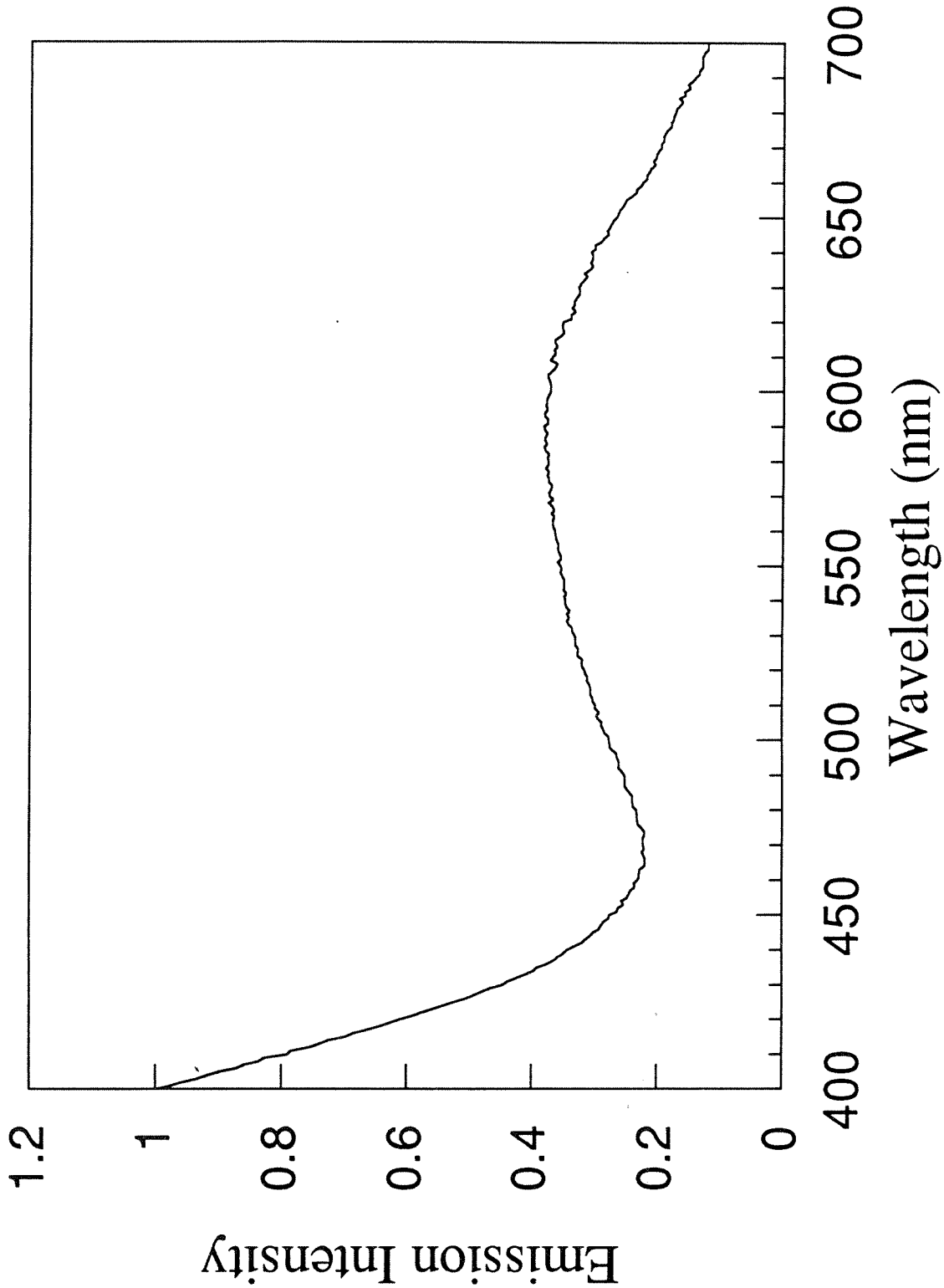

Emission Intensity
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
700
Wavelength (nm)

Figure 4.9. Luminescence decay of Au(I)-WT-azurin, 77 K glycerol:water glass.

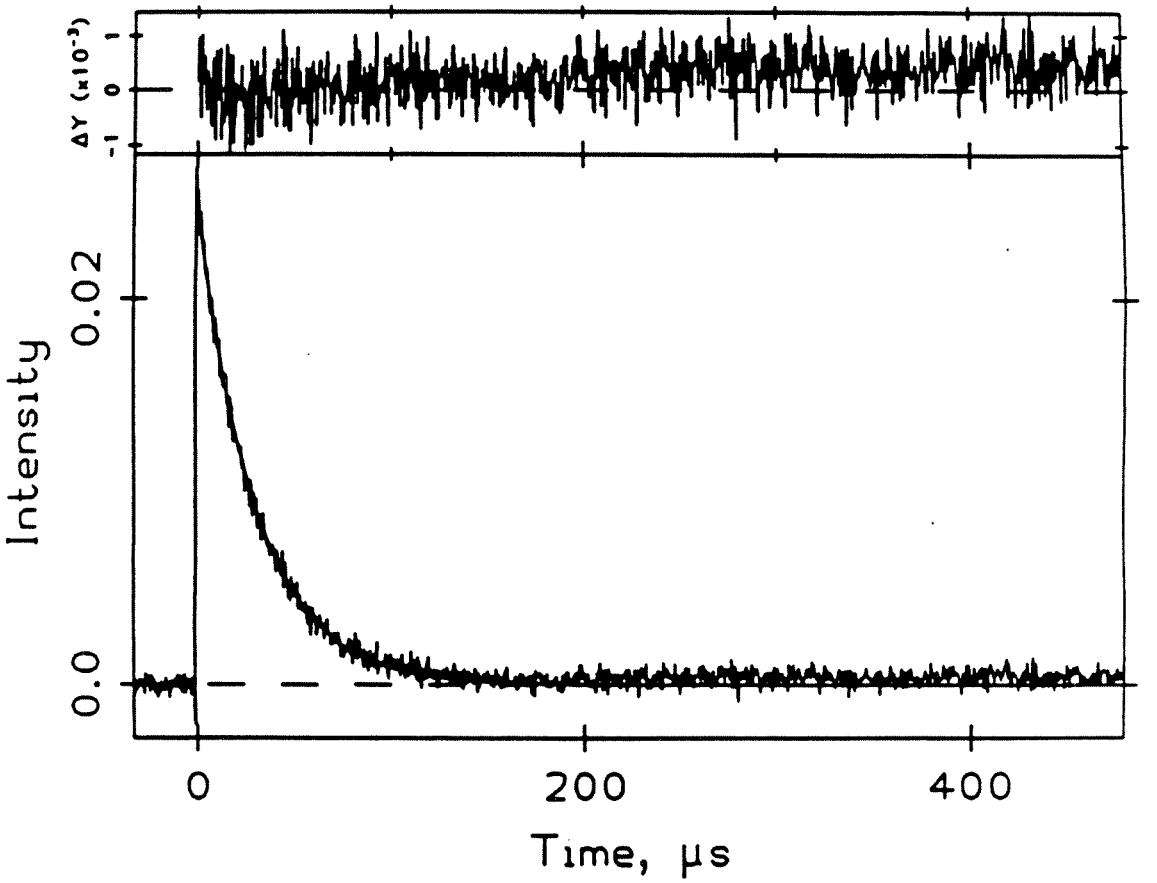
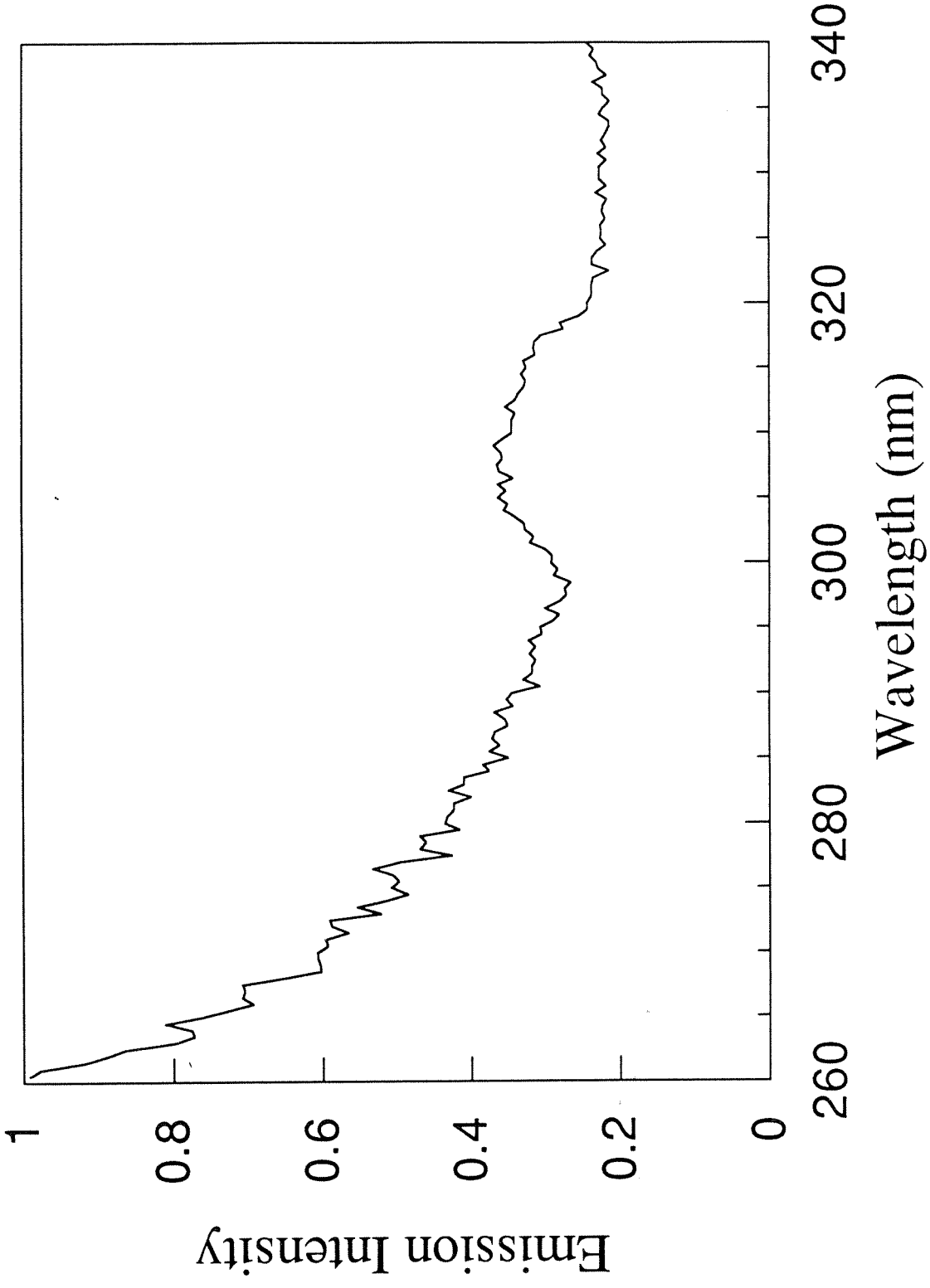

ΔY (x10⁻³)
1
0
-1
Intensity
0.02
0.0
0
200
400
Time, μs

Figure 4.10. Excitation spectrum of Au(I)-WT-azurin.


Emission Intensity
1
0.8
0.6
0.4
0.2
0
260
280
300
320
340
Wavelength (nm)

Au(I)-WT-azurin spectrum and that of reduced-holo- WT-azurin is that the Au(I)-WT-azurin has greater absorbance at 250 nm.[9]

Emission and Excitation Spectra

The emission spectra of holo-, reduced-holo-, and apo- azurins at 77 K in a 50:50 water:glycerol glass are nearly identical (excitation at 313 nm; Figures 4.5 to 4.7). The emission spectra consist of a combination of fluorescence and phosphorescence from the tryptophan residue. The tryptophan emission has been observed previously: the fluorescence maximum occurs at 310 nm with a lifetime of 12 ns and the phosphorescence maximum occurs at 445 nm with a lifetime of 210 ms (lifetimes measured at room temperature).[10,11] The emission spectrum of the Au(I)-WT- azurin shows the tryptophan emission as well as a new low energy emission band at 580 nm (Figure 4.8). This low energy emission has a lifetime of 30 μs, which corresponds well with the lifetime observed for the three coordinate gold(I) complexes discussed in chapter two (Figure 4.9). The excitation spectrum of the Au(I)-WT- azurin has a band at 308 nm (Figure 4.10). The fact that the band at 308 nm leads to emission with a lifetime of 30 μs supports the assignment of the band as the $^1A_1 \rightarrow E'$ ($^3E''$) transition.

Control Experiments for Active Site Binding

An excess of $CuSO_4$ was added to a solution of Au(I)-WT-azurin (100 μM) and the solution was left standing at 4° for one day. The solution was then repeatedly (3 times) reduced in volume by centrifuge filtration and diluted with buffer A to remove the $CuSO_4$. The absorption spectrum remain unchanged from the initial Au(I)-WT azurin spectrum indicating that the gold does indeed bind to the active site. If gold were not bound to the active site then a band at 628 nm would have appeared as the Cu^{2+} bound to the active site. The fact that Cu^{2+} does not displace the Au^{+} demonstrates that the gold is tightly bound to the active site.

A further test of active site binding was accomplished with a Cys112 to Asp112 mutant. The mutant is known to bind Cu(II) in the active site through Cu(II)-oxygen

binding.[12] The Au(I) soft metal center does not tend to bind oxygen, and would not be expected to bind the active site of the Asp112 mutant. The mutant azurin was placed in solution with two equivalents of $ClAuS(CH_2CH_2OH)_2$ for one day at 4 °C and then purified by FPLC. The purified protein showed no indication of binding Au(I) and readily bound Cu(II) upon addition of $CuSO_4$. The lack of Au(I) binding indicates that the cysteine of the active site is needed to bind Au(I) in the WT-azurin.

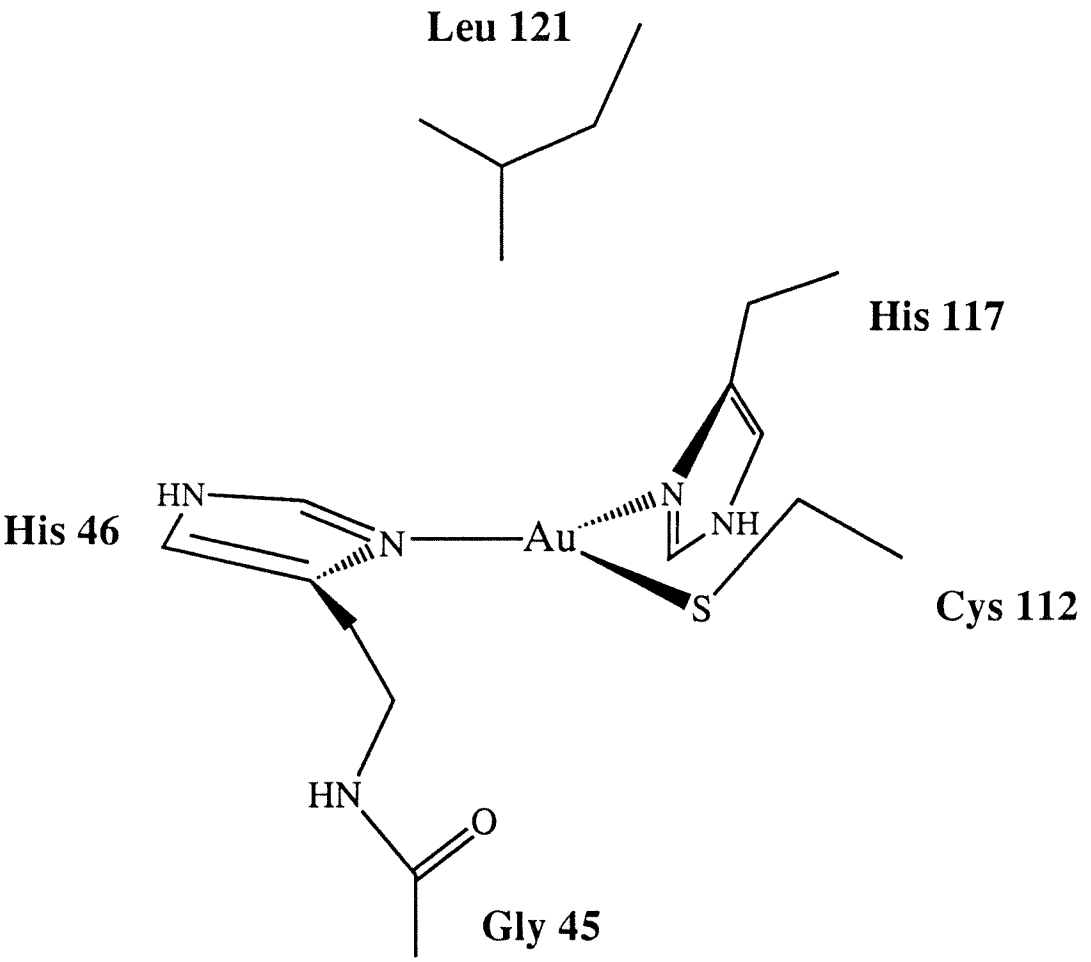
To ensure that surface binding is not present, the $ClAuS(CH_2CH_2OH)_2$ was added to a solution of holo-WT-azurin and the solution was allowed to stand for one day at 4 °C. After washing with buffer B, FPLC purification showed only one peak. The absorption spectra of the purified protein is identical to holo-WT- azurin, and the emission spectrum shows only trytophan emission. The absence of any low energy emission demonstrates that the 580 nm emission of Au(I)-WT-azurin is not due to surface bound Au(I).

Conclusions

We have synthesized a Au(I)-WT-azurin where the Au(I) center is bound to the active site. The Au(I)-WT-azurin has an emission band not present in holo, reduced-holo, or apo-azurins. As discussed in chapter two, isolated two coordinate Au(I) complexes such as $Au(PCy_3)_2^+$ and four coordinate complexes such as $Au(dcpe)_2^+$ do not emit, but three coordinate gold complexes are highly emissive. The low energy (λ_{max} = 580 nm) emission of the Au(I)-WT-azurin has been assigned as the $^1A_1 \leftarrow E'$ ($^3E''$) transition associated with the three coordinate Au(I). The corresponding absorption band appears as a shoulder at 308 nm. The large Stokes shift of 15,400 cm^{-1} for the Au(I)-WT-azurin is nearly twice that observed for the three coordinate model complexes, indicating a substantial amount of reorganizational energy in the excited state.

Based on the 580 nm emission of Au(I)-WT-azurin the geometry of the Au(I) site in azurin is believed to be three coordinate with the Au(I) bound to Cys112, His46, and His117. The Au(I) center is isoelectronic with Cu(I), so the Cu(I) site is also believed to

Figure 4.11. Theoretical active site for the Au(I)-Leu121 mutant.


Leu 121
His 117
His 46
HN
N
Au
N
NH
S
Cys 112
HN
O
Gly 45

be three coordinate with no bonding interaction between the Cu(I) center and the Met121. If there were any bonding interaction between the Cu(I) and Met121, one would expect the interaction to be even greater for the larger, softer Au(I) center since methionine is a soft ligand. Even a small amount of bonding interaction would move the $E_{\nu_o-\nu_o}$ energy to higher energy than the 430 nm $E_{\nu_o-\nu_o}$ energy observed for the three coordinate complexes in chapter two and any significant bonding interaction would shut off the emission completely. The partial bond suggested by Solomon for the 2.9 Å Cu(I) - methionine corresponds to bond energy of 7 kcal/mol. This interaction should shift the $E_{\nu_o-\nu_o}$ energy from 430 nm to 390 nm. The $E_{\nu_o-\nu_o}$ does shift 20 nm to higher energy for the Au(I)-WT-azurin ($E_{\nu_o-\nu_o}$ = 410 nm), but this is much smaller than the predicted shift and could also be explained by less electron density donation from the ligands. The cysteine and two histidines in Au(I)-WT-azurin would be expected to be less donating than three phosphines, so that the d orbitals of Au(I)-WT-azurin will be slightly lower in energy. The $E_{\nu_o-\nu_o}$ of the Au(I) substituted Leu121 mutant (Figure 4.11) will provide a better reference point than the model complexes and is in the process of being prepared.

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Appendix 1 X-ray data for $[Au_2(dcpe)_2](PF_6)_2$.

Table 1. **Final Refined Parameters for Bis(μ-DHPE) Digold bis-Hexafluorophosphate**

x, y, z and U_{eq}[a] $\times 10^4$

Atom	x	y	z	U_{eq}
Au	652(.3)	5652	2500	439(1)
P1	1058(1)	5593(1)	717(1)	481(4)
C1	458(4)	4959(5)	−262(5)	681(20)
C10	2116(6)	5166(6)	635(8)	533(24)
C11	2128(7)	4273(5)	1132(7)	810(27)
C12	3017(9)	3932(6)	1106(9)	1030(35)
C13	3626(7)	4503(8)	1673(9)	1052(35)
C14	3624(6)	5342(8)	1209(9)	951(33)
C15	2746(5)	5736(6)	1198(8)	768(26)
C20	1107(5)	6670(5)	219(6)	597(20)
C21	300(9)	7167(7)	439(10)	894(37)
C22	407(6)	8091(6)	119(9)	1006(34)
C23	697(8)	8193(6)	−994(9)	1077(36)
C24	1465(9)	7702(8)	−1196(11)	1442(48)
C25	1372(6)	6772(6)	−934(7)	907(27)
P2	3292(3)	8292	2500	899(8)
F1	3128(8)	8509(8)	1366(5)	2497(54)
F2	3924(9)	8924	2500	3533(72)
F3	2639(8)	7639	2500	2385(44)
F4	3854(8)	7670	2050(8)	2838(63)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

Table S2. Complete Distances and Angles for Bis(μ-DHPE) Digold bis-Hexafluorophosphate

	Distance(Å)		Distance(Å)
Au –Au	2.935(1)	C23 –H23A	0.953
Au –P1	2.314(2)	C23 –H23B	0.951
P1 –C1	1.848(7)	C24 –H24A	0.943
P1 –C10	1.819(10)	C24 –H24B	0.955
P1 –C20	1.825(8)	C25 –H25A	0.948
C1 –C1	1.463(9)	C25 –H25B	0.948
C10 –C11	1.550(13)		
C10 –C15	1.522(13)		
C11 –C12	1.516(15)		
C12 –C13	1.504(16)		
C13 –C14	1.456(16)		
C14 –C15	1.532(14)		
C20 –C21	1.534(14)		
C20 –C25	1.505(11)		
C21 –C22	1.535(16)		
C22 –C23	1.470(15)		
C23 –C24	1.472(17)		
C24 –C25	1.524(16)		
P2 –F1	1.477(14)		
P2 –F2	1.424(31)		
P2 –F3	1.469(27)		
P2 –F4	1.448(16)		
C1 –H1A	0.950		
C1 –H1B	0.950		
C10 –H10	0.951		
C11 –H11A	0.949		
C11 –H11B	0.949		
C12 –H12A	0.949		
C12 –H12B	0.952		
C13 –H13A	0.951		
C13 –H13B	0.948		
C14 –H14A	0.952		
C14 –H14B	0.950		
C15 –H15A	0.950		
C15 –H15B	0.950		
C20 –H20	0.952		
C21 –H21A	0.949		
C21 –H21B	0.949		
C22 –H22A	0.947		
C22 –H22B	0.954		

Table S2. (Cont.)

			Angle(°)				Angle(°)
P1	-Au	-P1	160.6(1)	H11B	-C11	-C10	109.5
Au	-P1	-C1	120.7(2)	H11A	-C11	-C12	109.4
Au	-P1	-C10	109.1(3)	H11B	-C11	-C12	109.3
Au	-P1	-C20	107.4(2)	H11B	-C11	-H11A	109.6
C10	-P1	-C1	103.8(4)	H12A	-C12	-C11	108.6
C20	-P1	-C1	108.2(3)	H12B	-C12	-C11	108.4
C20	-P1	-C10	107.0(4)	H12A	-C12	-C13	109.4
C1	-C1	-P1	117.8(5)	H12B	-C12	-C13	109.0
C11	-C10	-P1	109.4(6)	H12B	-C12	-H12A	109.4
C15	-C10	-P1	111.2(6)	H13A	-C13	-C12	109.0
C15	-C10	-C11	110.7(8)	H13B	-C13	-C12	109.4
C12	-C11	-C10	109.3(8)	H13A	-C13	-C14	108.6
C13	-C12	-C11	112.0(9)	H13B	-C13	-C14	108.7
C14	-C13	-C12	111.5(10)	H13B	-C13	-H13A	109.6
C15	-C14	-C13	112.4(9)	H14A	-C14	-C13	108.9
C14	-C15	-C10	111.2(8)	H14B	-C14	-C13	109.0
C21	-C20	-P1	112.8(6)	H14A	-C14	-C15	108.5
C25	-C20	-P1	115.9(6)	H14B	-C14	-C15	108.7
C25	-C20	-C21	110.4(7)	H14B	-C14	-H14A	109.3
C22	-C21	-C20	110.8(9)	H15A	-C15	-C10	109.1
C23	-C22	-C21	112.6(9)	H15B	-C15	-C10	109.1
C24	-C23	-C22	111.4(10)	H15A	-C15	-C14	109.1
C25	-C24	-C23	113.4(10)	H15B	-C15	-C14	108.9
C24	-C25	-C20	109.6(8)	H15B	-C15	-H15A	109.5
H1A	-C1	-P1	107.3	H20	-C20	-P1	102.3
H1B	-C1	-P1	107.4	H20	-C20	-C21	109.3
H1B	-C1	-H1A	109.5	H20	-C20	-C25	105.3
C1	-C1	-H1A	107.4	H21A	-C21	-C20	109.0
C1	-C1	-H1B	107.4	H21B	-C21	-C20	108.9
F2	-P2	-F1	87.7	H21A	-C21	-C22	109.2
F3	-P2	-F1	92.3	H21B	-C21	-C22	109.3
F4	-P2	-F1	84.2	H21B	-C21	-H21A	109.7
F1	-P2	-F1	175.3	H22A	-C22	-C21	108.9
F3	-P2	-F2	180.0	H22B	-C22	-C21	108.3
F4	-P2	-F2	92.6	H22A	-C22	-C23	109.0
F4	-P2	-F3	87.4	H22B	-C22	-C23	108.6
H10	-C10	-P1	108.5	H22B	-C22	-H22A	109.4
H10	-C10	-C11	109.3	H23A	-C23	-C22	108.9
H10	-C10	-C15	107.7	H23B	-C23	-C22	109.2
H11A	-C11	-C10	109.7	H23A	-C23	-C24	108.8

Table S2. (Cont.)

	Angle(°)
H23B -C23 -C24	109.4
H23B -C23 -H23A	109.1
H24A -C24 -C23	109.1
H24B -C24 -C23	108.4
H24A -C24 -C25	108.5
H24B -C24 -C25	107.7
H24B -C24 -H24A	109.7
H25A -C25 -C20	109.4
H25B -C25 -C20	109.2
H25A -C25 -C24	109.3
H25B -C25 -C24	109.4
H25B -C25 -H25A	109.8

1 k 0

1	3549	3731	-49

2 k 0

0	1410	1418	-6
1	881	848	-15
2	570	529	52

3 k 0

1	669	639	44
2	2276	2324	-30
3	1583	1554	17

4 k 0

0	739	743	-5
1	2116	2177	-40
2	149	132	14
3	2808	2816	-3
4	186	100	40

5 k 0

1	1016	1048	-33
2	1682	1705	-15
3	367	367	0
4	2211	2150	30
5	939	925	11

6 k 0

0	1786	1788	0
1	761	760	1
2	1174	1224	-46
3	924	914	9
4	132	77	24
5	885	877	8
6	1363	1386	-14

7 k 0

1	2029	2122	-52
2	189	176	9
3	1218	1260	-35
4	553	588	-43
5	1015	1030	-14
6	135	107	10
7	1377	1380	-1

8 k 0

0	2203	2331	-66
1	240	221	14
2	1279	1295	-12
3	376	402	-28
4	629	627	1
5	363	352	10
6	1146	1136	8
7	527	551	-23
8	993	1013	-13

9 k 0

1	1284	1276	6
2	594	598	-4
3	-81	67	-18
4	1089	1128	-34
5	835	810	24
6	561	554	6
7	896	871	22
8	143	101	12
9	479	488	-5

10 k 0

0	877	867	9
1	369	419	-47
2	346	353	-7
3	1251	1280	-22
4	317	305	8
5	1016	1027	-9
6	619	617	2
7	114	140	-8
8	374	363	7
9	451	438	8
10	-157	39	-17

11 k 0

1	156	143	5
2	848	891	-41
3	187	189	-1
4	1410	1424	-10
5	241	235	3
6	233	233	0
7	253	225	14
8	251	259	-4
9	187	120	19
10	633	617	11
11	272	216	15

12 k 0

0	226	182	22
1	455	466	-9
2	100	35	10
3	1090	1133	-35
4	29	21	0
5	809	816	-6
6	145	104	10
7	112	86	5
8	274	289	-7
9	477	462	9
10	206	199	2
11	533	527	4
12	12	87	-4

13 k 0

1	562	543	15
2	677	706	-25
3	203	207	-1
4	759	778	-16
5	139	161	-6
6	258	267	-4
7	483	455	18
8	85	126	-7
9	347	330	8
10	440	446	-3
11	81	143	-10
12	301	296	2
13	120	28	6

14 k 0

0	743	762	-16
1	257	271	-15
2	563	568	-3
3	535	550	-11
4	-40	79	-7
5	250	249	0
6	537	534	2
7	-47	30	-2
8	494	513	-12
9	321	309	5
10	239	252	-4
11	290	281	3
12	122	16	9
13	119	64	6
14	297	207	17

15 k 0

1	677	696	-14
2	250	232	7
3	239	216	9
4	151	171	-5
5	398	380	9
6	-86	48	-7
7	579	592	-8
8	-61	168	-22
9	383	381	1
10	170	142	6
11	-43	47	-2
12	-71	73	-6
13	147	179	-5
14	-36	15	0

16 k 0

0	742	731	7
1	44	67	-2
2	424	440	-8
3	169	32	22
4	109	123	-2
5	193	147	12
6	513	499	8
7	231	137	24
8	424	445	-10
9	52	4	1
10	197	204	-1
11	149	67	11
12	143	80	8
13	92	104	-1

17 k 0

1	508	521	-7
2	195	177	4
3	41	64	-1
4	235	285	-17
5	313	307	2
6	181	221	-10
7	318	354	-14
8	145	29	13
9	273	237	11
10	146	152	-1
11	73	6	3
12	181	172	1

18 k 0

0	387	398	-5
1	210	180	7
2	183	196	-3
3	428	356	34
4	125	143	-3
5	307	329	-8
6	205	231	-6
7	107	92	1
8	110	179	-11
9	173	147	4
10	65	14	2

19 k 0

1	148	158	-1
2	375	373	0
3	-77	24	-4
4	445	429	7
5	198	109	15
6	170	215	-9
7	131	64	7
8	126	83	5

20 k 0

0	10	114	-7
1	166	192	-5
2	181	52	16
3	411	391	7
4	-183	50	-19
5	311	290	6
6	128	46	7

0 k 1

1	2409	2441	-14
3	2887	2861	9
5	1415	1484	-54
7	2579	2657	-34
9	1255	1353	-82
11	309	290	13
13	562	576	-11
15	784	804	-15
17	493	487	3
19	-17	80	-4

1 k 1

0	2484	2511	-11
1	1555	1429	88
2	1934	1841	53
3	1456	1391	49
4	630	640	-14
5	960	940	20
6	1968	2010	-24
7	565	553	13
8	1533	1602	-49
9	280	284	-3
10	699	742	-45
11	589	577	11
12	155	188	-13
13	268	288	-10
14	763	806	-35
15	76	80	0
16	583	598	-10
17	120	124	0
18	225	238	-3
19	152	194	-9
20	93	100	0

2 k 1

1	1955	1849	60
2	2927	2869	19
3	180	186	-6
4	1726	1711	9
5	659	670	-14
6	1246	1222	20
7	1431	1446	-11
8	273	280	-6
9	910	972	-62
10	1031	1031	0
11	181	205	-11
12	806	817	-10
13	364	387	-15
14	388	387	0
15	457	467	-6
16	146	32	16
17	332	316	7
18	302	312	-3
19	-130	40	-11
20	271	276	-1

3 k 1

0	3031	2905	41
1	1275	1227	41
2	271	284	-19
3	2663	2615	20
4	439	450	-16
5	2098	2072	13
6	579	568	14
7	699	683	17
8	593	594	-1
9	804	819	-15
10	373	331	33

11	1161	1181	-16
12	167	169	0
13	820	845	-21
14	247	215	13
15	187	168	6
16	215	172	13
17	291	282	3
18	97	65	3
19	440	402	17
20	188	73	16

4 k 1

1	609	601	11
2	1824	1783	25
3	442	452	-14
4	2754	2662	37
5	487	440	58
6	1124	1141	-15
7	242	242	0
8	363	396	-34
9	422	427	-4
10	1119	1128	-7
11	316	310	4
12	1073	1090	-14
13	22	85	-6
14	499	511	-8
15	32	64	-2
16	226	192	11
17	93	94	0
18	396	411	-7
19	218	75	24
20	322	320	0

5 k 1

0	1407	1440	-26
1	983	969	15
2	603	593	13
3	2158	2092	34
4	439	438	1
5	1876	1902	-15
6	739	689	54
7	-7	83	-12
8	848	869	-21
9	650	681	-31
10	515	526	-9
11	928	941	-11
12	104	68	6
13	633	676	-35
14	274	268	2
15	69	65	0
16	323	298	10
17	309	297	4
18	260	194	18
19	312	344	-10
20	82	13	3

6 k 1

1	1878	1904	-15
2	1336	1326	7
3	563	503	72
4	1206	1207	0
5	718	691	30
6	370	374	-4
7	1273	1209	49
8	148	148	0
9	1223	1251	-22
10	660	687	-25
11	153	170	-5
12	448	458	-7
13	321	318	1
14	193	181	3
15	528	507	13
16	158	144	2
17	376	373	1
18	309	247	21
19	73	64	0
20	186	191	0

7 k 1

0	2606	2670	-28
1	617	614	3
2	1356	1359	-2
3	809	819	-11
4	293	272	19
5	224	195	19
6	1324	1265	44
7	191	201	-5
8	1455	1453	1
9	316	305	7
10	631	664	-30
11	307	289	10
12	150	152	0
13	117	67	8
14	580	553	18
15	99	107	-1
16	520	505	9
17	152	118	6
18	214	228	-3
19	239	113	25

8 k 1

1	1720	1754	-21
2	193	237	-32
3	532	529	2
4	381	398	-17
5	898	913	-14
6	99	120	-6
7	1505	1487	11
8	253	187	32
9	813	784	25
10	-70	113	-19
11	-93	70	-14
12	112	142	-7
13	400	389	6
14	147	173	-6
15	553	554	0
16	144	71	10
17	328	349	-8
18	127	21	9
19	-81	59	-5

9 k 1

0	1382	1463	-63
1	322	313	8
2	966	996	-28
3	852	845	6
4	450	466	-16
5	714	721	-7
6	1268	1302	-26
7	303	291	7
8	761	746	13
9	171	151	6
10	381	359	14
11	484	473	7
12	213	164	16
13	361	352	4
14	461	465	-2
15	184	141	9
16	403	354	22
17	-30	67	-3
18	74	139	-7

10 k 1

1	764	798	-35
2	1077	1080	-3
3	291	290	0
4	1121	1132	-9
5	588	595	-6
6	572	603	-28
7	687	711	-22
8	107	97	2
9	375	350	15
10	721	727	-4
11	142	74	13
12	567	556	7
13	290	271	7
14	231	273	-14
15	200	256	-16
16	128	65	7
17	-61	140	-13
18	228	218	2

11 k 1

0	355	320	27
1	630	625	5
2	283	254	17
3	1252	1272	-15
4	320	321	-1
5	958	969	-8
6	263	247	8
7	261	262	0
8	-32	90	-9
9	481	491	-7
10	93	68	3
11	662	657	3
12	167	152	3
13	435	419	8
14	53	129	-9
15	108	125	-2
16	172	41	16
17	196	181	3

12 k 1

1	220	256	-19
2	900	922	-19
3	167	171	-1
4	1188	1211	-18
5	127	63	12
6	472	465	5
7	163	150	3
8	163	139	6
9	119	167	-11
10	585	584	0
11	179	158	5
12	516	510	3
13	-72	26	-4
14	217	221	-1
15	77	104	-3
16	109	119	-1
17	-35	93	-5

13 k 1

0	648	678	-26
1	268	311	-23
2	395	438	-30
3	885	908	-19
4	102	93	1
5	708	699	6
6	351	343	4
7	126	25	14
8	443	440	2
9	366	372	-3
10	272	285	-5
11	457	425	17
12	-148	27	-15
13	154	242	-21
14	217	161	13
15	-185	56	-21
16	133	170	-6

14 k 1

1	824	848	-19
2	415	410	3
3	198	214	-5
4	512	527	-10
5	272	271	0
6	57	141	-14
7	596	581	10
8	208	188	6
9	458	485	-15
10	276	273	1
11	131	131	0
12	202	212	-2
13	175	156	3
14	-138	22	-11
15	306	273	9

15 k 1

0	866	872	-4
1	158	76	16
2	497	493	2
3	187	192	-1
4	-92	66	-11
5	-72	49	-6
6	539	541	-1
7	128	128	0
8	612	575	23
9	168	137	6
10	199	262	-18
11	142	110	5
12	183	102	14
13	60	63	0
14	350	270	25

16 k 1

1	644	647	-2
2	184	41	26
3	158	166	-2
4	178	208	-8
5	339	332	3
6	215	178	10
7	516	523	-3
8	112	88	3
9	357	347	4
10	126	79	6
11	-105	27	-7
12	153	141	2
13	228	163	13

17 k 1

0	518	512	3
1	165	148	3
2	315	318	-1
3	318	296	9
4	198	111	19
5	289	325	-14
6	436	392	21
7	144	138	1
8	324	324	0
9	116	83	4
10	109	110	0
11	288	197	24
12	163	90	9

18 k 1

1	189	246	-16
2	339	329	4
3	105	58	5
4	443	424	8
5	211	215	-1
6	255	244	3
7	249	212	10
8	-115	25	-8
9	86	110	-2
10	255	221	8

19 k 1

0	149	81	10
1	186	209	-5
2	-31	44	-1
3	456	415	18
4	121	87	4
5	364	341	8
6	-99	65	-8
7	157	96	9
8	-67	55	-4

20 k 1

1	117	112	0
2	299	292	2
3	161	75	11
4	339	321	5
5	129	12	9
6	-127	178	-24

0 k 2

0	1672	1567	69
2	1835	1758	47
4	527	537	-16
6	1851	1818	20
8	1608	1656	-32
10	1093	1089	3
12	415	405	7
14	758	774	-12
16	623	618	3
18	234	142	24
20	206	151	11

1 k 2

1	1699	1586	73
2	855	798	68
3	595	604	-14
4	912	923	-12
5	929	922	8
6	432	398	43
7	1560	1630	-49
8	323	285	33
9	1423	1450	-19
10	412	440	-26
11	191	210	-9
12	502	508	-5
13	521	561	-32
14	138	228	-28
15	711	695	11
16	170	139	7
17	349	358	-4
18	192	153	9
19	-24	96	-6
20	198	85	18

2 k 2

0	2287	2190	47
1	909	862	54
2	2027	1935	62
3	1581	1530	36
4	703	693	13
5	1845	1850	-2
6	1010	1059	-50
7	461	428	38
8	1003	1055	-50
9	467	464	2
10	611	635	-24
11	802	866	-62
12	151	171	-7
13	689	687	1
14	563	554	6
15	-93	30	-8
16	438	439	0
17	315	298	6
18	-84	85	-9
19	235	240	-1
20	127	120	1

3 k 2

1	465	470	-8
2	1595	1549	31
3	461	428	48
4	2121	2088	17
5	519	508	14
6	1338	1333	3
7	517	536	-23
8	69	35	6
9	413	457	-44
10	973	991	-16
11	171	52	32
12	960	996	-30
13	219	231	-5
14	366	374	-4
15	283	313	-14
16	234	240	-2
17	192	145	11
18	413	412	0
19	95	56	3
20	265	260	1

4 k 2

0	540	538	3
1	938	927	11
2	677	657	27
3	2141	2091	26
4	447	440	8
5	1842	1753	52
6	150	111	19
7	665	669	-4
8	142	115	11
9	677	673	4
10	178	150	11
11	1230	1241	-8
12	188	143	14
13	660	665	-4
14	105	7	10
15	85	107	-3
16	-70	37	-5
17	394	381	6
18	-175	28	-20
19	370	401	-12
20	78	37	2

5 k 2

1	880	862	19
2	1881	1867	8
3	534	525	11
4	1946	1848	55
5	174	147	16
6	1204	1171	27
7	713	704	9
8	-47	90	-16
9	253	252	0
10	1226	1235	-6
11	237	228	4
12	912	910	1
13	190	142	14
14	385	396	-5
15	289	320	-14
16	164	176	-3
17	136	160	-4
18	422	402	8
19	-84	29	-4
20	283	253	8

6 k 2

0	2011	1916	51
1	534	516	23
2	1022	1036	-13
3	1480	1471	6
4	208	122	53
5	1213	1203	8
6	1192	1197	-4
7	372	365	6
8	938	916	20
9	643	635	7
10	549	549	0
11	929	928	0
12	-106	71	-15
13	517	522	-3
14	519	517	1
15	-75	95	-11
16	382	410	-13
17	257	259	0
18	-110	159	-23
19	261	247	3

7 k 2

1	1647	1656	-6
2	516	507	10
3	483	507	-29
4	748	745	3
5	807	799	8
6	369	362	6
7	1503	1483	13
8	152	193	-17
9	1167	1150	13
10	385	387	-1
11	358	357	1
12	352	348	2
13	392	408	-8
14	-53	112	-12
15	636	607	18
16	155	159	0
17	394	373	9
18	-75	163	-18
19	198	83	18

8 k 2

0	1810	1807	1
1	320	273	40
2	1071	1116	-41
3	-26	86	-14
4	136	118	7
5	125	79	14
6	984	978	5
7	172	178	-2
8	1527	1531	-2
9	131	85	10
10	829	825	3
11	135	95	9
12	246	222	9
13	152	113	8
14	637	639	-1
15	51	121	-8
16	526	499	14
17	94	53	3
18	213	196	4
19	-132	22	-10

9 k 2

1	1495	1517	-15
2	476	485	-9
3	479	494	-15
4	703	696	6
5	343	332	8
6	576	589	-11
7	1207	1209	-1
8	142	93	12
9	1141	1154	-9
10	335	304	16
11	176	136	11
12	435	408	16
13	422	435	-7
14	280	248	11
15	540	497	24
16	82	28	3
17	311	286	8
18	201	119	14

10 k 2

0	1201	1191	8
1	407	433	-24
2	648	680	-32
3	987	1005	-16
4	179	190	-4
5	1247	1250	-2
6	601	602	0
7	370	368	2
8	816	820	-3
9	304	313	-4
10	414	397	10
11	632	594	27
12	158	166	-2
13	558	530	16
14	363	382	-8
15	99	132	-5
16	288	264	7
17	166	179	-2
18	111	68	4

11 k 2

1	291	286	3
2	860	905	-42
3	-40	55	-5
4	1331	1325	3
5	229	242	-6
6	908	901	5
7	357	368	-6
8	46	57	-1
9	149	151	0
10	644	622	15
11	76	69	0
12	765	730	23
13	181	171	2
14	288	293	-1
15	182	154	6
16	144	131	2
17	-108	39	-7

12 k 2

0	405	411	-4
1	556	563	-5
2	146	169	-8
3	1059	1082	-19
4	131	159	-7
5	940	939	1
6	-73	96	-13
7	350	341	5
8	226	244	-7
9	450	430	12
10	196	168	8
11	776	732	30
12	96	58	4
13	531	487	23
14	80	18	4
15	62	84	-2
16	-94	105	-11
17	292	221	18

13 k 2

1	561	606	-38
2	721	746	-20
3	205	222	-6
4	739	727	9
5	201	149	16
6	479	491	-8
7	466	437	18

8	133	124	1
9	453	452	0
10	569	544	15
11	240	181	17
12	528	492	19
13	57	117	-6
14	102	151	-7
15	266	243	6
16	14	139	-10

14 k 2

0	835	828	6
1	226	233	-2
2	518	545	-19
3	375	408	-20
4	164	11	25
5	387	386	0
6	556	548	5
7	92	109	-2
8	688	660	18
9	288	260	10
10	401	386	7
11	266	281	-5
12	-76	16	-4
13	176	137	7
14	292	290	0
15	116	81	3

15 k 2

1	743	743	0
2	74	29	4
3	288	305	-8
4	-55	87	-9
5	342	339	1
6	-46	103	-9
7	657	628	19
8	159	140	4
9	548	501	26
10	167	105	11
11	173	153	4
12	76	70	0
13	153	227	-15
14	133	91	5

16 k 2

0	655	657	-1
1	166	144	5
2	390	439	-27
3	223	232	-2
4	-90	60	-9
5	249	203	15
6	429	442	-6
7	211	179	8
8	545	495	27
9	140	26	12
10	276	247	8
11	76	137	-7
12	127	111	2
13	220	154	13

17 k 2

1	371	375	-1
2	344	306	16
3	117	134	-3
4	387	404	-8
5	237	199	11
6	222	265	-13
7	420	371	23
8	110	53	5
9	288	263	8
10	208	193	3
11	-85	41	-4
12	258	230	7

18 k 2

0	172	139	7
1	203	174	7
2	-70	81	-7
3	445	429	8
4	-89	51	-6
5	413	414	0
6	150	159	-1
7	188	160	5
8	86	174	-13
9	256	134	26
10	128	59	7

19 k 2

1	219	81	27
2	257	249	2
3	82	60	1
4	449	406	19
5	147	49	11
6	277	240	10
7	-116	72	-10
8	-71	36	-3

20 k 2

0	146	154	-1
1	109	93	1
2	202	116	15
3	252	264	-3
4	34	49	0
5	240	241	0

0 k 3

1	1117	1118	0
3	1021	1001	19
5	776	819	-52
7	1265	1310	-37
9	1384	1456	-54
11	356	342	10
13	695	681	11
15	801	827	-20
17	336	339	-1
19	-151	92	-19

1 k 3

0	1566	1555	7
1	1453	1431	17
2	2074	2017	31
3	560	561	-1
4	160	147	10
5	318	299	22
6	972	1010	-38
7	178	169	5
8	1494	1527	-23
9	434	444	-9
10	816	845	-28
11	644	617	25
12	322	327	-3
13	236	276	-18
14	690	702	-9
15	89	47	4
16	597	582	10
17	128	134	-1
18	-135	117	-21
19	187	136	10
20	180	136	7

2 k 3

1	2108	2046	33
2	1185	1124	54
3	1190	1173	15
4	1278	1246	26
5	625	616	11
6	855	883	-30
7	1108	1122	-13
8	274	186	60
9	1029	1031	-1
10	909	884	22
11	136	121	4
12	807	824	-14
13	500	517	-12
14	257	259	0
15	529	533	-3
16	171	187	-4
17	303	277	9
18	345	307	15
19	66	77	0
20	246	166	18

3 k 3

0	1020	1000	20
1	508	493	22
2	1164	1128	33
3	1573	1529	30
4	232	206	23
5	1593	1602	-6
6	516	487	34
7	896	869	27
8	861	864	-2
9	722	736	-14
10	590	408	-14
11	1093	1090	2
12	299	293	2
13	661	673	-9
14	288	271	8
15	142	92	9
16	247	271	-8
17	436	405	15
18	125	53	8
19	375	335	15
20	-120	71	-10

4 k 3

1	214	190	23
2	1318	1250	54
3	215	197	15
4	1935	1975	-23
5	266	236	25
6	1247	1249	-2
7	203	157	26
8	198	244	-29
9	209	268	-36
10	833	836	-3
11	104	62	7
12	1100	1101	0
13	61	25	2
14	403	408	-3
15	124	43	11
16	226	273	-16
17	56	42	0
18	385	407	-9
19	63	9	2
20	317	271	13

5 k 3

0	967	955	11
1	391	362	36
2	614	616	-2
3	1545	1556	-7
4	250	230	16
5	1605	1631	-17
6	353	302	45
7	546	526	20
8	636	653	-17
9	558	571	-12
10	400	387	10
11	1098	1100	-1
12	180	127	14
13	734	742	-6
14	278	261	7
15	-68	91	-10
16	253	212	13
17	366	356	4
18	177	101	13
19	363	311	18
20	173	52	14

6 k 3

1	1095	1105	-9
2	836	830	7
3	532	506	30
4	1325	1323	1
5	230	225	3
6	808	785	22
7	1064	1033	28
8	142	78	18
9	919	923	-3
10	869	894	-22
11	192	205	-5
12	911	904	5
13	388	367	11
14	264	265	0
15	453	439	8
16	111	201	-19
17	268	290	-7
18	315	284	10
19	-23	61	-2

7 k 3

0	1361	1382	-15
1	128	137	-4
2	1077	1077	0
3	848	844	4
4	167	145	11
5	569	549	22
6	1056	1017	33
7	369	390	-17
8	1447	1449	-1
9	321	342	-13
10	697	708	-9
11	622	597	20
12	192	158	10
13	206	173	10
14	672	614	40
15	108	43	7
16	546	539	3
17	160	165	-1
18	89	180	-13
19	137	118	2

8 k 3

1	1493	1518	-18
2	317	232	65
3	904	896	7
4	261	279	-14
5	585	602	-17
6	-49	99	-16
7	1440	1453	-8
8	243	253	-5
9	1141	1123	14
10	190	181	3
11	367	377	-6
12	179	146	9
13	549	524	16
14	191	107	18
15	731	695	23
16	-44	62	-3
17	392	336	23
18	-191	41	-21
19	-134	26	-9

9 k 3

0	1428	1471	-31
1	455	432	21
2	1049	1032	14
3	707	720	-13
4	210	240	-18
5	596	602	-5
6	860	895	-32
7	296	310	-8
8	1117	1113	3
9	168	158	3
10	630	603	20
11	434	412	13
12	167	178	-3
13	400	392	4
14	617	617	0
15	138	112	4
16	457	438	9
17	56	55	0
18	220	78	23

10 k 3

1	805	834	-28
2	890	849	37
3	444	430	12
4	810	819	-8
5	342	349	-5
6	867	887	-17
7	698	708	-8
8	138	162	-7
9	604	596	5
10	503	484	12
11	-133	45	-16
12	713	684	19
13	358	385	-12
14	319	325	-2
15	403	391	5
16	90	38	4
17	131	143	-1
18	254	212	9

11 k 3

0	373	361	8
1	628	596	28
2	124	149	-7
3	1043	1056	-11
4	93	41	7
5	1104	1103	0
6	217	186	12
7	587	594	-5
8	369	383	-8
9	445	406	24
10	53	53	0
11	808	794	10
12	202	205	0
13	610	589	12
14	255	223	9
15	-51	94	-7
16	145	93	7
17	200	230	-6

12 k 3

1	335	325	6
2	782	792	-9
3	251	284	-16
4	1091	1084	5
5	182	120	17
6	869	892	-18
7	205	162	14
8	173	152	6
9	178	194	-4
10	658	684	-18
11	174	209	-9
12	768	705	40
13	-27	61	-2
14	363	290	28
15	125	71	6
16	-93	135	-15

13 k 3

0	645	638	5
1	265	259	2
2	476	499	-16
3	620	643	-18
4	61	30	2
5	731	734	-2
6	403	384	10
7	228	168	19
8	531	527	2
9	358	400	-21
10	376	382	-3
11	598	581	10
12	108	54	5
13	407	400	2
14	137	186	-8
15	74	35	2
16	186	234	-9

14 k 3

1	638	662	-18
2	214	247	-12
3	200	252	-19
4	423	390	20
5	250	258	-3
6	276	266	4
7	585	604	-12
8	-73	98	-10
9	627	600	17
10	275	315	-14
11	231	218	3
12	309	292	6
13	196	177	3
14	-141	22	-11
15	338	280	17

15 k 3

0	808	815	-5
1	187	51	26
2	516	530	-8
3	84	57	3
4	158	29	20
5	24	90	-6
6	471	438	19
7	-88	26	-6
8	700	681	11
9	179	117	12
10	365	391	-10
11	-70	97	-9
12	90	62	2
13	-64	39	-3
14	283	275	2

16 k 3

1	587	572	10
2	193	176	4
3	310	265	18
4	262	274	-4
5	229	208	6
6	194	187	1
7	507	539	-17
8	182	65	18
9	461	433	12
10	137	33	10
11	52	87	-2
12	120	122	0
13	188	238	-11

17 k 3

0	301	318	-6
1	191	128	14
2	214	268	-17
3	395	404	-4
4	61	18	2
5	353	354	0
6	299	280	7
7	87	154	-10
8	391	338	21
9	-191	54	-22
10	149	149	0
11	290	225	17

18 k 3

1	168	97	13
2	301	297	1
3	87	56	2
4	436	411	12
5	-59	74	-5
6	271	280	-3
7	190	176	2
8	119	37	7
9	112	90	2
10	270	216	13

19 k 3

0	89	70	1
1	132	126	0
2	-85	67	-7
3	296	326	-9
4	-57	21	-2
5	332	306	8
6	-175	49	-18
7	144	124	2
8	-24	16	0

20 k 3

1	122	128	0
2	89	160	-9
3	66	68	0
4	251	262	-2
5	169	46	14

0 k 4

0	1770	1743	17
2	1977	1921	31
4	267	256	11
6	1206	1218	-10
8	1679	1709	-19
10	947	973	-23
12	368	346	14
14	635	667	-24
16	630	610	12
18	225	233	-2
20	-148	100	-17

1 k 4

1	2714	2651	26
2	479	454	34
3	800	794	6
4	875	896	-23
5	826	810	16
6	709	697	13
7	1592	1623	-21
8	356	332	21
9	1357	1364	-5
10	270	307	-24
11	373	400	-21
12	517	490	21
13	590	598	-6
14	189	191	0
15	682	661	15
16	51	57	0
17	403	396	3
18	173	159	2
19	134	39	9
20	157	139	2

2 k 4

0	1941	1856	48
1	464	447	23
2	1496	1443	38
3	1554	1540	9
4	337	347	-11
5	1423	1413	7
6	1075	1088	-11
7	536	554	-20
8	1284	1306	-17
9	607	625	-18
10	592	601	-8
11	826	856	-26
12	219	242	-10
13	637	672	-27
14	601	581	14
15	24	83	-5
16	435	435	0
17	307	263	16
18	61	114	-5
19	283	274	2
20	123	89	3

3 k 4

1	729	703	32
2	1604	1589	10
3	344	331	15
4	1694	1664	19
5	271	275	-3
6	1310	1295	12
7	496	486	11
8	362	394	-29
9	359	400	-34
10	978	1002	-21
11	158	182	-8
12	1143	1165	-16
13	241	248	-2
14	367	407	-23
15	313	341	-13
16	165	170	-1
17	80	83	0
18	367	374	-2
19	127	38	8
20	316	275	12

4 k 4

0	319	286	37
1	867	887	-22
2	341	361	-25
3	1603	1591	8
4	503	487	19
5	1719	1686	20
6	129	128	0
7	736	767	-32
8	222	222	0
9	786	778	6
10	168	175	-2
11	1209	1202	5
12	36	50	-1
13	719	735	-12
14	142	73	13
15	162	123	9
16	228	102	31
17	361	303	23
18	-17	83	-4
19	358	349	3

5 k 4

1	893	877	16
2	1321	1330	-7

3	266	280	-13
4	1615	1586	19
5	341	279	54
6	1147	1114	28
7	754	756	-2
8	184	176	3
9	644	638	5
10	971	983	-10
11	259	253	-6
12	885	880	3
13	213	183	10
14	341	308	15
15	343	322	9
16	187	188	0
17	242	239	0
18	334	356	-8
19	35	67	-1

6 k 4

0	1240	1221	15
1	620	610	11
2	1099	1094	4
3	1210	1207	2
4	77	117	-13
5	1123	1083	33
6	979	1033	-51
7	308	290	13
8	961	932	25
9	644	628	14
10	644	648	-3
11	731	723	6
12	17	120	-12
13	439	431	4
14	514	501	8
15	129	74	8
16	435	430	2
17	297	277	6
18	212	156	11
19	219	213	1

7 k 4

1	1549	1548	1
2	504	502	2
3	473	506	-37
4	704	718	-15
5	667	696	-30
6	258	257	0
7	1207	1189	14
8	308	302	4
9	1018	998	16
10	218	208	4
11	245	214	12
12	271	243	12
13	475	473	1
14	132	92	6
15	598	589	5
16	165	163	0
17	360	342	6
18	48	108	-5
19	-193	16	-19

8 k 4

0	1641	1627	8
1	365	339	22
2	1248	1244	2
3	406	421	-14
4	161	188	-13
5	262	230	20
6	888	867	18
7	298	309	-7
8	1291	1284	5
9	75	64	1
10	620	654	-27
11	239	216	9
12	260	219	16
13	-55	177	-25
14	556	567	-7
15	110	110	0
16	490	469	10
17	178	14	18
18	136	141	0

9 k 4

1	1242	1228	11
2	640	636	4
3	357	386	-24
4	756	745	10
5	565	557	6
6	639	644	-5
7	976	972	3
8	31	75	-4
9	791	775	12
10	343	326	9
11	91	93	0
12	393	379	7
13	424	430	-3
14	207	251	-12
15	476	454	11
16	69	29	2
17	200	242	-10
18	133	141	-1

10 k 4

0	830	852	-20
1	235	279	-27
2	529	527	1
3	976	959	14
4	187	151	14
5	983	971	10
6	596	596	0
7	251	257	-3
8	632	641	-6
9	326	310	8
10	93	111	-3
11	609	581	18
12	201	214	-4
13	535	500	20
14	353	337	6
15	116	133	-2
16	301	236	19
17	191	151	7

11 k 4

1	334	361	-19
2	751	778	-25
3	189	190	0
4	1148	1139	8
5	251	228	10
6	751	741	8
7	215	221	-2
8	228	221	2
9	187	76	25
10	566	577	-7
11	140	39	13
12	696	663	20
13	115	185	-13
14	338	301	14
15	161	152	1
16	176	89	13
17	-72	52	-4

12 k 4

0	369	334	22
1	450	430	14
2	210	255	-19
3	1053	1078	-19
4	-63	48	-5
5	851	854	-2
6	174	123	13
7	274	245	12
8	243	209	12
9	406	358	27
10	266	215	17
11	694	652	27
12	208	112	20
13	446	427	9
14	-28	26	0
15	80	31	3
16	-29	104	-6

13 k 4

1	572	560	9
2	601	615	-10
3	213	248	-14
4	668	671	-2
5	183	184	0
6	458	451	4
7	428	444	-9
8	168	152	4
9	426	405	11
10	504	482	12
11	179	182	0
12	458	430	13
13	-68	53	-4
14	152	120	4
15	-95	184	-22

14 k 4

0	569	587	-13
1	133	181	-13
2	557	560	-2
3	363	355	4
4	95	69	3
5	301	322	-9
6	472	465	3
7	125	98	4
8	528	525	1
9	275	245	10
10	329	323	2
11	224	310	-27
12	-53	14	-1
13	169	131	6
14	284	232	14

15 k 4

1	642	622	13
2	179	61	23
3	328	351	-11
4	110	123	-2
5	292	290	0
6	162	65	16
7	592	561	18
8	148	90	9
9	419	450	-14
10	182	146	7
11	162	153	1
12	141	51	10
13	153	187	-6

16 k 4

0	550	566	-9
1	143	38	14
2	442	426	8
3	171	164	1
4	94	87	0
5	152	157	-1
6	398	399	0
7	179	135	9
8	417	475	-27
9	-29	38	-1
10	282	254	8
11	128	65	7
12	79	105	-2

17 k 4

1	374	378	-1
2	234	241	-2
3	-72	96	-10
4	280	286	-2
5	245	202	12
6	313	256	19
7	350	343	2
8	83	26	3
9	325	269	18
10	130	137	-1
11	-173	52	-17

18 k 4

0	286	232	18
1	71	139	-9
2	82	117	-4
3	377	354	9
4	170	65	15
5	329	338	-3
6	-172	143	-28
7	-93	113	-12
8	165	172	-1
9	142	125	2

19 k 4

1	155	38	13
2	246	253	-1
3	145	28	11
4	339	339	0
5	78	48	2
6	232	218	3
7	-90	39	-5

20 k 4

0	-86	88	-8
1	147	126	3
2	56	82	-1
3	249	269	-5

0 k 5

1	2647	2600	20
3	745	749	-4
5	1106	1142	-32
7	1780	1796	-9
9	1011	1062	-46
11	431	423	5
13	464	462	1
15	712	726	-10
17	459	445	6
19	24	94	-4

1 k 5

0	2583	2558	10
1	1015	965	49
2	1482	1455	19
3	1182	1166	14
4	285	284	0
5	1005	981	22
6	1647	1648	0
7	432	422	9
8	1585	1615	-20
9	260	252	5
10	675	700	-23
11	469	479	-7
12	174	153	7
13	243	252	-4
14	604	595	6
15	145	114	6
16	541	548	-4
17	75	105	-3

18	278	256	7
19	134	199	-12

2 k 5

1	1376	1394	-13
2	1736	1713	14
3	89	5	16
4	1813	1793	11
5	804	815	-11
6	952	961	-8
7	1348	1380	-24
8	160	175	-6
9	841	844	-2
10	861	842	16
11	248	256	-3
12	757	751	5
13	424	419	2
14	340	352	-6
15	454	449	3
16	-85	50	-7
17	252	265	-4
18	333	298	13
19	106	34	5

3 k 5

0	604	628	-30
1	1208	1158	42
2	160	138	12
3	2260	2225	17
4	174	159	8
5	1635	1658	-15
6	431	437	-5
7	548	568	-20
8	601	595	5
9	838	851	-11
10	81	139	-14
11	1067	1089	-16
12	207	170	12
13	781	766	11
14	207	211	-1
15	204	209	-1
16	156	113	8
17	280	245	11
18	42	36	0
19	332	360	-9

4 k 5

1	312	291	21
2	1793	1759	21
3	156	150	3
4	2026	2027	0
5	82	84	0
6	1089	1087	2
7	269	266	2
8	527	553	-25
9	257	278	-12
10	855	865	-9
11	113	99	3
12	1049	1049	0
13	73	42	3
14	466	437	18
15	127	90	6
16	50	119	-8
17	-102	131	-17
18	350	334	5
19	61	81	-1

5 k 5

0	1168	1173	-4
1	955	935	19
2	825	825	0
3	1600	1608	-5
4	110	92	5
5	1344	1370	-19
6	617	591	26
7	218	210	4
8	897	901	-3
9	616	607	7
10	625	610	12
11	729	743	-11
12	-105	119	-22
13	554	554	0
14	241	230	3
15	110	12	9
16	367	329	15
17	261	267	-2
18	102	179	-11
19	315	290	7

6 k 5

1	1630	1622	5
2	938	945	-7
3	471	469	1
4	996	995	0
5	587	571	15
6	579	590	-10
7	1085	1091	-5
8	373	353	14
9	1078	1078	0
10	455	462	-4
11	276	262	7
12	412	418	-3
13	322	326	-1
14	19	61	-2
15	457	432	13
16	197	164	7
17	382	343	15
18	204	221	-3
19	88	70	1

7 k 5

0	1705	1706	0
1	402	390	11
2	1383	1387	-2
3	474	482	-8
4	282	269	9
5	143	156	-5
6	1054	1031	19
7	-65	57	-8
8	1208	1194	10
9	331	301	17
10	534	503	22
11	128	127	0
12	173	184	-3
13	172	94	17
14	453	444	4
15	87	97	-1
16	492	459	16
17	161	87	10
18	161	167	-1

8 k 5

1	1524	1542	-12
2	220	172	25
3	609	604	5
4	536	549	-12
5	891	886	4
6	345	356	-8
7	1185	1173	9
8	152	125	7
9	672	642	23
10	148	93	12
11	114	159	-10
12	238	221	6
13	334	332	0
14	112	145	-6
15	473	454	9
16	-87	48	-6
17	297	276	6
18	138	48	9

9 k 5

0	930	963	-30
1	269	262	4
2	800	779	19
3	808	824	-14
4	287	286	0
5	605	608	-2
6	1057	1065	-6
7	317	313	2
8	678	647	24
9	152	153	0
10	241	214	10
11	408	405	1
12	191	153	9
13	284	289	-2
14	387	350	16
15	149	115	5
16	273	287	-4
17	112	90	2

10 k 5

1	619	615	3
2	861	822	34
3	109	86	5
4	865	874	-7
5	582	598	-13
6	506	519	-10
7	456	465	-6
8	-57	113	-14
9	211	226	-5
10	492	483	6
11	104	11	8
12	488	476	7
13	248	221	8
14	262	235	8
15	143	195	-10
16	-110	8	-7
17	160	64	11

11 k 5

0	433	418	10
1	464	479	-11
2	194	228	-14
3	1029	1052	-19
4	161	92	17
5	726	704	17
6	215	222	-2
7	184	147	11
8	156	160	-6
9	427	406	12
10	67	3	3
11	599	572	17
12	140	119	3
13	360	342	7
14	50	65	-1
15	-70	79	-6
16	-83	39	-4

12 k 5

1	156	155	0
2	707	717	-7
3	209	166	14
4	977	971	4
5	109	115	-1
6	451	436	9
7	166	162	1
8	199	217	-6
9	141	139	0
10	494	454	22
11	126	117	1
12	393	367	12
13	106	8	7
14	195	131	11
15	157	79	10
16	96	104	0

13 k 5

0	455	462	-4
1	259	238	9
2	394	403	-5
3	726	734	-6
4	99	38	7
5	538	562	-16
6	304	290	6
7	110	136	-5
8	310	314	-1
9	260	265	-1
10	205	212	-2
11	368	344	10
12	104	10	7
13	166	178	-2
14	196	148	9
15	75	45	1

14 k 5

1	580	588	-5
2	323	332	-4
3	238	223	5
4	404	431	-16
5	216	218	0
6	100	104	0
7	426	405	11
8	181	133	11
9	338	350	-4
10	256	249	2
11	55	71	-1
12	220	153	14
13	216	160	12
14	117	5	7

15 k 5

0	659	696	-25
1	33	115	-9
2	423	435	-6
3	222	215	2
4	146	90	10
5	-119	24	-11
6	420	393	13
7	-130	82	-16
8	476	463	6
9	19	114	-8
10	196	209	-3
11	25	92	-4
12	-111	90	-11
13	-145	31	-11

16 k 5

1	529	521	4
2	112	76	5
3	80	131	-7
4	-72	84	-9
5	352	314	16
6	-53	142	-15
7	466	455	5
8	133	32	10
9	313	302	3
10	-48	28	-1
11	73	62	0
12	-120	91	-12

17 k 5

0	436	432	2
1	138	101	6
2	272	273	0
3	176	235	-15

4	-58	126	-12
5	285	243	13
6	360	339	8
7	128	99	3
8	337	291	15
9	-202	80	-26
10	30	90	-3

18 k 5

1	317	262	20
2	301	288	4
3	96	50	4
4	355	320	12
5	193	177	3
6	243	223	4
7	204	188	3
8	-92	50	-6

19 k 5

0	96	115	-2
1	146	192	-8
2	-86	50	-5
3	389	354	12
4	195	74	18
5	342	293	15
6	159	80	10

0 k 6

0	3102	3106	-1
2	1490	1501	-7
4	516	554	-44
6	1412	1451	-28
8	1590	1614	-15
10	646	642	2
12	193	252	-23
14	614	597	11
16	568	578	-5
18	339	280	20

1 k 6

1	2202	2233	-15
2	708	679	32
3	370	376	-6
4	1074	1080	-5
5	956	984	-27
6	565	564	0
7	1500	1524	-16
8	146	99	14
9	1017	1021	-4
10	329	336	-4
11	163	196	-11
12	451	417	22
13	382	382	0
14	243	240	1
15	588	598	-6
16	170	87	15
17	409	396	6
18	-31	158	-15
19	-35	76	-3

2 k 6

0	1303	1314	-8
1	664	668	-4
2	991	1005	-13
3	1614	1608	3
4	280	328	-41
5	1340	1348	-6
6	1148	1144	3
7	255	237	10
8	852	851	0
9	470	462	6
10	289	316	-15
11	710	701	7
12	74	86	-1
13	597	603	-4
14	376	383	-3
15	128	164	-7
16	325	339	-5
17	162	203	-9
18	102	160	-8
19	311	276	10

3 k 6

1	466	443	25
2	1625	1644	-12
3	161	90	29
4	2029	2016	7
5	521	533	-12
6	1114	1114	0
7	543	546	-2
8	382	376	5
9	184	108	25
10	900	871	23
11	33	51	-1
12	840	835	3
13	173	139	8
14	446	448	0
15	196	181	4
16	-79	87	-9
17	139	73	9
18	353	323	10
19	-56	27	-2

4 k 6

0	474	509	-40
1	1069	1084	-13
2	310	335	-22
3	2058	2042	8
4	54	39	2
5	1504	1483	14
6	-122	15	-21
7	315	307	5
8	363	335	20
9	763	745	16
10	188	162	9
11	1061	1033	21
12	116	102	2
13	589	575	9
14	-141	36	-16
15	164	147	3
16	189	124	13
17	268	240	8
18	-70	72	-5
19	362	359	0

5 k 6

1	958	963	-4
2	1381	1381	0
3	534	539	-5
4	1459	1453	3
5	618	623	-4
6	684	684	0
7	803	793	9
8	321	328	-5
9	513	508	3
10	806	782	19
11	240	231	3
12	557	554	1
13	107	102	0
14	269	239	11
15	357	301	24
16	168	116	9
17	266	235	9
18	328	292	11

6 k 6

0	1363	1399	-27
1	559	548	11
2	1174	1164	8
3	1138	1147	-7
4	110	29	16
5	696	685	10
6	1168	1157	8
7	127	112	4
8	909	891	14
9	352	325	16
10	475	478	-2
11	359	363	-2
12	-118	23	-12
13	192	215	-7
14	376	359	8
15	74	121	-6
16	420	409	5
17	263	188	19
18	188	196	-1

7 k 6

1	1595	1563	20
2	287	315	-20
3	566	554	11
4	340	325	11
5	813	804	7
6	114	69	9
7	1109	1113	-3
8	290	282	4
9	710	718	-6
10	131	137	-1
11	236	193	16
12	125	84	7
13	296	344	-21
14	41	79	-3
15	487	463	12
16	54	125	-7
17	261	296	-10
18	142	94	5

8 k 6

0	1691	1679	7
1	135	75	15
2	913	892	18
3	364	330	25
4	360	357	2
5	320	302	11
6	936	921	13
7	301	277	12
8	917	901	12
9	93	53	5
10	418	406	7
11	140	128	2
12	138	220	-22
13	141	124	3
14	398	392	2
15	219	130	20
16	370	357	4
17	-85	21	-4

9 k 6

1	1096	1096	0
2	431	442	-8
3	136	68	16
4	730	726	3
5	533	546	-10
6	387	330	36
7	715	701	10
8	12	56	-2
9	511	531	-14
10	307	280	12
11	104	71	4
12	376	342	16
13	296	287	3
14	258	213	13
15	269	312	-14
16	-123	52	-10
17	216	208	1

10 k 6

0	702	698	3
1	383	380	2
2	379	370	6
3	914	917	-2
4	196	171	9
5	775	763	9
6	459	469	-7
7	63	130	-11
8	385	414	-17
9	309	290	8
10	90	67	2
11	489	487	0
12	220	164	15
13	374	347	11
14	204	173	7
15	116	100	1
16	162	136	4

11 k 6

1	202	229	-11
2	750	761	-9
3	-64	65	-7
4	1017	1030	-10
5	296	241	25
6	415	381	21
7	237	208	11
8	198	153	13
9	-100	35	-9
10	503	491	7
11	73	88	-1
12	449	437	6
13	152	67	12
14	189	191	0
15	-64	52	-3
16	158	98	8

12 k 6

0	281	230	23
1	433	423	6
2	126	72	9
3	867	871	-3
4	167	90	17
5	576	558	12
6	-113	56	-13
7	-120	92	-19
8	154	206	-14
9	359	348	5
10	162	158	0
11	458	446	6
12	69	38	2
13	246	228	5
14	138	36	10
15	145	65	9

13 k 6

1	416	398	11
2	615	623	-5
3	108	135	-5
4	587	600	-9
5	166	116	11
6	202	232	-10
7	361	358	1
8	152	130	4
9	317	296	8
10	390	356	15
11	109	78	3
12	233	227	1
13	147	81	8
14	-43	69	-3

14 k 6

0	612	623	-7
1	189	243	-17
2	447	406	24
3	443	469	-15
4	160	43	18
5	218	240	-7
6	389	371	8
7	181	73	20
8	448	425	11
9	215	219	-1
10	240	190	13
11	198	194	0
12	-97	43	-6
13	122	65	5

15 k 6

1	568	604	-22
2	-54	170	-23
3	170	176	-1
4	92	172	-15
5	294	322	-11
6	161	119	8
7	486	485	0
8	180	133	9
9	349	325	9
10	186	97	14
11	-62	57	-4
12	-172	55	-17

16 k 6

0	577	585	-4
1	160	89	12
2	322	347	-10
3	63	120	-7
4	103	135	-5
5	74	136	-8
6	410	421	-5
7	210	134	16
8	412	361	20
9	82	45	2
10	99	127	-3
11	138	109	3

17 k 6

1	388	404	-7
2	219	219	0
3	129	69	7
4	232	248	-4
5	294	250	14
6	201	219	-4
7	290	294	-1
8	65	10	2
9	220	187	7

18 k 6

0	308	295	4
1	107	166	-9
2	208	165	9
3	353	333	7
4	152	82	9
5	337	301	12
6	238	207	7
7	124	86	4

19 k 6

1	48	92	-3
2	311	294	5
3	99	33	4
4	416	367	18

0 k 7

1	1461	1489	-19
3	1089	1082	6
5	903	932	-27
7	1436	1452	-11
9	846	865	-16
11	197	201	-1
13	418	439	-12
15	664	651	8
17	365	350	6
19	-155	99	-12

1 k 7

0	1472	1504	-23
1	267	255	9
2	1343	1365	-16
3	509	511	-2
4	171	138	15
5	497	506	-9
6	1211	1231	-15
7	290	288	1
8	1074	1076	-2
9	196	220	-10
10	577	594	-13
11	484	469	10
12	-74	144	-23
13	282	246	14
14	607	590	11
15	37	61	-1
16	502	462	21
17	-103	107	-14
18	-35	163	-15

2 k 7

1	1369	1429	-45
2	977	987	-9
3	309	324	-11
4	1028	1029	0
5	336	344	-6
6	722	696	25
7	714	739	-23
8	113	85	6
9	751	746	4
10	743	732	8
11	133	85	9
12	565	571	-4
13	296	284	5
14	283	270	5
15	373	374	0
16	-29	100	-7
17	198	251	-13
18	182	236	-12

3 k 7

0	1142	1150	-7
1	516	503	12
2	357	374	-15
3	1739	1739	0
4	209	202	3
5	1304	1288	12
6	117	156	-13
7	268	239	17
8	359	377	-13
9	405	394	7
10	236	208	11
11	842	825	12
12	204	175	8
13	602	591	7
14	166	138	6
15	-108	116	-18
16	167	162	1
17	255	269	-4
18	-180	88	-21

4 k 7

1	167	158	4
2	1078	1073	4
3	211	186	13
4	1761	1795	-20
5	87	78	1
6	752	744	6
7	96	156	-18
8	250	218	15
9	-70	29	-5
10	791	785	4
11	133	153	-4
12	722	714	5
13	137	11	14
14	366	375	-4
15	103	50	5
16	217	203	3
17	94	38	4
18	380	349	11

5 k 7

0	906	912	-4
1	541	590	-51
2	295	294	0
3	1368	1355	9
4	111	74	9
5	1090	1094	-3
6	397	379	13
7	113	21	14
8	458	475	-12
9	464	456	5
10	273	234	16
11	755	751	2
12	95	54	5
13	500	517	-10
14	223	203	6
15	-82	176	-25
16	224	194	7
17	255	263	-2
18	172	111	9

6 k 7

1	1248	1237	8
2	807	808	-1
3	120	109	3
4	842	812	27
5	417	408	7
6	351	412	-45
7	795	802	-5
8	-57	65	-7
9	743	735	6
10	573	582	-6
11	-84	114	-16
12	361	400	-20
13	235	252	-5
14	116	206	-19
15	435	407	13
16	171	139	6
17	313	271	12
18	225	206	4

7 k 7

0	1497	1470	18
1	307	327	-14
2	790	815	-24
3	332	318	10
4	113	187	-26
5	157	119	11
6	849	835	11
7	167	167	-6
8	984	994	-8
9	173	206	-11
10	431	423	4
11	307	310	-1
12	147	174	-6
13	109	114	0
14	452	463	-5
15	-97	83	-10
16	427	401	10
17	127	115	1

8 k 7

1	1144	1157	-10
2	43	61	-2
3	359	355	2
4	206	159	17
5	549	557	-6
6	-83	13	-7
7	1000	1005	-3
8	34	48	0
9	671	678	-5
10	120	68	8
11	106	127	-4
12	139	107	5
13	338	347	-3
14	116	141	-4
15	510	461	23
16	-144	61	-13
17	359	282	24

9 k 7

0	921	963	-36
1	261	233	14
2	830	821	7
3	449	413	25
4	-82	35	-8
5	400	408	-5
6	778	783	-4
7	118	187	-18
8	695	695	0
9	193	160	9
10	315	296	8
11	373	365	3
12	226	184	12
13	290	276	4
14	408	405	1
15	-45	99	-6
16	374	314	20

10 k 7

1	692	683	7
2	722	764	-34
3	298	245	25
4	812	819	-5
5	309	295	7
6	546	584	-27
7	478	447	19
8	84	46	4
9	273	300	-11
10	530	507	14
11	118	47	8
12	497	453	23
13	254	256	0
14	148	223	-16
15	322	258	19
16	24	64	-1

11 k 7

0	249	249	0
1	506	474	22
2	24	106	-9
3	895	903	-5
4	175	165	2
5	785	792	-5
6	165	154	2
7	273	289	-7
8	62	110	-6
9	398	367	16
10	-112	48	-10

6	400	399	0
7	270	255	6
8	520	525	-3
9	244	221	7
10	261	231	9
11	430	441	-5
12	142	139	0
13	431	396	14
14	309	300	3
15	161	103	7

11 k 8

1	207	171	12
2	566	578	-8
3	229	191	12
4	963	943	14
5	133	132	0
6	561	547	9
7	285	271	5
8	105	81	3
9	74	162	-14
10	465	439	13
11	138	42	11
12	546	534	6
13	245	151	20
14	258	273	-3

12 k 8

0	336	293	20
1	321	328	-3
2	183	192	-2
3	703	683	14
4	-53	88	-7
5	687	692	-3
6	95	83	1
7	236	251	-5
8	197	151	11
9	292	301	-3
10	-90	149	-19
11	540	536	1
12	201	70	20
13	444	388	21

13 k 8

1	437	450	-7
2	420	432	-6
3	210	208	0
4	560	542	10
5	127	117	1
6	436	393	21
7	390	372	8
8	112	49	6
9	323	324	0
10	453	400	24
11	145	153	-1
12	400	384	5

14 k 8

0	574	577	-1
1	43	163	-17
2	411	419	-4
3	269	250	6
4	59	48	0
5	265	267	0
6	424	418	2
7	143	106	5
8	520	462	28
9	201	209	-1
10	316	299	5
11	297	267	8

15 k 8

1	495	505	-5
2	-56	68	-5
3	231	225	1
4	187	124	13
5	233	194	10
6	153	112	6
7	501	466	16
8	-160	76	-17
9	441	397	17
10	126	95	3

16 k 8

0	478	456	10
1	137	76	5
2	304	322	-6
3	243	180	16
4	-158	36	-16
5	168	175	-1
6	244	297	-15
7	186	94	14
8	352	378	-9

17 k 8

1	261	268	-1
2	180	196	-3
3	29	100	-5
4	299	320	-6
5	104	95	1
6	276	206	18

18 k 8

0	180	137	7
1	137	95	5
2	172	77	12
3	265	287	-6

0 k 9

1	888	897	-8
3	627	643	-15
5	604	612	-7
7	1058	1082	-18
9	820	825	-3
11	238	302	-26
13	400	427	-13
15	503	508	-2
17	211	265	-13

1 k 9

0	862	884	-20
1	466	494	-25
2	675	670	4
3	479	484	-4
4	198	220	-11
5	239	242	-1
6	727	756	-25
7	247	281	-17
8	935	936	0
9	174	205	-10
10	520	514	3
11	344	329	7
12	178	216	-11
13	240	178	18
14	523	489	19
15	113	51	6
16	403	367	14
17	223	92	23

2 k 9

1	655	668	-12
2	793	808	-14
3	250	214	19
4	621	623	-1
5	259	268	-5
6	587	575	9
7	683	713	-25
8	146	129	4
9	657	652	3
10	550	576	-17
11	198	153	12
12	474	478	-2
13	319	322	-1
14	239	230	2
15	315	349	-12
16	-166	113	-23
17	109	179	-10

3 k 9

0	613	623	-9
1	411	425	-11
2	215	198	8
3	949	969	-17
4	119	73	10
5	916	928	-10
6	276	242	17
7	432	434	-1
8	501	511	-7
9	457	455	0
10	246	276	-11
11	735	722	9
12	94	135	-6
13	502	501	0
14	253	205	14
15	145	133	2
16	-114	142	-18
17	194	255	-14

4 k 9

1	219	245	-14
2	555	544	9
3	30	79	-5
4	1308	1304	2
5	146	123	6
6	829	838	-7
7	203	216	-4
8	227	248	-9
9	128	116	2
10	681	679	1
11	115	75	5
12	726	706	13
13	-149	20	-15
14	321	311	3
15	148	78	9
16	200	216	-3
17	-117	54	-8

5 k 9

0	629	660	-27
1	236	203	15
2	305	270	20
3	895	887	7
4	157	118	11
5	1077	1058	14
6	245	248	-1
7	332	320	6
8	482	497	-10
9	438	420	11
10	314	293	9
11	717	705	8
12	25	130	-11
13	502	491	5
14	185	178	1
15	100	64	3
16	237	171	14

6 k 9

1	727	746	-16
2	512	514	-1
3	249	255	-2
4	786	811	-21
5	91	177	-21
6	498	498	0
7	663	675	-8
8	78	106	-4
9	670	675	-3
10	457	451	3
11	156	181	-6
12	504	488	9
13	277	250	8
14	171	159	2
15	339	324	4
16	200	133	12

7 k 9

0	1061	1056	4
1	317	296	11
2	675	686	-9
3	414	431	-11
4	209	190	7
5	304	299	2
6	654	660	-4
7	182	175	2
8	911	888	16
9	168	181	-3
10	530	509	12
11	330	297	14
12	122	132	-1
13	110	166	-9
14	425	403	9
15	-158	30	-14
16	364	340	7

8 k 9

1	924	916	6
2	128	168	-11
3	503	500	1
4	252	271	-8
5	437	448	-7
6	151	148	0
7	884	877	5
8	198	29	29
9	704	704	0
10	109	139	-5
11	163	241	-21
12	93	110	-2
13	289	298	-3
14	55	94	-3
15	461	434	11

9 k 9

0	755	781	-20
1	242	217	10
2	615	621	-5
3	484	474	6
4	132	82	9
5	466	462	2
6	663	649	9
7	212	199	3
8	697	699	-1
9	82	65	1
10	383	391	-3
11	316	296	7
12	46	101	-5
13	255	244	3
14	354	377	-7
15	155	71	9

10 k 9

1	464	476	-7
2	568	562	4
3	308	257	22
4	678	649	21

11	551	550	0
12	44	140	-11
13	354	372	-6
14	142	131	1
15	-54	120	-9

12 k 7

1	98	152	-12
2	619	619	0
3	232	175	19
4	765	787	-16
5	-44	58	-4
6	395	391	2
7	130	182	-12
8	95	138	-7
9	199	187	3
10	475	460	8
11	165	138	5
12	480	440	18
13	109	45	5
14	251	220	7

13 k 7

0	442	454	-7
1	288	274	5
2	277	317	-17
3	635	657	-15
4	130	17	13
5	531	531	0
6	300	273	10
7	150	77	12
8	369	365	1
9	315	291	9
10	264	263	0
11	347	372	-10
12	-87	47	-5
13	289	266	6

14 k 7

1	651	628	15
2	320	308	5
3	173	158	3
4	408	405	1
5	208	234	-7
6	78	177	-17
7	501	503	-1
8	128	158	-5
9	435	419	7
10	144	226	-17
11	178	135	7
12	97	206	-17

15 k 7

0	721	691	19
1	8	69	-3
2	428	401	13
3	58	128	-9
4	134	65	9
5	-93	167	-24
6	511	446	33
7	180	98	14
8	475	472	1
9	-86	94	-9
10	210	247	-8
11	185	110	12

16 k 7

1	499	495	2
2	125	116	1
3	192	152	9
4	219	214	1
5	290	224	20
6	189	178	2
7	406	403	1
8	145	53	10
9	266	295	-8
10	229	71	26

17 k 7

0	284	380	-34
1	188	122	12
2	242	255	-4
3	300	284	5
4	-84	58	-6
5	254	285	-8
6	219	276	-14
7	48	117	-6
8	180	265	-19

18 k 7

1	163	168	-1
2	291	263	8
3	184	84	14
4	367	356	11
5	176	125	7
6	109	215	-17

19 k 7

0	-17	96	-3

0 k 8

0	1896	1897	0
2	685	681	4
4	136	183	-20
6	695	724	-27
8	1221	1216	3
10	628	626	1
12	309	307	1
14	508	545	-22
16	441	432	4
18	-51	155	-14

1 k 8

1	1113	1128	-12
2	98	96	0
3	399	400	0
4	671	676	-4
5	473	484	-9
6	179	220	-19
7	869	873	-3
8	93	87	1
9	948	956	-6
10	302	259	20
11	175	185	-3
12	323	302	10
13	380	436	-29
14	161	148	2
15	486	480	2
16	84	79	0
17	264	263	0
18	-109	94	-11

2 k 8

0	826	799	26
1	210	234	-14
2	772	765	6
3	727	716	10
4	143	134	3
5	787	784	2
6	571	571	0
7	191	196	-2
8	743	749	-4
9	310	308	1
10	392	403	-6
11	580	572	5
12	102	171	-14
13	408	397	5
14	393	403	-5
15	-87	83	-9
16	307	316	-3
17	213	194	4
18	170	99	10

3 k 8

1	430	442	-11
2	727	755	-27
3	602	609	-7
4	1131	1144	-11
5	344	313	22
6	702	739	-34
7	494	483	8
8	-37	91	-9
9	269	306	-18
10	732	722	7
11	228	190	12
12	640	644	-2
13	118	196	-17
14	283	237	16
15	280	231	16
16	225	188	9
17	-98	102	-11
18	299	286	3

4 k 8

0	173	149	10
1	694	718	-24
2	146	158	-4
3	1109	1174	-54
4	-45	16	-2
5	962	967	-4
6	179	180	0
7	635	633	1
8	116	95	4
9	451	457	-4
10	122	71	8
11	898	908	-7
12	127	75	8
13	527	519	4
14	134	56	10
15	112	147	-5
16	182	48	19
17	343	321	7

5 k 8

1	466	448	16
2	808	810	-2
3	317	289	18
4	1012	1033	-17
5	124	164	-12
6	737	701	30
7	326	314	6
8	99	14	9
9	228	236	-3
10	824	842	-14
11	-127	99	-20
12	705	690	10
13	121	126	0
14	285	278	2
15	200	189	2
16	73	170	-13
17	149	97	6

6 k 8

0	760	763	-2
1	214	220	-2
2	584	558	22
3	743	775	-29
4	240	173	30
5	733	724	7
6	634	629	4
7	219	244	-10
8	673	676	-2
9	358	379	-11
10	368	367	0
11	550	549	0
12	-64	71	-6
13	421	406	7
14	384	402	-7
15	-50	94	-6
16	338	299	12
17	144	209	-11

7 k 8

1	899	890	7
2	154	123	9
3	441	448	-5
4	662	678	-14
5	418	372	30
6	280	260	9
7	927	924	2
8	-28	128	-15
9	764	756	6
10	249	259	-3
11	247	264	-6
12	288	259	10
13	360	364	-1
14	125	106	2
15	489	468	9
16	236	90	25

8 k 8

0	1212	1204	6
1	70	64	0
2	750	733	15
3	161	154	2
4	-95	60	-12
5	119	77	8
6	723	709	11
7	111	117	-1
8	1002	971	22
9	50	19	1
10	510	513	-1
11	108	108	0
12	215	142	18
13	67	45	1
14	485	457	13
15	105	73	3
16	415	384	11

9 k 8

1	977	980	-2
2	316	296	10
3	321	323	-1
4	472	495	-16
5	246	266	-8
6	370	375	-2
7	774	779	-4
8	-69	30	-4
9	670	675	-3
10	138	225	-21
11	203	157	11
12	304	298	2
13	369	317	20
14	233	208	6
15	439	407	12

10 k 8

0	629	654	-19
1	247	248	0
2	397	414	-10
3	735	743	-6
4	180	74	23
5	842	866	-18

5	299	266	14
6	397	432	-18
7	508	508	0
8	81	118	-5
9	409	391	8
10	417	367	23
11	-99	77	-9
12	466	408	26
13	184	218	-7
14	238	218	4

11 k 9

0	272	281	-4
1	301	318	-8
2	133	146	-3
3	693	674	13
4	-90	60	-8
5	664	680	-11
6	105	164	-11
7	248	298	-18
8	262	254	2
9	276	287	-3
10	108	89	2
11	529	486	20
12	113	90	2
13	367	357	3

12 k 9

1	200	218	-5
2	457	447	5
3	141	120	4
4	706	690	10
5	-85	120	-15
6	526	492	19
7	114	144	-5
8	7	90	-5
9	197	125	15
10	419	404	6
11	89	87	0
12	470	422	19

13 k 9

0	386	417	-15
1	172	154	4
2	311	310	0
3	444	452	-4
4	-67	17	-3
5	470	482	-6
6	206	242	-10
7	166	168	0
8	283	294	-3
9	221	232	-2
10	163	215	-10
11	395	354	14

14 k 9

1	460	458	0
2	219	188	8
3	244	191	15
4	307	287	7
5	142	152	-1
6	264	179	22
7	403	382	8
8	152	80	9
9	418	367	19
10	220	212	1

15 k 9

0	485	471	7
1	171	45	17
2	378	328	20
3	-93	107	-12
4	-125	65	-12
5	160	52	13
6	271	302	-9
7	-45	13	-1
8	434	418	6
9	-136	69	-11

16 k 9

1	386	344	16
2	45	99	-4
3	99	149	-7
4	221	201	4
5	129	146	-2
6	132	112	2
7	346	335	3

17 k 9

0	247	233	3
1	-26	76	-3
2	173	165	1
3	227	240	-3
4	148	43	10

0 k 10

0	1384	1437	-37
2	862	885	-19
4	329	334	-2
6	751	777	-21
8	938	960	-16
10	555	543	7
12	235	219	5
14	486	454	16
16	391	386	1

1 k 10

1	1137	1172	-26
2	305	237	36
3	395	403	-5
4	654	645	7
5	394	417	-15
6	319	347	-15
7	952	947	4
8	203	173	9
9	714	718	-2
10	189	199	-3
11	184	194	-3
12	269	254	5
13	349	329	8
14	141	140	0
15	416	418	-1
16	98	70	2

2 k 10

0	822	837	-13
1	256	228	13
2	610	615	-4
3	917	903	10
4	99	150	-12
5	990	999	-6
6	691	691	0
7	257	273	-7
8	658	627	23
9	349	353	-2
10	350	313	17
11	489	516	-15
12	-191	99	-31
13	448	438	4
14	372	345	10
15	61	107	-4
16	319	254	19

3 k 10

1	340	335	3
2	863	866	-3
3	175	187	-4
4	1066	1077	-8
5	277	277	0
6	713	700	9
7	364	365	0
8	234	261	-10
9	147	172	-6
10	643	639	2
11	-63	37	-3
12	674	649	15
13	169	135	6
14	290	319	-9
15	199	162	7
16	-48	126	-9

4 k 10

0	357	354	1
1	623	619	2
2	183	157	8
3	1023	1039	-12
4	138	51	16
5	853	859	-5
6	183	219	-12
7	333	354	-11
8	244	239	2
9	468	481	-8
10	121	154	-6
11	695	676	12
12	-81	84	-9
13	500	482	9
14	-114	56	-9
15	-84	127	-13
16	206	83	19

5 k 10

1	494	452	30
2	939	950	-9
3	264	295	-15
4	843	827	13
5	292	308	-7
6	606	618	-8
7	515	517	-1
8	167	225	-17
9	408	410	-1
10	573	556	9
11	182	203	-5
12	486	477	4
13	77	115	-4
14	129	188	-10
15	243	234	2

6 k 10

0	815	796	15
1	316	324	-4
2	707	694	10
3	655	656	0
4	182	213	-10
5	539	577	-27
6	636	657	-15
7	152	186	-8
8	623	613	6
9	352	313	17
10	394	376	8
11	343	356	-5
12	154	127	4
13	219	206	3
14	324	305	6
15	79	44	2

7 k 10

1	936	946	-7
2	233	228	1
3	391	383	4
4	317	317	0
5	449	474	-15
6	141	178	-9
7	713	710	1
8	237	167	21
9	612	613	-1
10	159	138	4
11	165	191	-6
12	164	130	6
13	267	262	1
14	106	51	4
15	368	334	11

8 k 10

0	935	936	-1
1	145	169	-6
2	611	597	10
3	217	265	-19
4	252	230	9
5	241	248	-3
6	547	558	-7
7	203	168	10
8	661	679	-11
9	-75	64	-6
10	371	352	8
11	-43	111	-9
12	209	174	8
13	127	118	1
14	376	332	15

9 k 10

1	643	661	-13
2	371	371	0
3	136	155	-4
4	470	478	-4
5	351	359	-3
6	388	322	33
7	611	590	13
8	207	68	27
9	477	439	20
10	182	236	-14
11	193	71	21
12	294	240	15
13	310	249	18
14	119	150	-4

10 k 10

0	497	490	4
1	232	183	16
2	241	281	-15
3	599	584	10
4	50	143	-13
5	547	528	11
6	344	356	-5
7	176	146	6
8	342	338	1
9	293	242	18
10	-100	113	-14
11	394	355	15
12	117	116	0
13	281	278	0

11 k 10

1	-59	174	-25
2	453	464	-6
3	-137	54	-15
4	642	628	8
5	209	179	8
6	355	343	5
7	190	177	3
8	194	112	16
9	197	52	23
10	377	354	8
11	-83	37	-4

12	409	374	13

12 k 10

0	218	209	2
1	236	234	0
2	84	87	0
3	607	593	8
4	54	73	-1
5	466	460	3
6	147	139	1
7	207	148	13
8	72	160	-13
9	261	227	9
10	-83	107	-10
11	355	374	-6

13 k 10

1	334	298	14
2	407	396	5
3	78	118	-5
4	446	440	2
5	70	113	-4
6	180	216	-8
7	287	241	13
8	151	104	7
9	278	234	12
10	227	277	-12

14 k 10

0	432	408	11
1	-152	127	-24
2	311	311	0
3	295	289	1
4	172	53	17
5	206	191	3
6	282	282	0
7	76	60	1
8	282	311	-8
9	116	145	-3

15 k 10

1	393	381	4
2	-13	94	-5
3	218	160	12
4	170	124	7
5	190	214	-5
6	-66	17	-2
7	287	315	-8

16 k 10

0	384	355	10
1	132	59	7
2	231	237	-1
3	-97	121	-13
4	199	82	18

0 k 11

1	1202	1230	-20
3	528	549	-15
5	543	578	-25
7	957	938	14
9	615	622	-4
11	221	232	-3
13	260	289	-9
15	451	419	13

1 k 11

0	1207	1232	-18
1	336	330	2
2	901	897	3
3	506	505	1
4	147	134	3
5	379	384	-3
6	800	814	-11
7	210	161	14
8	739	742	-2
9	211	192	5
10	373	366	3
11	282	266	5
12	58	130	-9
13	186	178	1
14	328	350	-7
15	-76	66	-5

2 k 11

1	870	891	-17
2	805	814	-7
3	220	199	7
4	862	875	-10
5	369	397	-16
6	535	538	-2
7	645	630	10
8	166	143	5
9	407	410	-1
10	484	448	20
11	149	107	7
12	465	445	9
13	211	207	0
14	252	226	7
15	276	243	8

3 k 11

0	507	541	-25
1	513	514	0
2	149	176	-7
3	1064	1049	11
4	164	139	6
5	904	871	24
6	187	201	-4
7	199	249	-18
8	287	256	12
9	450	464	-8
10	124	61	8
11	557	547	5
12	168	97	12
13	374	430	-23
14	-123	98	-14
15	103	140	-4

4 k 11

1	129	133	0
2	868	864	3
3	162	134	7
4	1042	1045	-2
5	177	127	12
6	469	465	2
7	135	163	-6
8	306	313	-2
9	196	149	12
10	456	469	-7
11	118	83	4
12	548	516	17
13	-84	21	-4
14	243	249	-1
15	-116	71	-10

5 k 11

0	556	572	-11
1	367	378	-6
2	409	393	9
3	891	878	10
4	135	136	0
5	690	701	-8
6	304	343	-17
7	140	127	2
8	448	420	15
9	347	362	-6
10	246	268	-7
11	412	407	2
12	-146	64	-15
13	316	286	9
14	241	164	16

6 k 11

1	837	813	17
2	505	513	-5
3	243	215	10
4	460	464	-2
5	314	343	-13
6	237	200	12
7	582	571	7
8	199	184	4
9	442	457	-7
10	234	270	-11
11	37	148	-13
12	213	221	-1
13	249	175	18
14	39	54	0

7 k 11

0	959	934	18
1	118	154	-7
2	640	622	12
3	190	213	-7
4	198	173	7
5	50	79	-3
6	597	572	16
7	-84	65	-8
8	605	586	12
9	32	125	-9
10	269	261	2
11	154	104	8
12	171	134	6
13	-128	26	-9

8 k 11

1	708	709	0
2	165	147	4
3	259	265	-2
4	300	290	4
5	444	428	9
6	-79	169	-24
7	583	587	-2
8	116	12	9
9	350	338	4
10	58	58	0
11	122	81	5
12	209	127	15
13	135	225	-16

9 k 11

0	606	589	11
1	157	180	-5
2	400	392	3
3	415	447	-17
4	185	157	6
5	359	365	-2
6	501	459	24
7	144	117	4
8	325	335	-3
9	159	131	5
10	164	125	6
11	196	233	-8
12	161	132	4

10 k 11

1	327	349	-9
2	457	429	14
3	69	58	0
4	436	466	-15
5	292	269	8
6	226	260	-10
7	180	239	-15
8	107	71	4
9	-25	128	-10
10	263	291	-8
11	-103	61	-7

11 k 11

0	161	238	-21
1	282	262	7
2	-60	99	-9
3	560	534	15
4	159	85	12
5	406	401	2
6	125	127	0
7	159	119	7
8	-178	54	-20
9	178	237	-13
10	-243	46	-33
11	363	328	11

12 k 11

1	15	142	-13
2	457	439	8
3	-187	90	-27
4	511	507	2
5	91	57	3
6	269	229	11
7	188	118	12
8	173	136	6
9	198	119	13

13 k 11

0	273	293	-6
1	36	175	-18
2	264	202	17
3	417	428	-4
4	99	25	5
5	262	283	-6
6	210	164	9
7	-149	57	-14
8	249	218	7

14 k 11

1	353	353	0
2	222	228	-1
3	191	106	14
4	250	257	-1
5	219	159	12
6	-104	51	-7

15 k 11

0	420	423	-1
1	43	69	-1
2	293	245	13
3	120	158	-5
4	115	78	3

0 k 12

0	1075	1098	-16
2	626	645	-14
4	228	211	6
6	636	629	4
8	740	737	2
10	399	365	15
12	152	165	-2
14	356	304	17

1 k 12

1	868	882	-10
2	301	294	3
3	188	202	-4
4	390	405	-8
5	439	449	-5
6	190	185	1
7	680	683	-1
8	74	81	0
9	496	501	-2
10	204	172	7
11	96	138	-6
12	206	220	-3
13	225	238	-3
14	148	109	5

2 k 12

0	665	673	-6
1	310	296	6
2	460	469	-5
3	724	717	5
4	77	128	-8
5	612	597	9
6	512	505	4
7	128	122	1
8	414	433	-9
9	212	250	-11
10	180	192	-2
11	399	376	9
12	204	117	16
13	363	294	23
14	186	214	-5

3 k 12

1	227	250	-8
2	747	727	14
3	164	127	8
4	847	850	-2
5	255	226	10
6	427	422	2
7	245	235	3
8	203	132	17
9	164	96	12
10	412	412	0
11	160	42	15
12	487	445	19
13	32	94	-4
14	208	205	0

4 k 12

0	194	177	4
1	421	427	-3
2	79	109	-4
3	866	863	2
4	87	18	5
5	683	673	6
6	-157	44	-20
7	179	160	4
8	203	134	16
9	345	339	2
10	-134	84	-15
11	480	469	5
12	-20	40	-1
13	327	286	12

5 k 12

1	426	429	-1
2	644	635	6
3	182	205	-6
4	695	680	10
5	86	152	-11
6	335	318	7
7	392	350	19
8	170	133	7
9	240	235	1
10	355	377	-9
11	14	91	-4
12	331	334	0
13	-117	63	-9

6 k 12

0	617	605	7
1	293	214	30
2	527	497	19
3	468	458	5
4	56	63	0
5	361	324	16
6	478	465	7
7	132	30	11
8	431	407	11
9	241	240	0
10	278	230	14
11	276	262	4
12	-50	38	-2
13	250	156	20

7 k 12

1	707	678	19
2	236	157	23
3	223	224	0
4	233	184	14
5	394	391	1
6	106	21	7
7	543	536	3
8	124	87	5
9	423	385	17
10	53	102	-4
11	197	102	16
12	98	73	2

8 k 12

0	769	750	12
1	30	67	-2
2	462	449	7
3	-28	108	-9
4	228	162	18
5	52	104	-5
6	441	442	0
7	42	73	-2
8	505	470	17
9	137	25	10
10	232	235	0
11	-130	81	-12

9 k 12

1	565	530	20
2	213	252	-12
3	-119	103	-16
4	360	327	13
5	260	271	-3
6	263	219	13
7	435	393	19
8	-129	31	-10
9	326	288	12
10	162	154	1
11	-87	68	-6

10 k 12

0	373	394	-9
1	165	181	-3
2	199	216	-4
3	425	440	-7
4	157	97	9
5	392	382	4
6	237	254	-5
7	34	114	-6
8	223	242	-5
9	-94	156	-18
10	-150	48	-13

11 k 12

1	121	148	-4
2	423	410	5
3	100	42	5
4	533	505	14
5	135	120	2
6	306	279	9
7	113	121	-1
8	52	96	-3
9	24	49	-1

12 k 12

0	159	170	-2
1	210	228	-4
2	86	128	-5
3	515	490	11
4	215	47	25
5	340	358	-6
6	-78	47	-4
7	106	63	4

13 k 12

1	290	260	9
2	301	320	-6
3	-149	110	-19
4	370	320	17
5	158	70	10
6	99	146	-6

14 k 12

0	402	336	24
1	148	118	4
2	273	236	9
3	252	235	4

0 k 13

1	539	571	-20
3	238	237	0
5	377	360	8
7	572	566	3
9	462	433	13
11	106	114	-1

1 k 13

0	544	570	-17
1	-70	110	-13
2	387	426	-21
3	238	220	6
4	-50	78	-6
5	240	182	18
6	477	459	10
7	-75	73	-7
8	504	492	6
9	-27	114	-8
10	298	266	10
11	211	191	4
12	79	120	-4

2 k 13

1	417	440	-12
2	405	394	5
3	187	143	11
4	462	440	12
5	179	195	-4
6	275	282	-2
7	358	362	-1
8	-103	25	-7
9	383	341	17
10	353	300	19
11	143	69	8
12	229	273	-11

3 k 13

0	301	279	9
1	235	250	-5
2	31	157	-18
3	598	597	0
4	-57	53	-4
5	547	532	9
6	153	114	7
7	197	167	7
8	222	212	2
9	263	218	13
10	105	108	0
11	420	395	9
12	62	81	-1

4 k 13

1	110	46	7
2	477	484	-4
3	-93	49	-8
4	680	674	3
5	121	24	10
6	390	379	5
7	-57	31	-2
8	77	36	3
9	132	23	10
10	365	349	5
11	-118	34	-8
12	431	386	17

5 k 13

0	351	329	10
1	204	209	-1
2	214	195	5
3	560	565	-3
4	119	17	10
5	539	513	14
6	-99	120	-16
7	197	136	13
8	236	207	7
9	197	222	-5
10	88	134	-5
11	399	388	4

6 k 13

1	449	458	-4
2	340	328	4
3	-86	106	-12
4	359	402	-19
5	-148	145	-28
6	276	213	20
7	323	356	-12
8	94	52	3
9	365	349	5
10	285	280	1
11	135	94	5

7 k 13

0	621	592	17
1	93	90	0
2	410	381	13
3	204	204	0
4	85	54	2
5	115	166	-9
6	400	368	13
7	-58	64	-4
8	509	505	1
9	145	119	3
10	273	267	1

8 k 13

1	573	538	20
2	119	35	8
3	279	213	21
4	-71	47	-4
5	209	239	-8
6	114	46	6
7	531	515	8
8	-66	8	-2
9	416	375	16
10	-79	41	-4

9 k 13

0	509	492	8
1	49	111	-6
2	370	379	-3
3	285	220	20
4	-157	17	-15
5	176	213	-8
6	362	374	-4
7	55	118	-6
8	417	378	15
9	51	73	-1

10 k 13

1	299	310	-3
2	374	319	20
3	-52	121	-10
4	404	381	8
5	-104	161	-20
6	280	285	-1
7	296	278	5
8	120	36	7

11 k 13

0	-68	146	-15
1	186	203	-3
2	80	77	0
3	445	440	2
4	-146	46	-12
5	447	408	15
6	173	108	9

12 k 13

1	-101	118	-13
2	296	305	-2
3	88	83	0
4	413	413	0

0 k 14

0	639	597	-27
2	389	373	7
4	-17	52	-2
6	204	309	-33
8	523	497	13
10	225	259	-8

1 k 14

1	467	459	4
2	169	102	13
3	201	207	-1
4	239	207	9
5	131	150	-3
6	153	115	6
7	409	409	0
8	-74	37	-4
9	450	383	28
10	166	111	8

2 k 14

0	379	358	10
1	220	96	28
2	281	303	-8
3	302	322	-7
4	116	55	7
5	327	333	-2
6	217	239	-6
7	148	106	6
8	354	325	11
9	121	142	-3
10	177	192	-2

3 k 14

1	250	205	14
2	360	324	15
3	207	166	10
4	490	460	16
5	169	75	15
6	307	331	-8
7	238	202	9
8	77	62	1
9	188	147	7
10	303	320	-5

4 k 14

0	162	72	15
1	158	203	-11
2	67	78	-1
3	494	459	18
4	108	15	7
5	451	464	-6
6	114	64	5
7	290	237	15
8	-160	68	-17
9	195	234	-9
10	180	36	16

5 k 14

1	212	171	10
2	364	334	13
3	1	79	-4
4	443	461	-8
5	80	65	1
6	390	346	17
7	198	181	3
8	154	79	10
9	169	142	4

6 k 14

0	310	330	-7
1	202	109	19
2	197	252	-15
3	334	333	0
4	-80	47	-5
5	315	355	-14
6	266	258	2
7	176	119	9
8	301	335	-11
9	84	165	-10

7 k 14

1	416	422	-2
2	132	111	3
3	206	210	0
4	269	254	4
5	118	161	-7
6	-44	124	-9
7	438	425	5
8	-62	36	-2

8 k 14

0	552	514	19
1	-35	32	-1
2	342	339	1
3	161	85	11
4	211	48	25
5	155	107	7
6	319	327	-2
7	-209	45	-24

9 k 14

1	432	399	14
2	-42	139	-11
3	79	148	-8
4	241	242	0
5	126	131	0
6	143	173	-4

10 k 14

0	230	274	-11
1	133	122	1
2	234	193	9
3	385	326	20
4	81	20	3

0 k 15

1	459	478	-9
3	326	276	17
5	277	207	20
7	477	467	4

1 k 15

0	471	469	1
1	138	95	6
2	381	344	15
3	170	177	-1
4	55	84	-2
5	214	170	9
6	329	340	-3
7	164	107	8
8	439	408	13

2 k 15

1	325	326	0
2	285	263	7
3	-78	126	-13
4	342	326	5
5	210	117	18
6	303	256	14
7	278	309	-9
8	124	98	3

3 k 15

0	273	258	4
1	84	156	-10
2	135	117	2
3	369	418	-20
4	87	21	4
5	426	425	0
6	170	118	8
7	158	172	-2
8	225	175	10

4 k 15

1	115	104	1
2	296	299	0
3	-51	23	-1
4	531	511	10
5	89	36	3
6	271	316	-13
7	81	89	0

5 k 15

0	211	224	-3
1	176	144	6
2	125	130	0
3	361	397	-13
4	165	35	15
5	429	395	13
6	160	152	1

6 k 15

1	347	339	2
2	179	237	-13
3	177	131	8
4	276	295	-5
5	207	136	13
6	209	191	3

7 k 15

0	482	453	13
1	150	107	6
2	290	303	-4
3	217	154	12
4	119	77	4

8 k 15

1	412	382	11
2	105	108	0
3	197	166	6

0 k 16

0	591	558	16
2	377	317	21
4	192	105	14

1 k 16

1	449	425	10
2	207	124	15
3	194	139	10
4	280	243	10

2 k 16

0	300	310	-2
1	103	121	-2
2	130	195	-11
3	402	354	18
4	-146	79	-14

3 k 16

1	87	117	-3
2	379	351	10
3	-122	33	-8

4 k 16

0	143	103	5
1	237	237	0
2	147	75	8

Appendix 2 X-ray data for $[Au_2(dcpe)_3]$ $[Au(CN)_2]_2$.

[(Au(dcpe))2 mu-(dcpe)]2+ 2[Au(CN)2]-

-14	2	1	
1	169	178	-1
-14	3	1	
1	-149	166	-28
2	244	284	-9
3	-129	224	-36
4	342	385	-12
-14	4	1	
1	347	336	3
2	373	407	-11
3	53	70	-1
4	209	246	-8
-14	5	1	
1	199	201	0
2	283	253	14
3	191	239	-19
4	380	401	-11
-14	6	1	
1	348	345	2
2	417	396	12
3	91	116	-5
4	289	294	-2
-14	7	1	
1	165	162	1
2	267	254	6
3	192	243	-22
4	471	474	-2
-14	8	1	
1	284	288	-1
2	272	269	1
-13	1	1	
1	265	260	2
2	-90	22	-10
3	332	316	8
4	519	505	8
5	-43	100	-12
6	249	268	-8
7	303	305	0
-13	2	1	
1	622	606	11
2	-102	84	-19
3	160	231	-25
4	-74	137	-24
5	112	205	-26
6	429	445	-9
7	383	403	-10
-13	3	1	
1	421	460	-23
2	-128	157	-41
3	449	484	-20
4	307	344	-18
5	-130	104	-26
6	268	318	-22
7	-136	137	-35
8	352	363	-5
-13	4	1	
1	618	622	-2
2	-93	12	-9
3	276	277	0
4	-152	127	-42
5	346	368	-11
6	545	557	-7
7	166	205	-12
8	175	264	-31
-13	5	1	
1	318	367	-31
2	173	202	-11
3	496	494	1
4	216	274	-26
5	214	291	-36
6	333	333	0
7	-94	120	-23
8	364	383	-10
-13	6	1	
1	450	451	0
2	-86	21	-10
3	330	312	9
4	38	35	0
5	666	659	5
6	455	458	-2
7	25	67	-3
-13	7	1	
1	221	217	1
2	34	91	-8
3	494	477	11
4	103	128	-6
5	444	446	-1
6	195	216	-8
7	244	238	2
-13	8	1	
1	388	380	5
2	88	93	-1
3	167	137	10
4	188	193	-1
5	451	450	0
6	368	355	7
-13	9	1	
1	221	191	13
2	399	412	-8
3	277	209	31
4	111	130	-5
5	198	185	5
-13	10	1	
1	223	204	8
2	300	321	-12
3	147	85	15
-12	1	1	
1	104	98	1
2	332	296	22
3	512	522	-7
4	-112	63	-20
5	347	354	-3
6	400	389	7
7	184	215	-11
8	510	523	-7
9	-156	118	-39
-12	2	1	
1	323	334	-6
2	-127	120	-35
3	159	208	-17
4	326	349	-12
5	465	493	-18
6	495	533	-24
7	-121	115	-29
8	346	362	-8
9	-158	43	-27
10	440	463	-12
-12	3	1	
1	-157	23	-31
2	529	541	-8
3	386	417	-19
4	86	134	-10
5	219	292	-33
6	-77	141	-26
7	416	426	-6
8	473	489	-9
9	-119	83	-21
10	247	276	-12
-12	4	1	
1	79	129	-13
2	269	265	2
3	161	218	-23
4	473	482	-5
5	538	551	-9
6	113	197	-26
7	284	292	-3
8	142	212	-22
9	-36	193	-35
10	360	354	2
-12	5	1	
1	124	133	-3
2	502	520	-13
3	480	497	-12
4	230	292	-33
5	325	327	-1
6	31	93	-8
7	631	628	1
8	182	239	-22
9	-132	68	-22
10	-103	146	-30
-12	6	1	
1	126	95	9
2	173	211	-18
3	173	182	-4
4	543	536	5
5	621	627	-4
6	-87	31	-10
7	397	407	-6
8	-133	48	-22
9	174	219	-16
-12	7	1	
1	232	205	13
2	480	470	7
3	348	355	-4
4	360	342	11
5	221	192	12
6	217	270	-26
7	559	570	-7
8	253	301	-23
9	28	126	-15
-12	8	1	
1	151	130	7
2	283	271	6
3	74	33	5
4	545	546	0
5	300	281	10
6	-82	38	-9
7	369	377	-4
8	144	110	8
-12	9	1	
1	473	470	2
2	458	452	-9
3	105	7	13
4	237	236	0
5	111	42	12
6	217	228	-4
7	475	496	-13
-12	10	1	
1	352	364	-8
2	203	221	-8
3	255	257	-1
4	423	407	10
5	-21	94	-10
6	129	145	-4
-12	11	1	
1	483	480	2
2	285	298	-7
3	-44	52	-5
4	213	235	-9
-12	12	1	
1	294	288	3
2	136	101	9
-11	1	1	
1	314	315	-1
2	639	645	-5
3	89	105	-4
4	168	194	-10
5	266	310	-25
6	204	247	-20
7	646	629	11
8	410	448	-23
9	307	333	-13
10	-73	144	-27
11	289	289	0
-11	2	1	
1	177	217	-16
2	436	448	-7
3	218	310	-48
4	574	608	-24
5	511	522	-7
6	-114	58	-19
7	418	433	-9
8	-155	25	-28
9	488	522	-22
10	315	354	-20
11	-32	117	-14
12	338	356	-9
-11	3	1	
1	306	321	-10
2	785	806	-15
3	-142	48	-29
4	313	371	-35
5	204	230	-11
6	478	502	-15
7	527	551	-15
8	65	179	-29
9	190	250	-24
10	-35	142	-21

11	262	291	-12
12	493	509	-9

-11 4 1

1	258	267	-5
2	327	313	9
3	474	500	-20
4	671	659	8
5	420	439	-12
6	249	272	-11
7	260	283	-11
8	109	187	-23
9	449	448	0
10	-60	193	-40
11	-109	95	-20

-11 5 1

1	682	674	6
2	577	586	-7
3	231	249	-10
4	388	413	-17
5	-108	68	-21
6	729	747	-13
7	548	555	-6
8	-142	24	-24
9	61	158	-22
10	-203	2	-46
11	290	340	-24

-11 6 1

1	86	141	-19
2	395	406	-8
3	456	454	1
4	636	646	-8
5	-23	65	-6
6	559	562	-2
7	112	176	-20
8	294	292	0
9	415	420	-3
10	-80	111	-20
11	114	247	-45

-11 7 1

1	547	525	17
2	552	549	2
3	131	168	-14
4	171	196	-11
5	285	290	-3
6	700	723	-18
7	365	377	-7
8	44	133	-17
9	248	294	-23
10	174	204	-10

-11 8 1

1	308	307	1
2	130	133	-1
3	534	540	-4
4	325	329	-2
5	-44	61	-7
6	326	310	9
7	96	136	-10
8	350	353	-2
9	429	438	-5
10	49	100	-8

-11 9 1

1	657	635	17
2	229	224	2
3	317	327	-6
4	115	95	5
5	305	321	-10
6	528	486	28
7	267	281	-7
8	151	171	-6
9	210	184	9

-11 10 1

1	380	380	0
2	183	153	12
3	506	515	-6
4	78	106	-6
5	95	122	-7
6	215	253	-18
7	159	111	13

-11 11 1

1	442	435	5
2	23	50	-2
3	193	221	-12
4	-39	33	-3
5	405	378	16
6	451	433	11

-11 12 1

1	179	157	8
2	161	84	21
3	326	338	-7
4	78	124	-10

-11 13 1

1	243	226	8

-10 1 1

1	1098	1102	-3
2	238	229	5
3	108	133	-8
4	170	202	-15
5	440	454	-10
6	688	704	-12
7	633	665	-24
8	146	215	-27
9	288	350	-35
10	266	278	-5
11	527	528	0
12	261	275	-6
13	36	141	-18

-10 2 1

1	702	739	-28
2	196	277	-42
3	581	601	-15
4	586	585	0
5	-19	143	-26
6	398	429	-21
7	261	316	-31
8	676	667	6
9	455	469	-9
10	-165	0	-32
11	294	310	-8
12	-171	80	-39
13	390	371	9

-10 3 1

1	1052	1054	-2
2	-130	89	-38
3	264	272	-4
4	-94	15	-12
5	560	576	-11
6	821	848	-20
7	188	283	-46
8	445	432	8
9	-114	90	-24
10	187	212	-9
11	554	534	12
12	192	211	-7
13	319	325	-3

-10 4 1

1	532	521	10
2	473	492	-16
3	623	624	0
4	656	665	-7
5	390	402	-8
6	481	484	-2
7	242	274	-17
8	616	628	-8
9	310	336	-14
10	-193	14	-44
11	359	360	0
12	-143	52	-24
13	561	550	7

-10 5 1

1	793	792	1
2	150	201	-27
3	290	281	6
4	43	1	2
5	966	975	-6
6	533	532	1
7	-52	102	-16
8	298	317	-11
9	-123	42	-20
10	233	284	-24
11	468	461	4
12	-159	22	-27

-10 6 1

1	447	470	-21
2	221	221	0
3	743	771	-24
4	171	188	-8
5	470	461	7
6	108	155	-16
7	392	387	3
8	658	666	-6
9	-62	173	-39
10	64	128	-13
11	107	120	-2
12	326	312	7

-10 7 1

1	644	658	-12
2	187	183	2
3	258	250	5
4	135	146	-4
5	737	734	2
6	522	537	-11
7	90	97	-1
8	413	440	-18
9	-115	67	-21
10	430	430	0
11	227	230	-1

-10 8 1

1	267	241	16
2	616	638	-18
3	423	443	-16
4	-63	4	-6
5	299	303	-2
6	-56	38	-6
7	295	301	-3
8	691	677	10
9	186	169	6
10	231	262	-14
11	-127	2	-17

-10 9 1

1	389	385	2
2	372	382	-7
3	120	55	15
4	410	431	-15
5	501	496	3
6	206	191	6
7	149	119	9
8	330	352	-13
9	197	174	8
10	373	360	7

-10 10 1

1	-49	2	-3
2	636	636	0
3	287	259	16
4	58	113	-12
5	261	224	18
6	-74	98	-19
7	499	498	0
8	407	378	16
9	-91	55	-12

-10 11 1

1	223	166	26
2	322	323	-1
3	32	21	0
4	292	269	12
5	486	501	-10
6	99	5	11
7	303	297	3

-10 12 1

1	117	147	-9
2	414	426	-8
3	257	231	12
4	113	80	7
5	252	270	-9
6	343	321	12

-10 13 1

1	92	18	9
2	147	137	3
3	106	43	10

-9 1 1

1	589	596	-5
2	101	98	0
3	370	374	-2
4	348	352	-2
5	741	732	7
6	862	875	-10
7	-110	45	-19
8	473	484	-7
9	-87	59	-14
10	737	718	13
11	274	304	-16
12	-129	141	-42
13	398	406	-4
14	-165	59	-33

-9 2 1

1	207	262	-29
2	899	889	7
3	412	434	-14
4	-131	109	-41
5	-33	84	-11
6	358	399	-30
7	520	520	0
8	705	735	-23

9	-172	2	-40
10	285	317	-18
11	-105	52	-16
12	358	386	-16
13	570	551	12
14	-130	73	-23

-9 3 1

1	194	167	13
2	400	380	14
3	184	196	-5
4	887	891	-3
5	957	969	-9
6	515	562	-38
7	340	366	-17
8	-106	40	-17
9	210	246	-17
10	608	590	12
11	303	333	-17
12	292	318	-13
13	353	368	-8
14	202	193	3

-9 4 1

1	94	28	13
2	470	432	29
3	1085	1067	13
4	400	401	0
5	793	810	-14
6	133	160	-11
7	811	816	-4
8	283	327	-27
9	-90	111	-25
10	128	201	-25
11	-192	1	-45
12	512	508	2
13	490	502	-7
14	38	94	-7

-9 5 1

1	256	257	0
2	117	27	20
3	310	310	0
4	906	891	11
5	900	920	-15
6	157	157	0
7	549	566	-13
8	25	120	-17
9	329	360	-19
10	415	419	-2
11	-80	80	-14
12	264	318	-26
13	212	182	10

-9 6 1

1	570	544	21
2	783	771	9
3	642	642	0
4	453	465	-10
5	73	113	-11
6	316	322	-3
7	912	898	10
8	435	443	-5
9	37	121	-16
10	229	279	-25
11	255	282	-13
12	555	532	14
13	171	229	-20

-9 7 1

1	191	187	2
2	312	320	-6
3	94	102	-2
4	855	868	-10
5	435	446	-8
6	-105	35	-19
7	413	428	-11
8	-94	45	-14
9	471	466	3
10	475	450	15
11	147	171	-7
12	312	305	3

-9 8 1

1	699	724	-22
2	641	625	14
3	149	111	14
4	329	335	-4
5	58	90	-7
6	342	351	-5
7	747	746	0
8	314	289	14
9	260	264	-1
10	-42	93	-12
11	433	422	6

-9 9 1

1	482	474	7
2	268	231	23
3	327	331	-2
4	602	619	-13
5	137	166	-11
6	76	63	2
7	365	367	-1
8	34	109	-13
9	477	471	3
10	227	242	-6
11	108	151	-11

-9 10 1

1	799	782	13
2	486	469	12
3	76	3	8
4	302	295	4
5	148	168	-7
6	482	489	-4
7	489	496	-5
8	-129	19	-21
9	-119	121	-33

-9 11 1

1	376	396	-15
2	116	96	6
3	214	204	5
4	545	526	13
5	54	100	-9
6	364	345	11
7	127	116	2
8	387	378	5

-9 12 1

1	470	491	-16
2	207	241	-17
3	153	79	20
4	242	255	-6
5	150	145	1
6	589	564	16
7	232	230	0

-9 13 1

1	235	211	11
2	136	49	19
3	163	136	8
4	347	349	-1

-9 14 1

1	481	436	29

-8 1 1

1	127	140	-5
2	518	498	16
3	731	745	-11
4	625	617	6
5	835	835	0
6	-81	48	-12
7	564	566	0
8	256	276	-12
9	825	838	-10
10	480	498	-13
11	108	133	-7
12	452	440	8
13	-134	2	-21
14	377	369	4
15	298	293	2

-8 2 1

1	1074	1052	15
2	1084	1081	1
3	219	243	-13
4	-80	116	-28
5	175	207	-14
6	749	771	-16
7	941	939	0
8	379	436	-44
9	345	363	-12
10	140	192	-20
11	333	341	-4
12	800	798	1
13	102	128	-6
14	357	334	12
15	177	193	-5

-8 3 1

1	172	135	18
2	463	446	13
3	913	907	4
4	1083	1073	7
5	510	499	8
6	494	484	7
7	350	284	37
8	134	211	-34
9	636	632	2
10	463	478	-10
11	-144	21	-27
12	466	443	15
13	-152	68	-32
14	540	523	10
15	313	295	8

-8 4 1

1	391	353	31
2	1145	1136	6
3	262	222	24
4	492	491	1
5	71	89	-4
6	1311	1298	8
7	575	563	9
8	120	153	-11
9	321	300	12
10	-133	72	-29
11	375	360	8
12	604	594	7
13	-63	2	-4
14	310	313	-1

-8 5 1

1	81	79	0
2	460	429	25
3	639	635	3
4	1059	1030	21
5	473	452	15
6	690	682	5
7	159	216	-29
8	565	568	-2
9	738	748	-7
10	-90	95	-22
11	209	245	-16
12	197	223	-10
13	366	355	5
14	418	419	0

-8 6 1

1	568	568	0
2	949	930	15
3	329	300	20
4	123	132	-3
5	320	317	2
6	907	890	13
7	623	622	0
8	56	101	-9
9	395	402	-4
10	85	152	-19
11	589	570	13
12	272	261	5
13	196	234	-15

-8 7 1

1	271	266	3
2	274	207	41
3	973	968	4
4	477	480	-2
5	-39	75	-12
6	364	380	-12
7	-89	15	-12
8	441	427	10
9	722	703	14
10	-97	36	-13
11	225	258	-15
12	-132	51	-23
13	406	405	0

-8 8 1

1	807	807	0
2	412	393	16
3	509	494	13
4	152	156	-1
5	464	473	-7
6	685	682	2
7	357	361	-3
8	262	266	-2
9	342	352	-6
10	323	308	8
11	364	383	-11
12	98	103	-1

-8 9 1

1	340	335	3
2	175	155	10
3	853	860	-5
4	226	224	1
5	-84	19	-11
6	255	248	4
7	144	158	-5
8	582	589	-5
9	457	457	0
10	62	53	1
11	144	177	-10

-8 10 1

1	593	587	5

2	166	161	2
3	383	372	8
4	85	111	-7
5	422	436	-10
6	561	547	10
7	87	32	8
8	167	201	-13
9	-106	32	-14
10	202	218	-6

-8 11 1

1	89	106	-4
2	168	183	-7
3	608	613	-4
4	272	257	8
5	203	207	-1
6	224	233	-4
7	452	450	1
8	443	438	2
9	108	134	-6

-8 12 1

1	225	207	9
2	135	110	7
3	263	270	-3
4	25	20	0
5	455	451	2
6	443	409	22
7	179	198	-7

-8 13 1

1	112	36	14
2	217	190	12
3	394	391	1
4	19	60	-3
5	70	134	-15

-8 14 1

1	151	71	20
2	135	120	4

-7 1 1

1	899	908	-7
2	660	673	-10
3	899	903	-3
4	1044	1055	-8
5	46	128	-21
6	336	349	-8
7	325	337	-8
8	835	846	-7
9	819	828	-7
10	-122	0	-22
11	535	549	-11
12	-168	13	-39
13	554	565	-7
14	558	517	27
15	-122	22	-17
16	192	222	-11

-7 2 1

1	1691	1707	-9
2	192	209	-9
3	-77	38	-12
4	430	426	3
5	891	904	-10
6	961	965	-2
7	647	664	-12
8	293	321	-17
9	-69	74	-16
10	256	294	-23
11	803	809	-4
12	364	385	-13
13	421	432	-7
14	403	395	4
15	307	288	9

-7 3 1

1	1022	1008	11
2	709	687	19
3	920	920	0
4	904	911	-6
5	523	529	-4
6	474	460	10
7	127	126	0
8	763	764	0
9	239	265	-15
10	-124	79	-31
11	436	430	3
12	-103	46	-16
13	588	588	0
14	476	458	11
15	43	162	-25

-7 4 1

1	1584	1580	2
2	271	265	4
3	365	348	14
4	139	164	-12
5	1421	1411	6
6	969	977	-5
7	152	198	-20
8	270	279	-5
9	-161	78	-51
10	435	440	-3
11	591	588	2
12	-98	20	-12
13	353	375	-13
14	79	177	-26
15	160	196	-12

-7 5 1

1	652	630	20
2	903	874	24
3	966	966	0
4	712	710	1
5	679	682	-2
6	306	309	-2
7	403	410	-4
8	1080	1069	7
9	272	280	-5
10	-129	49	-27
11	76	117	-9
12	415	401	8
13	581	565	10
14	178	238	-23

-7 6 1

1	1019	1011	5
2	313	277	27
3	367	332	27
4	114	104	3
5	1064	1064	0
6	636	640	-3
7	-82	70	-19
8	672	664	5
9	-56	48	-7
10	516	521	-3
11	454	451	1
12	291	295	-1
13	161	201	-14
14	-151	41	-26

-7 7 1

1	239	247	-6
2	889	893	-3
3	810	800	7
4	238	237	0
5	344	340	2
6	66	63	0
7	475	461	11
8	852	847	3
9	209	245	-19
10	311	329	-10
11	-111	37	-17
12	468	457	7
13	460	423	22

-7 8 1

1	698	671	22
2	603	580	19
3	125	32	22
4	435	432	3
5	830	843	-11
6	271	292	-14
7	-98	71	-23
8	421	438	-12
9	268	257	5
10	469	457	8
11	256	241	7
12	174	213	-15
13	251	259	-3

-7 9 1

1	-60	37	-10
2	973	980	-5
3	466	478	-11
4	-16	53	-5
5	221	243	-13
6	206	195	6
7	502	529	-21
8	642	631	8
9	-109	3	-15
10	-108	90	-24
11	-105	14	-12
12	386	382	2

-7 10 1

1	267	249	12
2	584	586	-2
3	68	99	-8
4	433	411	17
5	567	588	-17
6	30	46	-1
7	349	360	-7
8	85	126	-10
9	278	268	5
10	287	258	13

-7 11 1

1	273	249	15
2	722	733	-8
3	324	334	-7
4	131	26	22
5	336	334	0
6	468	475	-4
7	614	614	0
8	297	249	24
9	-106	51	-16

-7 12 1

1	107	82	6
2	195	200	-2
3	143	92	15
4	307	295	7
5	457	460	-2
6	167	185	-6
7	251	259	-3
8	-113	13	-14

-7 13 1

1	265	264	0
2	511	507	2
3	195	152	16
4	-41	5	-2
5	-77	31	-8
6	304	319	-8

-7 14 1

1	153	133	6
2	331	299	18
3	222	182	16

-6 1 1

1	505	515	-9
2	996	1015	-15
3	1259	1270	-8
4	-19	97	-17
5	187	193	-3
6	423	409	11
7	971	968	2
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10	504	490	11
11	-122	51	-26
12	440	453	-9
13	769	767	1
14	98	140	-11
15	296	305	-5
16	-132	80	-26

-6 2 1

1	249	250	-1
2	88	136	-20
3	382	368	11
4	1010	1025	-11
5	1043	1033	7
6	697	719	-17
7	756	735	16
8	398	410	-8
9	195	235	-20
10	685	676	7
11	436	459	-17
12	173	200	-12
13	604	585	14
14	231	255	-11
15	464	446	11
16	97	104	-1

-6 3 1

1	719	708	10
2	857	854	2
3	1520	1519	0
4	370	380	-8
5	394	375	14
6	98	109	-3
7	1436	1406	18
8	621	623	-1
9	-104	98	-28
10	318	334	-11
11	-106	126	-38
12	616	620	-3
13	715	696	13
14	-127	59	-23
15	275	279	-1
16	-132	38	-20

-6 4 1

1	383	377	6
2	143	123	10
3	116	101	6

[(Au(dcpe))2 mu-(dcpe)]2+ 2[Au(CN)2]-

4	1518	1491	17
5	1060	1065	-3
6	324	326	-1
7	837	805	24
8	67	113	-11
9	354	350	2
10	759	756	2
11	100	193	-34
12	406	411	-3
13	273	284	-5
14	309	300	4
15	296	340	-24

-6 5 1

1	606	602	3
2	755	765	-9
3	989	1001	-9
4	446	436	9
5	210	182	16
6	719	712	5
7	1217	1202	10
8	559	557	1
9	-108	57	-23
10	396	395	0
11	335	355	-13
12	638	645	-4
13	276	251	11
14	-97	110	-23
15	208	221	-5

-6 6 1

1	185	171	9
2	319	290	23
3	310	274	28
4	1332	1347	-10
5	279	270	6
6	217	194	12
7	565	560	4
8	88	110	-6
9	752	732	15
10	576	584	-6
11	182	192	-4
12	211	230	-8
13	-127	47	-21
14	299	289	4

-6 7 1

1	1000	1005	-4
2	951	962	-9
3	420	427	-5
4	424	421	2
5	261	264	-2
6	433	414	14
7	1270	1264	4
8	265	259	4
9	278	304	-17
10	153	163	-3
11	499	458	28
12	442	444	-1
13	146	161	-4
14	250	264	-6

-6 8 1

1	596	580	14
2	210	163	26
3	307	310	-2
4	773	762	8
5	366	361	4
6	-44	16	-3
7	460	473	-11
8	118	152	-12
9	643	623	15
10	414	417	-1
11	-48	105	-15
12	183	226	-17
13	-91	70	-14

-6 9 1

1	1097	1077	14
2	576	555	17
3	8	69	-8
4	362	366	-3
5	464	456	6
6	502	507	-4
7	667	652	12
8	80	22	7
9	109	162	-17
10	-145	19	-28
11	306	301	2
12	416	388	16

-6 10 1

1	472	480	-7
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3	192	200	-4
4	777	798	-17
5	139	75	19
6	312	333	-13
7	180	164	6
8	470	469	0
9	309	318	-5
10	243	246	-1
11	-79	98	-17

-6 11 1

1	691	726	-31
2	400	419	-15
3	209	187	11
4	327	328	0
5	220	238	-9
6	594	607	-10
7	345	339	3
8	117	132	-4
9	95	101	-1

-6 12 1

1	358	362	-3
2	86	40	8
3	205	226	-11
4	516	520	-2
5	-17	33	-1
6	240	223	8
7	-30	30	-2
8	392	375	10

-6 13 1

1	546	538	6
2	165	150	6
3	99	20	11
4	125	139	-4
5	304	274	16
6	353	344	5

-6 14 1

1	302	287	8
2	161	160	0
3	353	321	19

-5 1 1

1	955	957	-1
2	1906	1949	-24
3	-74	73	-21
4	-117	24	-30
5	393	387	5
6	1128	1137	-6
7	1184	1167	12
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9	496	499	-2
10	-144	22	-33
11	525	543	-14
12	919	885	25
13	239	273	-18
14	372	392	-12
15	284	298	-7
16	266	269	-1
17	298	293	2

-5 2 1

1	149	104	24
2	852	825	23
3	968	957	9
4	844	849	-4
5	1010	1003	5
6	680	661	16
7	351	353	-1
8	73	108	-9
9	911	889	16
10	176	256	-41
11	55	102	-10
12	654	664	-7
13	-124	60	-25
14	670	636	24
15	323	297	14
16	168	222	-20

-5 3 1

1	1702	1662	24
2	1816	1794	12
3	118	106	5
4	-59	104	-30
5	46	80	-8
6	1596	1603	-4
7	1069	1077	-5
8	237	246	-4
9	-97	27	-14
10	338	346	-4
11	533	567	-27
12	1004	977	19
13	-119	62	-23
14	393	387	3
15	61	106	-8
16	306	297	4

-5 4 1

1	121	73	22
2	1208	1152	42
3	806	808	-1
4	1433	1417	10
5	542	508	30
6	1427	1400	17
7	219	205	8
8	197	221	-12
9	639	595	32
10	411	416	-3
11	343	343	0
12	303	296	3
13	537	519	12
14	495	491	2
15	262	289	-13
16	184	146	11

-5 5 1

1	373	372	0
2	2098	2085	6
3	149	63	36
4	322	278	35
5	452	453	-1
6	1454	1432	13
7	486	494	-6
8	198	213	-7
9	617	597	16
10	235	245	-5
11	587	565	16
12	321	306	8
13	136	190	-20
14	192	211	-7
15	-94	121	-25

-5 6 1

1	405	388	17
2	89	7	17
3	1654	1657	-1
4	682	646	31
5	277	293	-12
6	340	341	0
7	250	243	4
8	713	698	11
9	1005	985	15
10	171	168	1
11	212	241	-14
12	-106	28	-15
13	479	452	17
14	349	341	4
15	121	168	-13

-5 7 1

1	1143	1146	-2
2	790	796	-4
3	778	763	13
4	426	435	-8
5	462	443	15
6	1016	1017	0
7	669	683	-12
8	185	189	-1
9	365	366	-1
10	423	418	3
11	601	605	-2
12	106	207	-35
13	162	229	-26
14	154	185	-10

-5 8 1

1	522	532	-9
2	177	136	21
3	1132	1141	-6
4	146	136	4
5	138	136	0
6	541	547	-5
7	192	177	7
8	521	504	13
9	438	462	-18
10	79	109	-7
11	113	136	-6
12	-124	10	-18
13	483	474	5

-5 9 1

1	876	876	0
2	327	341	-11
3	360	328	23
4	155	167	-6
5	757	769	-9
6	957	950	6
7	16	12	0
8	195	198	-1
9	23	75	-6
10	257	258	0
11	308	323	-8
12	155	145	3

-5 10 1

1	113	128	-6

[(Au(dcpe))2 mu-(dcpe)]2+ 2[Au(CN)2]- Page 6

2	110	105	1
3	872	908	-30
4	380	382	-1
5	208	210	-1
6	188	223	-18
7	530	517	9
8	553	536	12
9	304	308	-2
10	-99	8	-11
11	-84	79	-14

-5 11 1

1	210	193	10
2	118	67	14
3	399	405	-4
4	215	199	7
5	410	412	-1
6	509	518	-6
7	171	210	-16
8	147	188	-15
9	-80	37	-9
10	280	312	-16

-5 12 1

1	111	52	13
2	332	335	-1
3	512	539	-21
4	111	76	8
5	152	144	2
6	131	65	15
7	427	421	3
8	377	363	8

-5 13 1

1	154	130	8
2	123	1	19
3	230	235	-2
4	242	231	4
5	318	316	1
6	208	198	4

-5 14 1

1	149	127	7
2	357	336	13
3	347	314	18

-4 1 1

1	2655	2700	-19
2	371	384	-12
3	132	144	-5
4	539	535	3
5	1232	1262	-22
6	1239	1242	-1
7	1093	1106	-9
8	568	576	-7
9	177	198	-10
10	241	283	-26
11	959	925	24
12	321	327	-3
13	289	323	-22
14	445	465	-14
15	227	234	-3
16	351	353	0
17	107	103	0

-4 2 1

1	1240	1221	15
2	1730	1721	5
3	1062	1088	-22
4	1190	1211	-16
5	611	612	0
6	488	475	11
7	128	151	-10
8	1354	1343	7
9	553	542	8
10	134	215	-37
11	497	506	-7
12	-110	2	-18
13	736	713	17
14	541	550	-6
15	121	173	-17
16	168	189	-7
17	-151	25	-26

-4 3 1

1	2266	2232	16
2	246	222	21
3	243	238	3
4	218	239	-16
5	2147	2131	8
6	1253	1256	-1
7	242	259	-12
8	583	583	0
9	120	135	-5
10	308	296	7
11	1007	971	26
12	72	183	-38
13	466	468	-1
14	157	248	-40
15	277	283	-2
16	394	369	14

-4 4 1

1	1004	971	29
2	194	8	80
3	1228	1218	7
4	909	894	13
5	1241	1230	8
6	68	58	2
7	591	608	-14
8	1234	1223	7
9	338	325	9
10	-57	32	-7
11	395	409	-10
12	328	336	-4
13	543	521	15
14	347	362	-9
15	-82	109	-21
16	270	276	-2

-4 5 1

1	1587	1583	2
2	259	207	43
3	102	88	6
4	153	76	34
5	1507	1502	3
6	872	880	-6
7	78	68	2
8	797	761	27
9	360	362	-1
10	782	785	-2
11	583	565	14
12	181	209	-12
13	244	244	0
14	-172	3	-36
15	247	271	-11

-4 6 1

1	500	502	-2
2	1447	1447	0
3	588	589	0
4	536	537	-1
5	381	348	27
6	-47	27	-5
7	244	241	1
8	1426	1400	15
9	260	262	-1
10	411	423	-9
11	94	166	-24
12	581	590	-6
13	413	425	-7
14	104	127	-5
15	153	162	-2

-4 7 1

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-4 8 1

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-4 10 1

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-4 11 1

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-4 14 1

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-3 2 1

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-3 3 1

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3	142	199	-23
4	165	235	-32
5	179	223	-21
6	709	737	-20
7	379	399	-12
8	-33	183	-38
9	464	509	-30
10	-164	53	-33
11	-122	30	-16

10 -1 1

0	252	219	22
1	255	218	23
2	652	664	-9
3	286	274	6
4	590	592	-1
5	545	555	-6
6	692	707	-10
7	-128	106	-31
8	-147	98	-35
9	592	587	3
10	-48	149	-24
11	-127	18	-16

10 0 1

-13	-74	143	-25
-12	-194	58	-46
-11	446	426	11
-10	-160	67	-35
-9	672	674	-1
-8	254	246	4
-7	395	382	8
-6	294	308	-8
-5	-106	26	-19
-4	769	768	1
-3	496	496	0
-2	33	49	-2
-1	277	258	13
0	454	464	-8
1	528	522	4
2	829	822	5
3	-76	26	-9
4	284	318	-20
5	153	188	-13
6	822	825	-1
7	108	150	-11
8	-144	48	-24
9	510	511	0
10	-186	18	-36

10 1 1

-12	351	354	-1
-11	520	549	-19
-10	-73	31	-7
-9	256	265	-4
-8	-79	49	-11
-7	599	582	12
-6	692	701	-7
-5	115	107	2
-4	729	719	8
-3	120	36	20
-2	465	438	21
-1	655	634	18
0	130	99	11
1	283	274	5
2	352	338	9
3	558	557	1
4	535	534	0
5	187	243	-25
6	486	499	-8
7	-141	2	-22
8	42	149	-20
9	679	668	7

10 2 1

-12	357	358	0
-11	151	134	5
-10	267	260	3
-9	386	382	2
-8	287	269	10
-7	274	269	2
-6	360	351	6
-5	225	224	0
-4	896	893	2
-3	218	215	1

-2	155	153	0
-1	271	309	-27
0	452	438	10
1	533	531	1
2	511	495	12
3	339	343	-2
4	106	145	-12
5	-102	13	-13
6	605	595	6
7	32	153	-23
8	-40	99	-11

10 3 1

-11	304	252	25
-10	122	146	-7
-9	169	162	2
-8	129	159	-10
-7	533	519	10
-6	457	443	10
-5	106	14	15
-4	501	492	6
-3	189	143	20
-2	461	469	-6
-1	571	562	7
0	239	205	18
1	277	302	-16
2	-77	52	-12
3	582	593	-8
4	209	222	-6
5	150	176	-9
6	255	281	-12
7	-59	108	-15

10 4 1

-10	332	311	11
-9	354	320	19
-8	22	8	0
-7	390	352	24
-6	114	44	14
-5	355	346	6
-4	576	553	17
-3	109	75	8
-2	109	130	-6
-1	290	270	11
0	531	525	4
1	561	550	8
2	134	92	11
3	459	464	-3
4	-8	39	-1
5	-18	29	-1

10 5 1

-8	257	239	8
-7	540	526	9
-6	92	90	0
-5	182	189	-3
-4	233	235	-1
-3	187	157	11
-2	339	332	4
-1	429	424	3
0	287	268	10
1	224	190	15
2	206	146	22
3	603	594	6

10 6 1

-4	356	363	-4
-3	86	33	7
-2	207	145	23
-1	80	47	5

11 -13 1

0	466	442	16

1	192	193	0
2	174	113	20
3	287	249	20
4	321	311	5

11 -12 1

0	297	324	-16
1	123	65	13
2	269	274	-2
3	287	278	5
4	207	216	-4
5	237	204	15
6	163	113	16
7	482	498	-11

11 -11 1

0	553	560	-5
1	177	109	24
2	199	167	14
3	106	69	8
4	315	291	14
5	308	282	15
6	192	152	16
7	552	555	-2
8	167	69	28
9	185	146	14

11 -10 1

0	365	369	-3
1	441	436	3
2	343	340	1
3	224	215	4
4	261	244	10
5	167	168	0
6	160	100	19
7	611	628	-13
8	110	57	11
9	49	53	0

11 -9 1

0	522	536	-11
1	231	241	-5
2	248	269	-13
3	87	91	0
4	617	599	14
5	165	171	-2
6	193	159	15
7	459	456	2
8	113	64	11
9	110	130	-5
10	484	477	4

11 -8 1

0	240	244	-2
1	522	514	6
2	563	571	-6
3	250	212	22
4	560	579	-16
5	125	38	20
6	363	324	26
7	596	608	-9
8	95	107	-3
9	139	113	7
10	407	397	6
11	310	306	2

11 -7 1

0	470	477	-5
1	275	271	2
2	371	351	14
3	148	127	8
4	710	719	-7

5	112	34	16	9	-142	133	-39	6	-46	95	-11	4	219	197	11
6	247	238	5	10	-184	56	-39					5	315	279	22
7	537	505	24						11 3 1			6	662	637	19
8	295	259	20		11 -1 1							7	176	151	9
9	298	265	18					-8	299	301	0	8	174	161	5
10	457	424	21	0	294	320	-22	-7	273	262	5	9	374	345	17
11	328	322	3	1	576	583	-6	-6	96	11	11				
				2	238	261	-12	-5	484	470	10		12 -7 1		
	11 -6 1			3	470	492	-15	-4	78	26	7				
				4	537	544	-4	-3	342	332	6	0	292	288	3
0	114	40	17	5	398	416	-11	-2	472	442	21	1	326	322	2
1	797	794	2	6	-112	121	-28	-1	39	36	0	2	118	77	11
2	513	506	6	7	-149	104	-34	0	327	307	12	3	639	644	-4
3	153	84	24	8	510	558	-30	1	157	106	15	4	258	211	25
4	460	451	6	9	94	177	-20	2	653	637	11	5	156	118	13
5	189	227	-21					3	372	345	16	6	485	467	13
6	449	450	0		11 0 1			4	-66	138	-26	7	244	237	3
7	604	576	21									8	360	329	18
8	344	328	10	-11	-141	89	-28		11 4 1			9	403	426	-15
9	225	261	-18	-10	413	421	-4								
10	183	195	-4	-9	407	406	0	-6	357	334	14		12 -6 1		
11	402	431	-17	-8	101	180	-24	-5	510	467	29				
				-7	240	270	-15	-4	135	103	9	0	588	591	-1
	11 -5 1			-6	-117	81	-26	-3	150	110	12	1	538	540	-1
				-5	801	796	3	-2	254	222	16	2	66	18	6
0	163	104	23	-4	564	556	6	-1	288	255	17	3	631	602	23
1	696	714	-16	-3	61	78	-3	0	447	439	5	4	105	37	13
2	121	51	19	-2	364	344	14	1	248	167	34	5	267	244	13
3	186	156	15	-1	240	238	1	2	452	420	20	6	476	494	-14
4	727	698	23	0	514	491	18					7	246	188	26
5	-117	37	-24	1	663	674	-9		12 -12 1			8	348	349	-1
6	267	293	-16	2	48	41	0					9	429	417	7
7	536	523	9	3	310	336	-16	0	154	55	23				
8	552	565	-9	4	345	358	-7	1	323	319	2		12 -5 1		
9	408	431	-15	5	698	706	-5	2	337	336	0				
10	80	151	-17	6	183	258	-31	3	149	122	8	0	426	422	3
11	448	448	0	7	-150	56	-27	4	169	117	17	1	151	151	0
				8	440	464	-14					2	363	343	14
	11 -4 1								12 -11 1			3	758	756	1
					11 1 1							4	145	84	18
0	280	253	17					0	61	53	1	5	142	74	19
1	909	919	-8	-10	267	270	-1	1	301	301	0	6	349	337	7
2	412	418	-5	-9	165	182	-6	2	183	118	22	7	386	391	-3
3	75	54	4	-8	291	300	-4	3	233	243	-5	8	488	497	-6
4	343	339	2	-7	414	387	17	4	239	225	7	9	351	368	-9
5	325	339	-9	-6	43	72	-4	5	263	223	20				
6	346	333	8	-5	497	481	11	6	445	405	26		12 -4 1		
7	569	573	-2	-4	237	264	-16								
8	409	400	6	-3	460	439	15		12 -10 1			0	798	801	-2
9	368	339	16	-2	632	627	4					1	245	236	5
10	-104	74	-17	-1	138	69	20	0	347	338	5	2	291	293	-1
11	508	495	7	0	168	192	-11	1	460	460	0	3	457	460	-2
				1	306	301	3	2	216	205	5	4	220	198	10
	11 -3 1			2	301	305	-2	3	248	244	2	5	242	242	0
				3	435	429	3	4	167	127	14	6	496	478	12
0	70	63	1	4	421	414	4	5	150	2	28	7	388	404	-9
1	736	743	-6	5	390	408	-11	6	516	502	10	8	401	398	1
2	98	104	-1	6	-49	72	-7	7	147	119	9	9	-66	135	-23
3	421	417	2	7	94	127	-7	8	102	85	3				
4	571	570	0										12 -3 1		
5	165	234	-30		11 2 1				12 -9 1						
6	175	207	-12									0	584	586	-1
7	153	194	-14	-10	442	427	8	0	214	173	18	1	130	36	22
8	596	600	-3	-9	251	231	9	1	384	374	6	2	451	461	-7
9	275	296	-10	-8	121	136	-4	2	114	121	-2	3	600	588	9
10	-73	147	-27	-7	67	99	-6	3	568	554	10	4	-112	44	-17
				-6	125	63	14	4	254	249	3	5	186	210	-9
	11 -2 1			-5	769	753	12	5	151	65	23	6	215	246	-13
				-4	412	395	11	6	495	477	13	7	539	550	-7
0	558	580	-19	-3	242	248	-3	7	176	124	18	8	403	388	8
1	976	980	-3	-2	240	203	19	8	220	167	22				
2	-180	41	-49	-1	373	366	4						12 -2 1		
3	-94	131	-34	0	588	552	27		12 -8 1						
4	379	412	-20	1	475	455	14					0	779	767	9
5	442	491	-32	2	318	323	-3	0	377	364	9	1	59	58	0
6	370	410	-24	3	164	177	-5	1	555	537	13	2	174	235	-24
7	118	208	-29	4	126	57	13	2	359	343	11	3	343	391	-27
8	516	526	-6	5	417	414	1	3	428	426	0	4	197	274	-31

5	305	355	-25
6	96	173	-19
7	440	466	-15
8	-122	116	-28

12 -1 1

0	400	398	1
1	259	261	-1
2	532	519	9
3	664	659	3
4	179	220	-16
5	225	250	-10
6	-157	119	-39
7	578	587	-5

12 0 1

-9	-139	2	-20
-8	279	295	-7
-7	-113	6	-14
-6	547	539	5
-5	490	505	-11
-4	56	19	3
-3	432	423	6
-2	74	24	6
-1	328	336	-5
0	386	375	7
1	103	61	9
2	333	299	20
3	447	429	11
4	385	411	-15
5	304	341	-19
6	-173	38	-32

12 1 1

-8	357	380	-13
-7	194	195	0
-6	286	300	-7
-5	351	325	15
-4	328	288	23
-3	696	673	17
-2	123	45	16
-1	177	153	9
0	230	176	24
1	339	356	-11
2	459	444	9
3	392	386	4
4	255	250	2
5	-77	91	-14

12 2 1

-6	455	454	0
-5	488	466	15
-4	188	105	27
-3	381	360	13
-2	194	134	22
-1	366	366	0
0	368	355	8
1	313	279	19
2	289	276	6
3	77	74	0

12 3 1

-3	437	418	12
-2	112	73	8
-1	188	178	3

13 -11 1

0	333	325	5
1	218	195	9
2	328	311	10

13 -10 1

0	573	550	16
1	313	292	11
2	189	188	0
3	91	100	-2
4	109	38	12
5	476	444	21

13 -9 1

0	453	422	20
1	183	164	7
2	382	358	15
3	376	367	6
4	114	50	13
5	433	403	20
6	135	78	14

13 -8 1

0	400	392	5
1	347	354	-4
2	377	353	15
3	328	302	15
4	243	163	36
5	529	524	3
6	149	64	21
7	276	240	18

13 -7 1

0	225	200	11
1	160	129	11
2	580	572	6
3	366	320	29
4	72	82	-1
5	437	418	13
6	177	154	8
7	428	385	27

13 -6 1

0	385	411	-18
1	171	120	18
2	467	454	9
3	134	88	13
4	204	166	16
5	411	400	7
6	175	142	11
7	343	319	13

13 -5 1

0	234	219	7
1	208	243	-18
2	670	652	13
3	210	168	18
4	35	39	0
5	218	208	4
6	256	284	-14
7	383	396	-7

13 -4 1

0	359	348	6
1	262	246	9
2	557	541	11
3	103	83	4
4	147	174	-9
5	290	308	-9
6	165	180	-4
7	344	344	0

13 -3 1

0	-43	101	-13
1	534	502	23
2	673	650	16
3	-15	15	0
4	-172	79	-38
5	152	212	-19
6	391	400	-4

13 -2 1

0	184	149	13
1	351	342	5
2	381	392	-6
3	-128	80	-22
4	368	376	-3
5	173	291	-44

13 -1 1

0	174	161	5
1	355	341	8
2	585	557	19
3	-110	20	-13
4	267	304	-17

13 0 1

-5	64	35	3
-4	516	511	3
-3	80	62	3
-2	385	385	0
-1	336	314	13
0	95	87	1
1	245	229	7
2	420	391	18

13 1 1

-2	225	178	20

14 -8 1

0	253	229	11
1	193	171	8
2	387	350	22
3	135	46	18

14 -7 1

0	104	65	7
1	434	423	7
2	435	416	12
3	48	0	2
4	357	322	20

14 -6 1

0	89	51	6
1	427	425	1
2	197	187	4
3	169	161	3
4	414	392	14

14 -5 1

0	240	175	27
1	597	574	16
2	204	171	14
3	185	174	4

14 -4 1

0	126	122	0
1	517	460	24
2	-32	63	-3
3	330	328	1

14 -3 1

0	300	330	-8
1	600	559	18
2	-184	14	-23

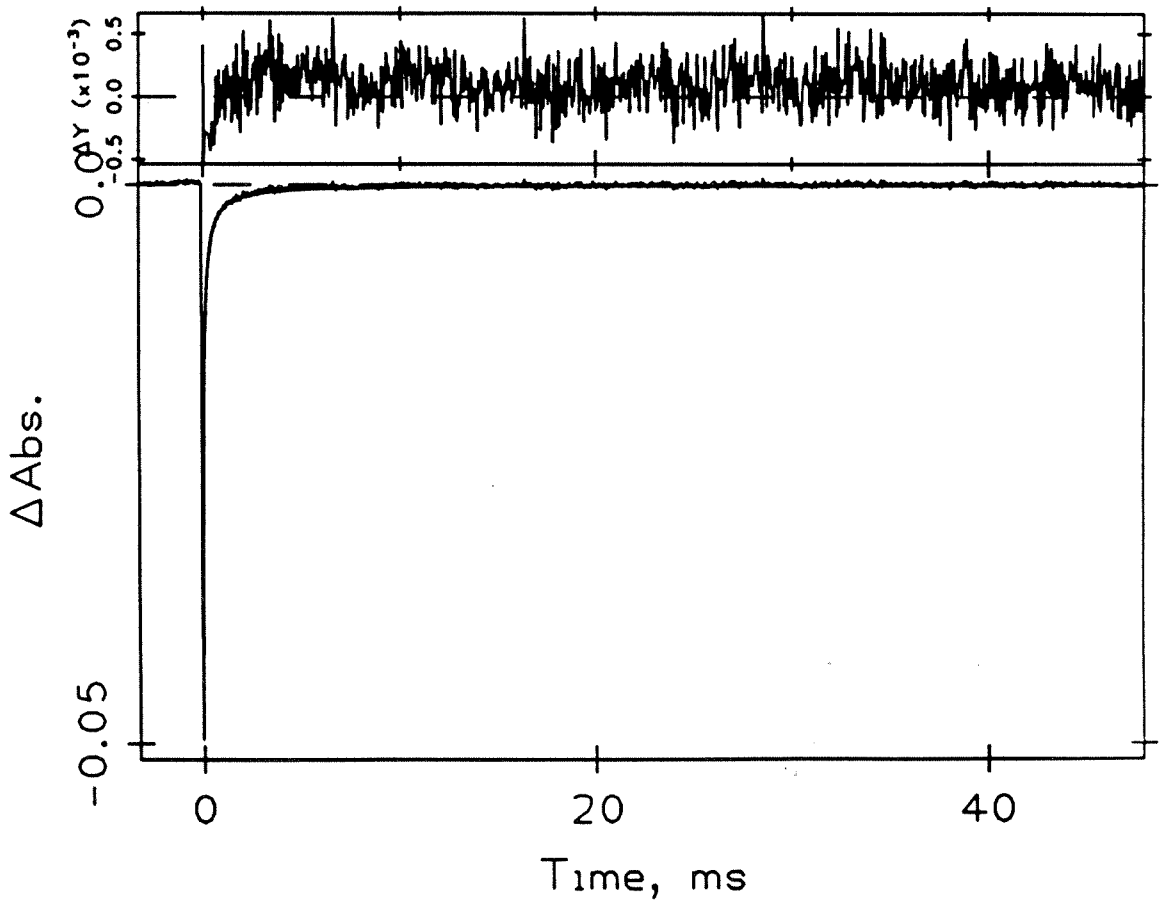
Appendix 3 Absorbance traces forrecombination rates.

```
DATA FILE: num0.000                    USER:
TIME RANGE:  25  ms     INPUT V RANGE:  1.60  V      INPUT OFFSET:       0 %
EXPERIMENT:  TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP   GAINS:  PRE-AMP:     x 100    POST-
NULL OUTPUT
SHOTS PER CYCLE:   50        CYCLES:    1
EXCITATION WAVELENGTH: 532 nm            OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT: tbapf6 0.1M
COMMENT:

                # ---> FIXED PARAMETER;  ! ---> FIXED SIGN

                        y(t) = 1/(C0+C1*t)

              C0 = -3.686E+01
              C1 = -4.257E+05
```

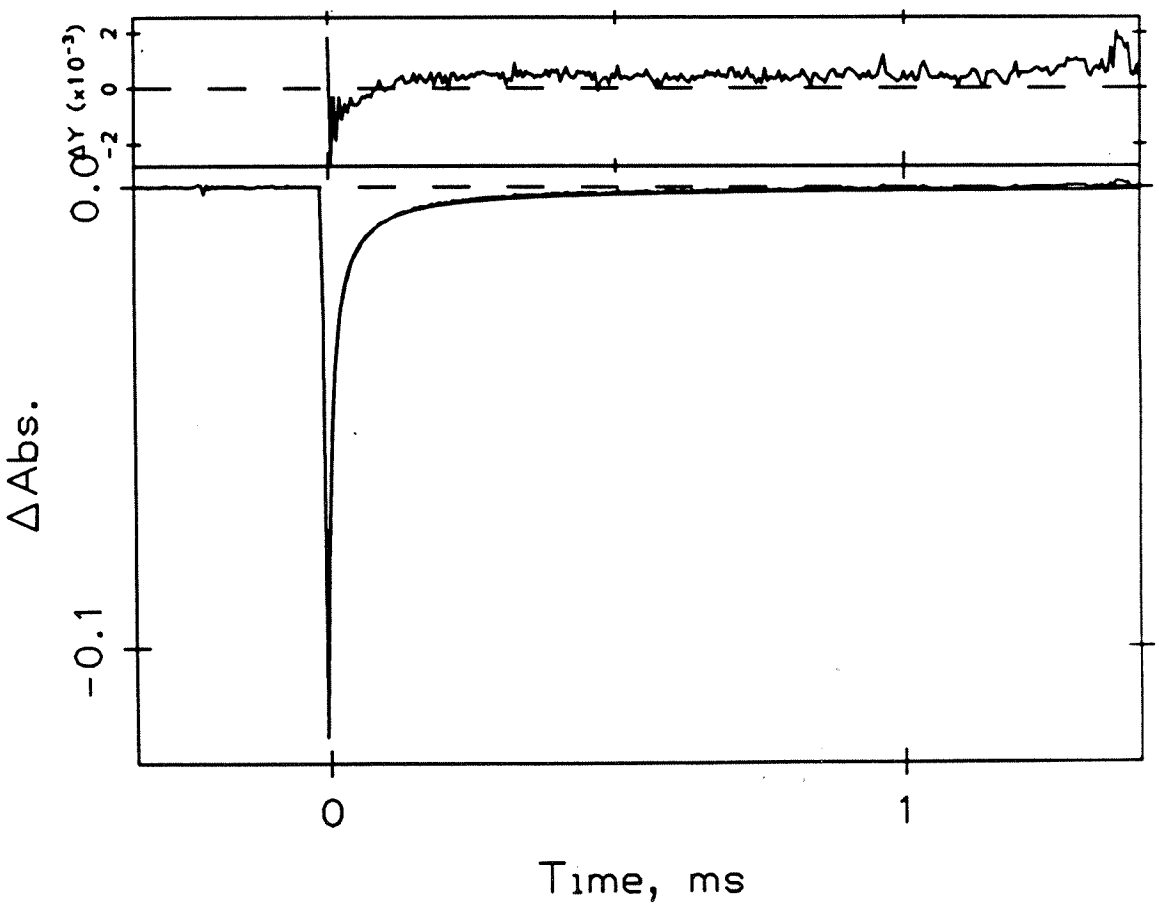


DATA FILE: 251-1.002 USER:
TIME RANGE: 5.0 ms INPUT V RANGE: 1.60 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP GAINS: PRE-AMP: x 100 POST-
NULL OUTPUT
SHOTS PER CYCLE: 20 CYCLES: 6
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

$$y(t) = 1/(C0+C1*t)$$

C0 = -1.273E+01
C1 = -1.257E+06

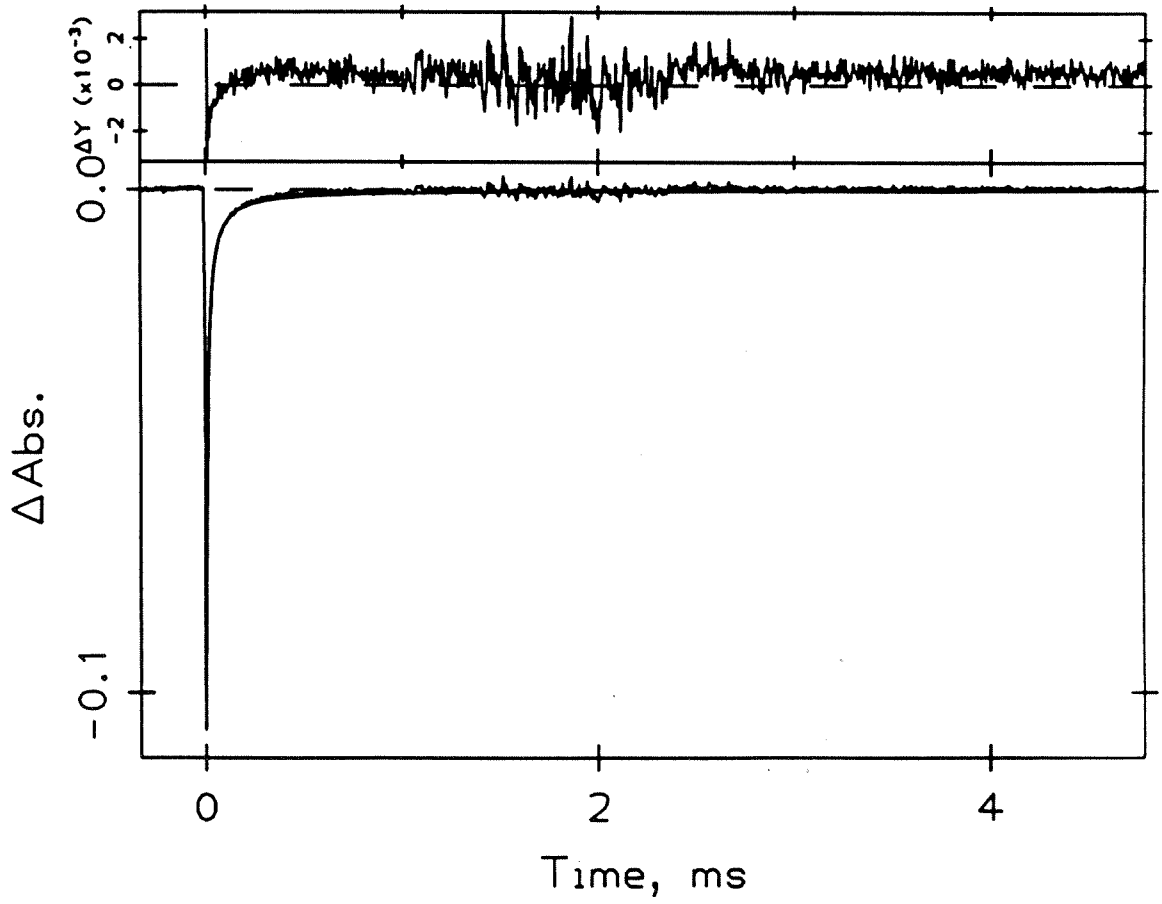


DATA FILE: 251-2.001 USER:
TIME RANGE: 2.5 ms INPUT V RANGE: 1.60 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP GAINS: PRE-AMP: x 100 POST-
NULL OUTPUT
SHOTS PER CYCLE: 20 CYCLES: 2
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

$$y(t) = 1/(C0+C1*t)$$

C0 = -6.842E+00
C1 = -1.408E+06

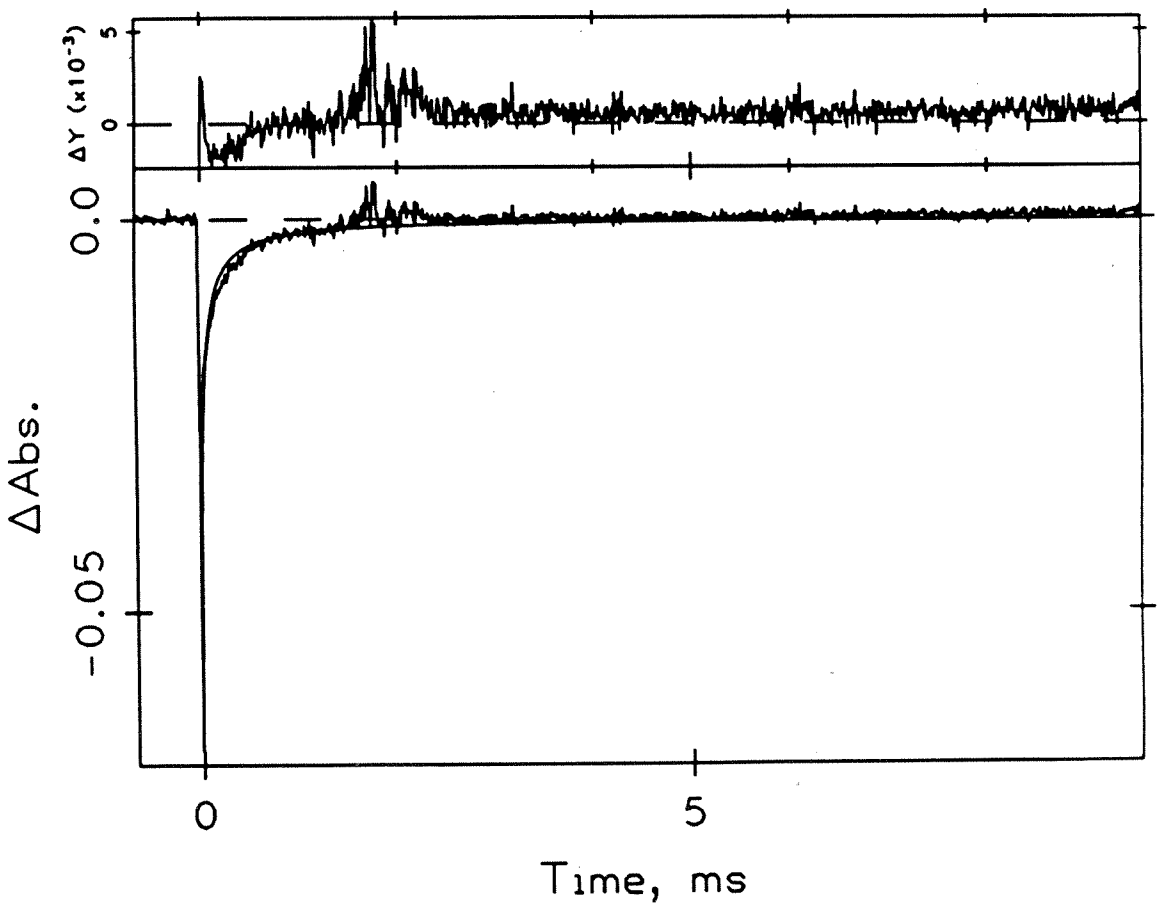


DATA FILE: 251-3.002 USER:
TIME RANGE: 7.5 ms INPUT V RANGE: 1.60 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP GAINS: PRE-AMP: x 100 POST-
NULL OUTPUT
SHOTS PER CYCLE: 20 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

$$y(t) = 1/(C0+C1*t)$$

C0 = -3.045E+01
C1 = -5.434E+05

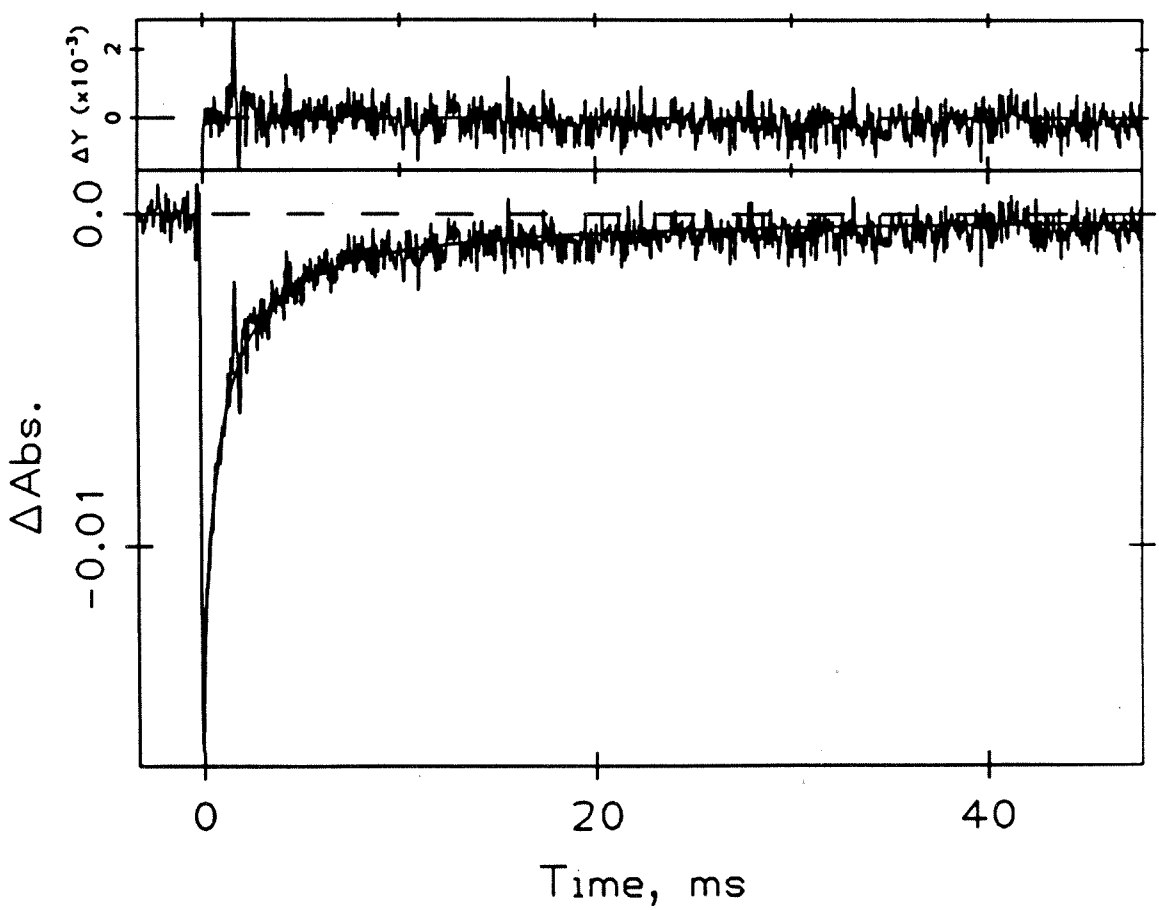


DATA FILE: br211-6.004 USER:
TIME RANGE: 50 ms INPUT V RANGE: 1.60 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP GAINS: PRE-AMP: x 100 POST-
NULL OUTPUT
SHOTS PER CYCLE: 1 CYCLES: 30
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT: 10 mg num 06
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

$$y(t) = 1/(C0+C1*t)$$

C0 = -7.468E+01
C1 = -8.076E+04

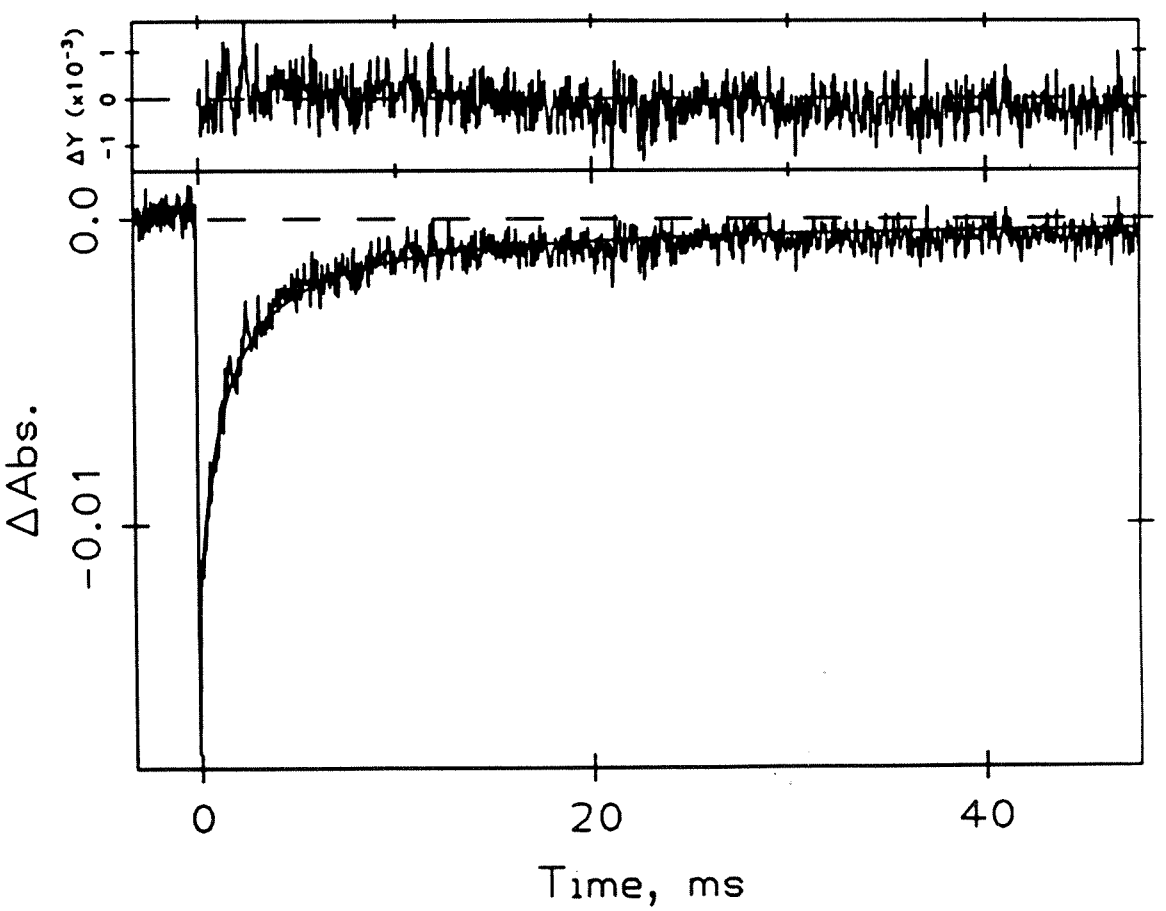


```
DATA FILE: br211-7.001                    USER:
TIME RANGE:   50  ms     INPUT V RANGE:  1.60  V      INPUT OFFSET:       0 %
EXPERIMENT:  TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP   GAINS:  PRE-AMP:     x 100   POST-
NULL OUTPUT
SHOTS PER CYCLE:     1        CYCLES:    30
EXCITATION WAVELENGTH: 532 nm             OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT: 11 mg num 07
COMMENT:

                # ---> FIXED PARAMETER;  ! ---> FIXED SIGN

                        y(t) = 1/(C0+C1*t)

              C0 = -8.217E+01
              C1 = -6.412E+04
```

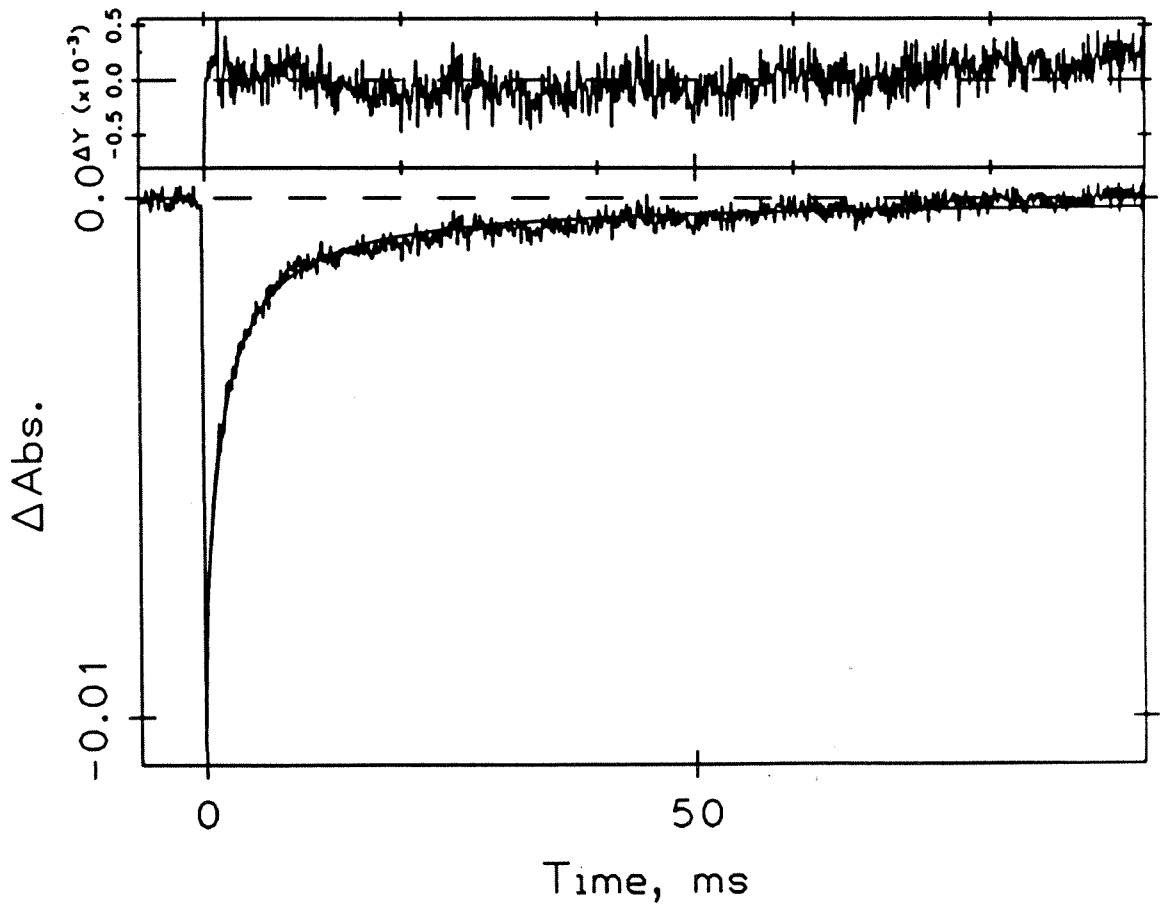


DATA FILE: br211-10.006 USER:
TIME RANGE: 75 ms INPUT V RANGE: 1.60 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
SLOW (100 kHz) VARIABLE GAIN OFFSETTING AMP GAINS: PRE-AMP: x 100 POST-
NULL OUTPUT
SHOTS PER CYCLE: 1 CYCLES: 30
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT: 25 mg num 10
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

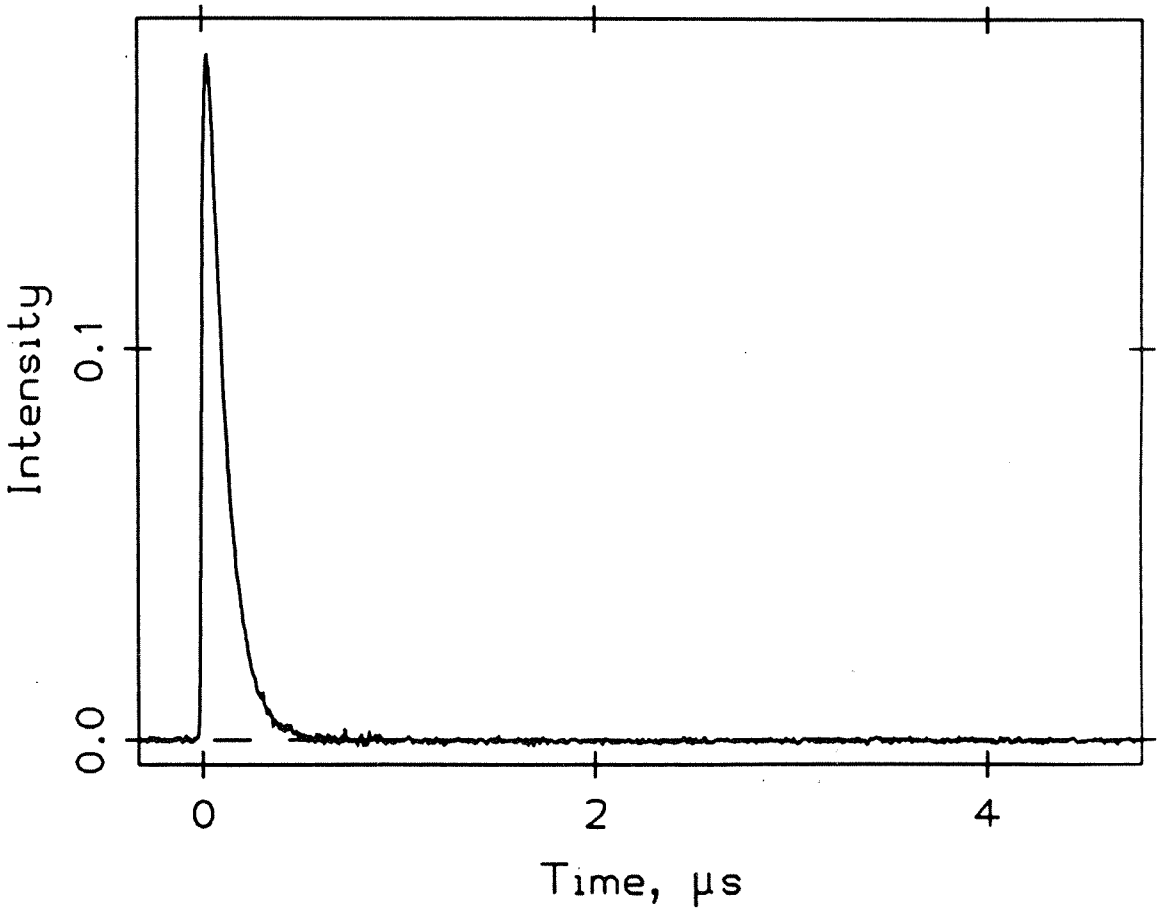
$$y(t) = 1/(C0+C1*t)$$

C0 = -1.181E+02
C1 = -6.187E+04

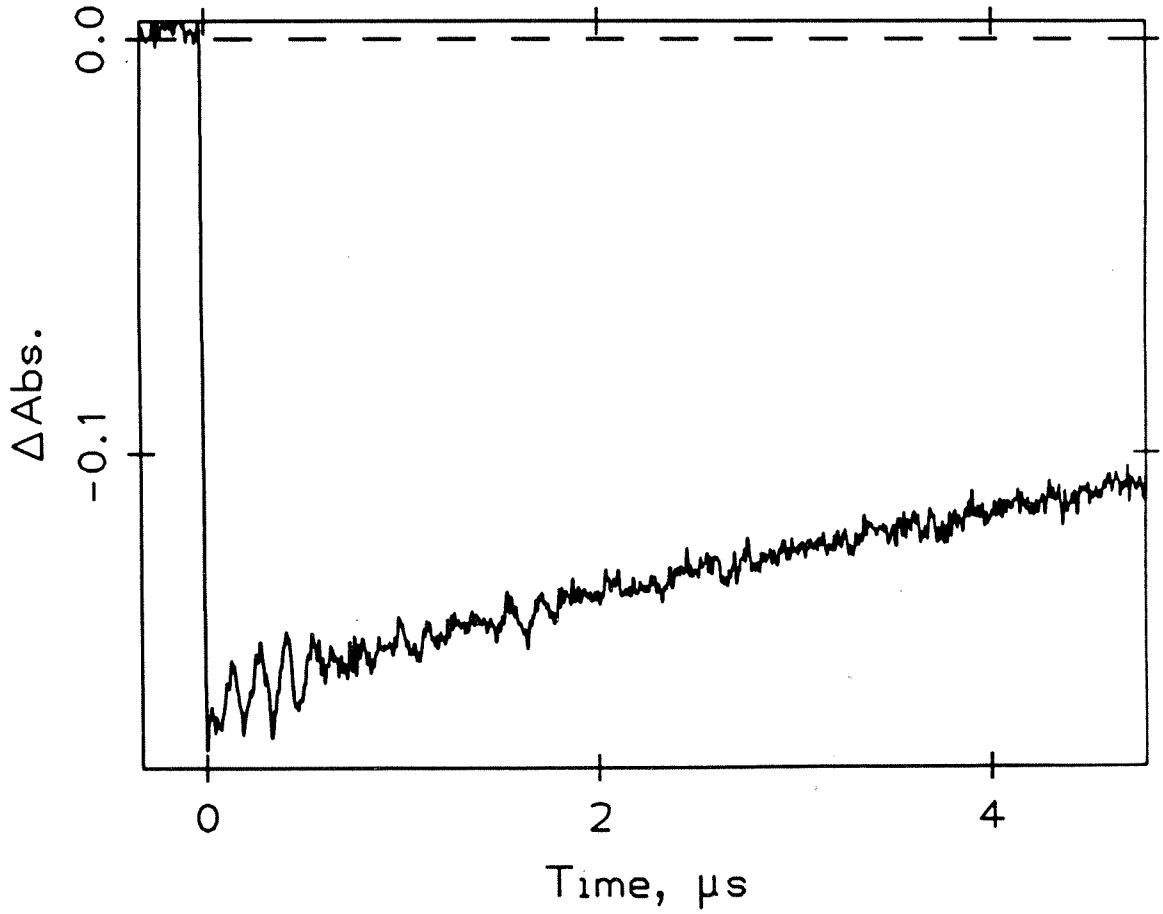


Appendix 4 Absorbance traces used to determine quantum yields.

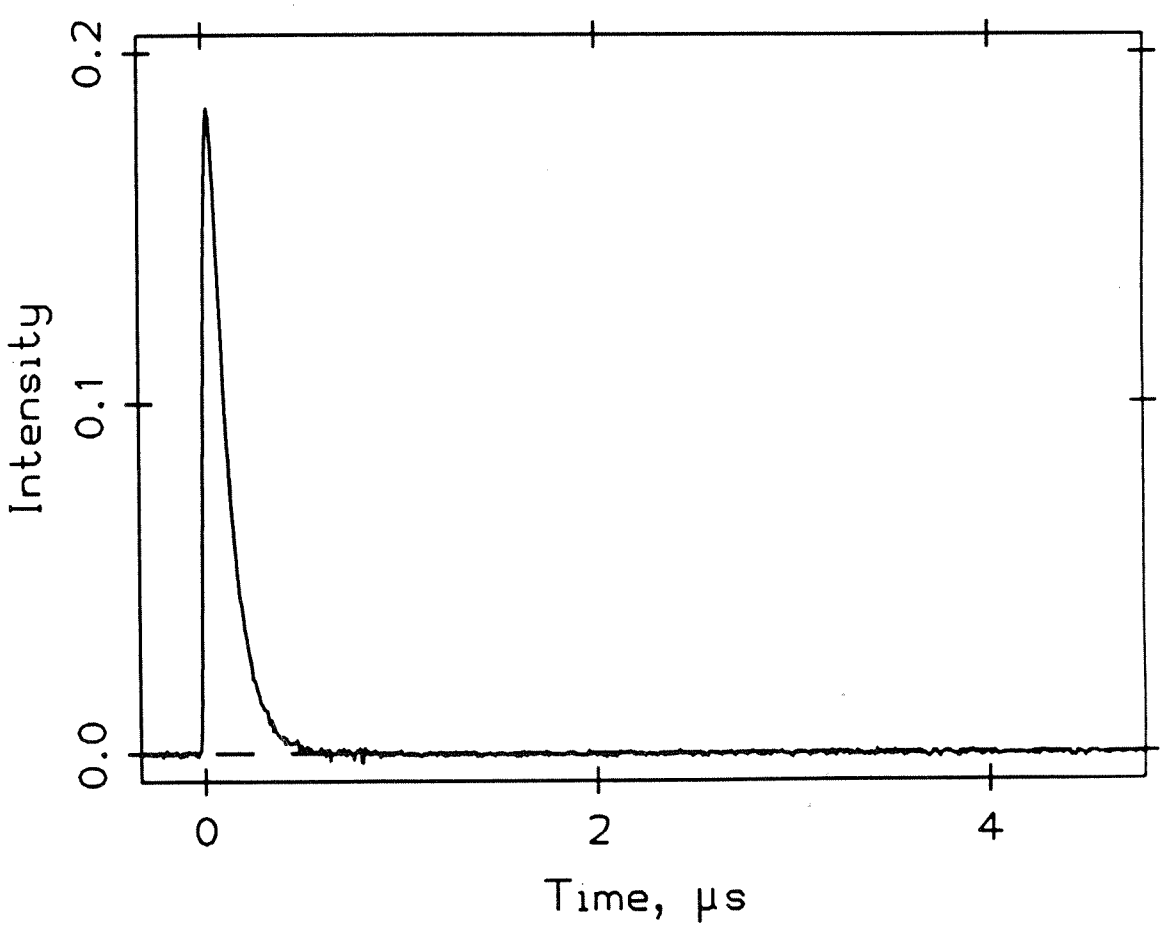
DATA FILE: 247-0.001 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



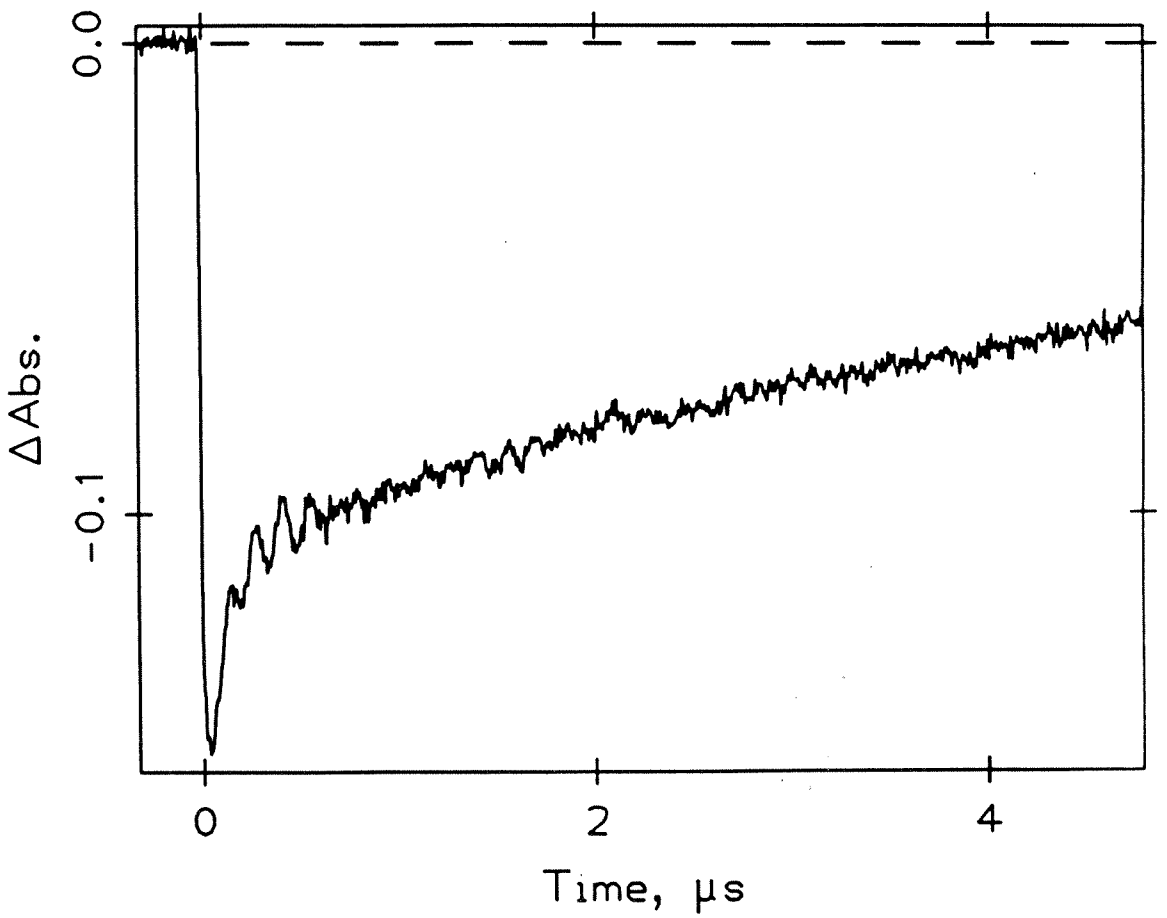
DATA FILE: 247-0.006 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



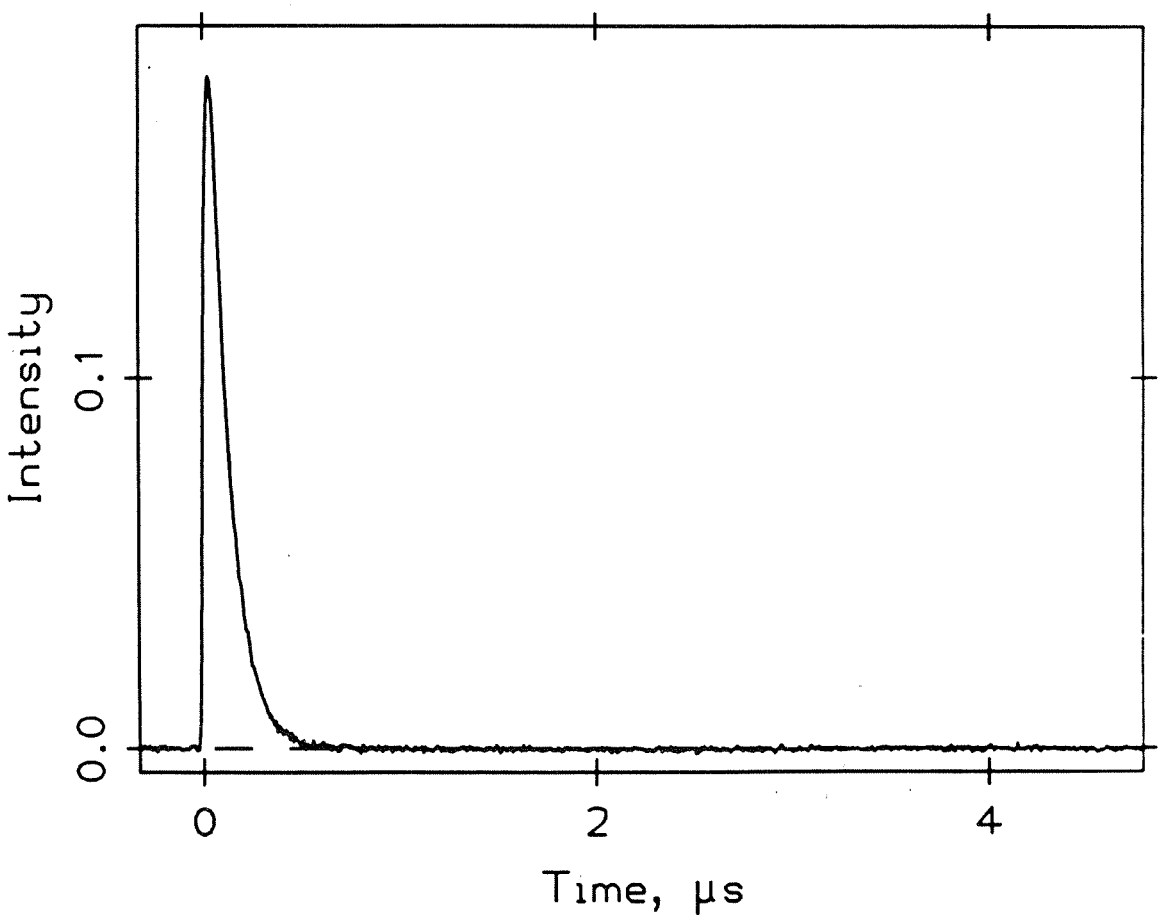
DATA FILE: 247-1.001 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



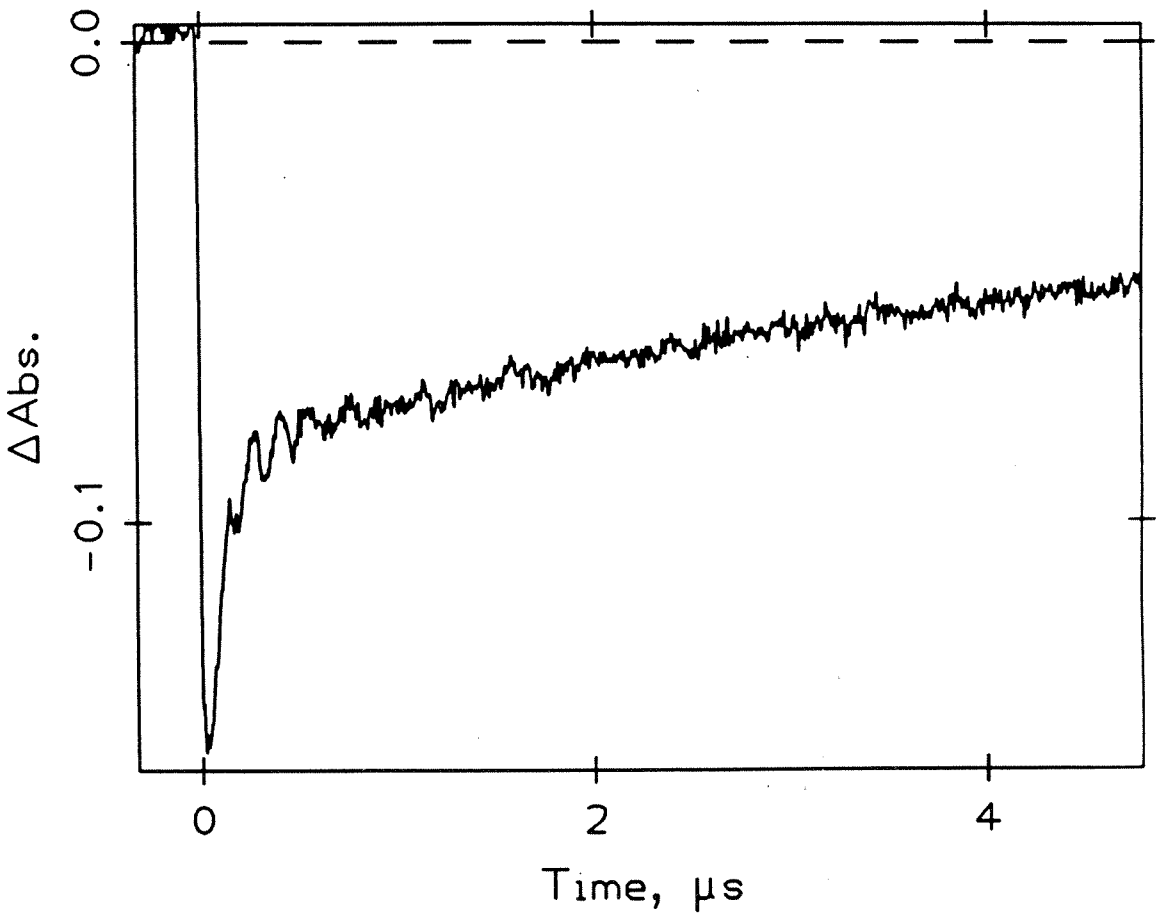
DATA FILE: 247-1.003 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 2
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



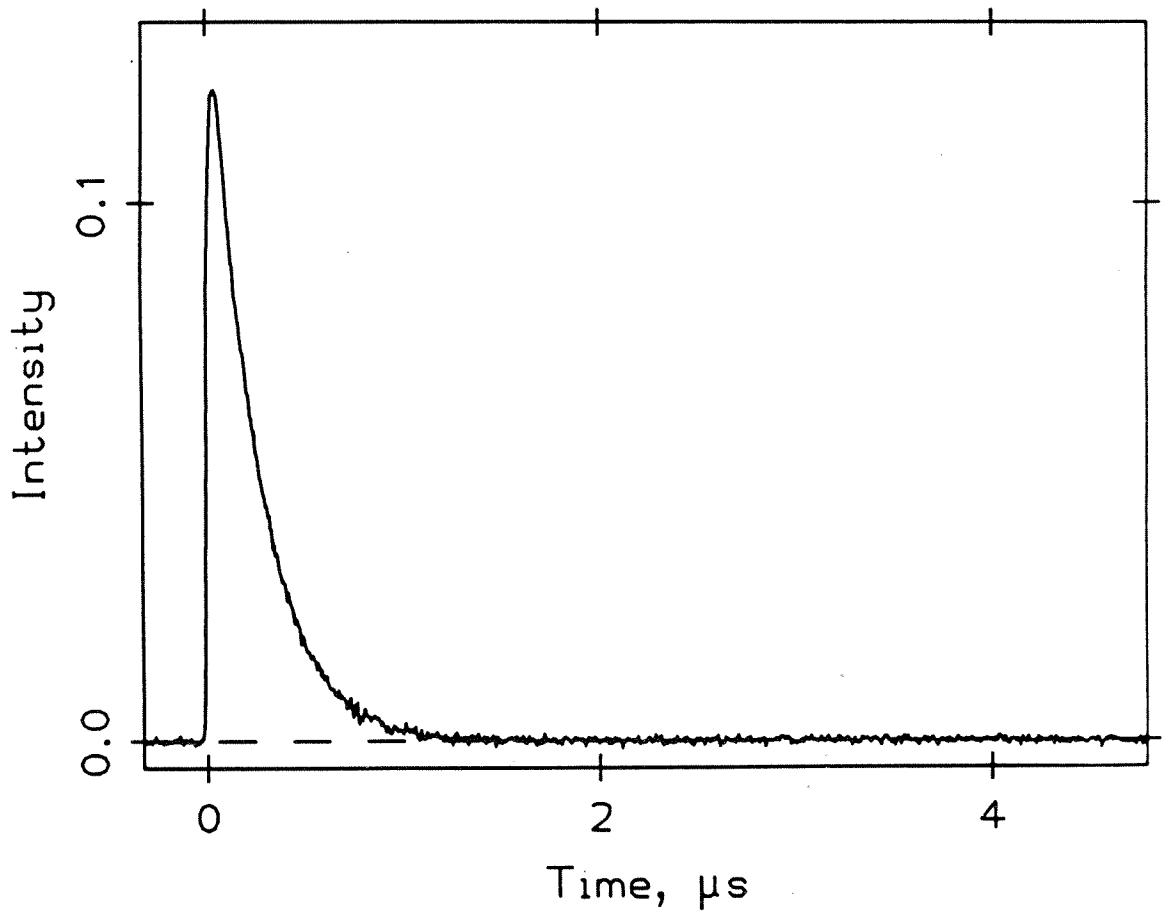
DATA FILE: 247-2.002 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



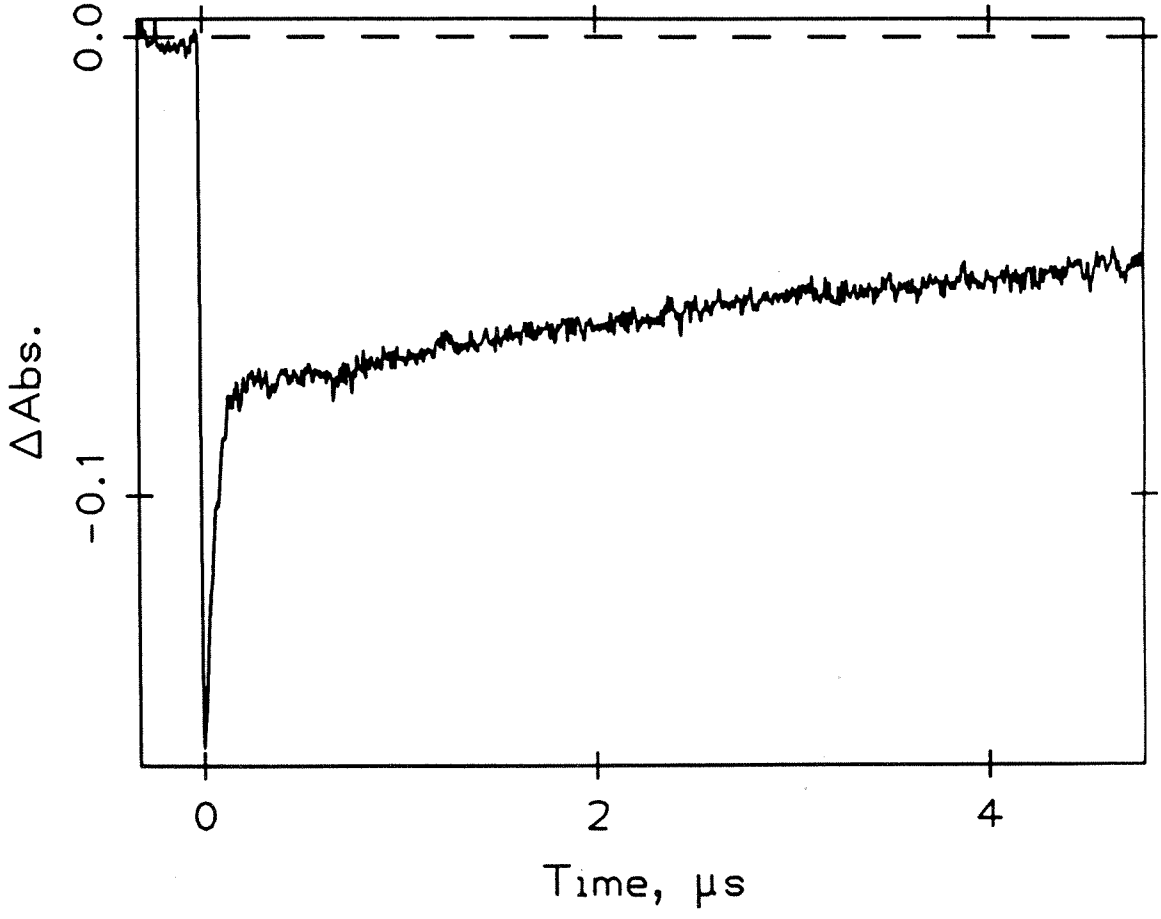
DATA FILE: 247-2.003 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 2
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 250 ul



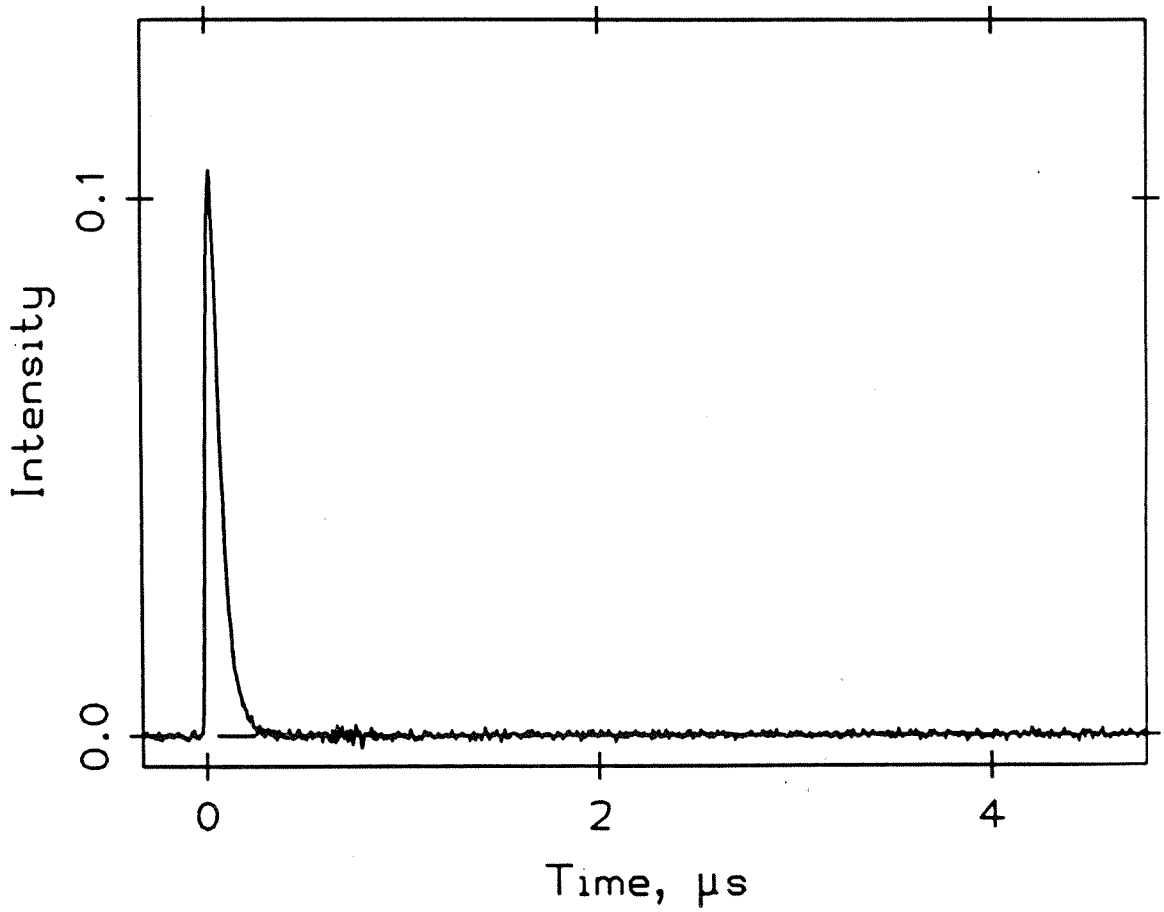
DATA FILE: 247-3.001 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: no q



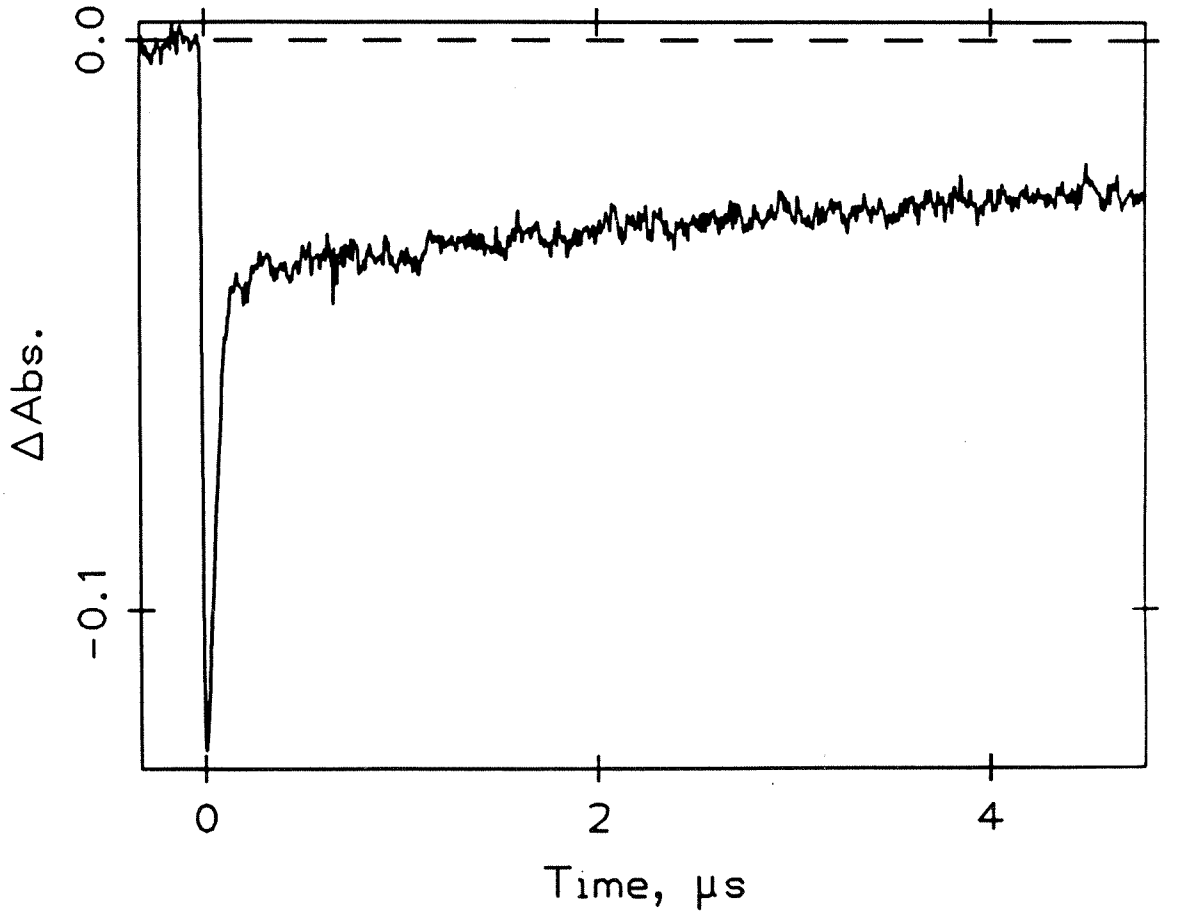
DATA FILE: 247-3.003 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 0030mgq



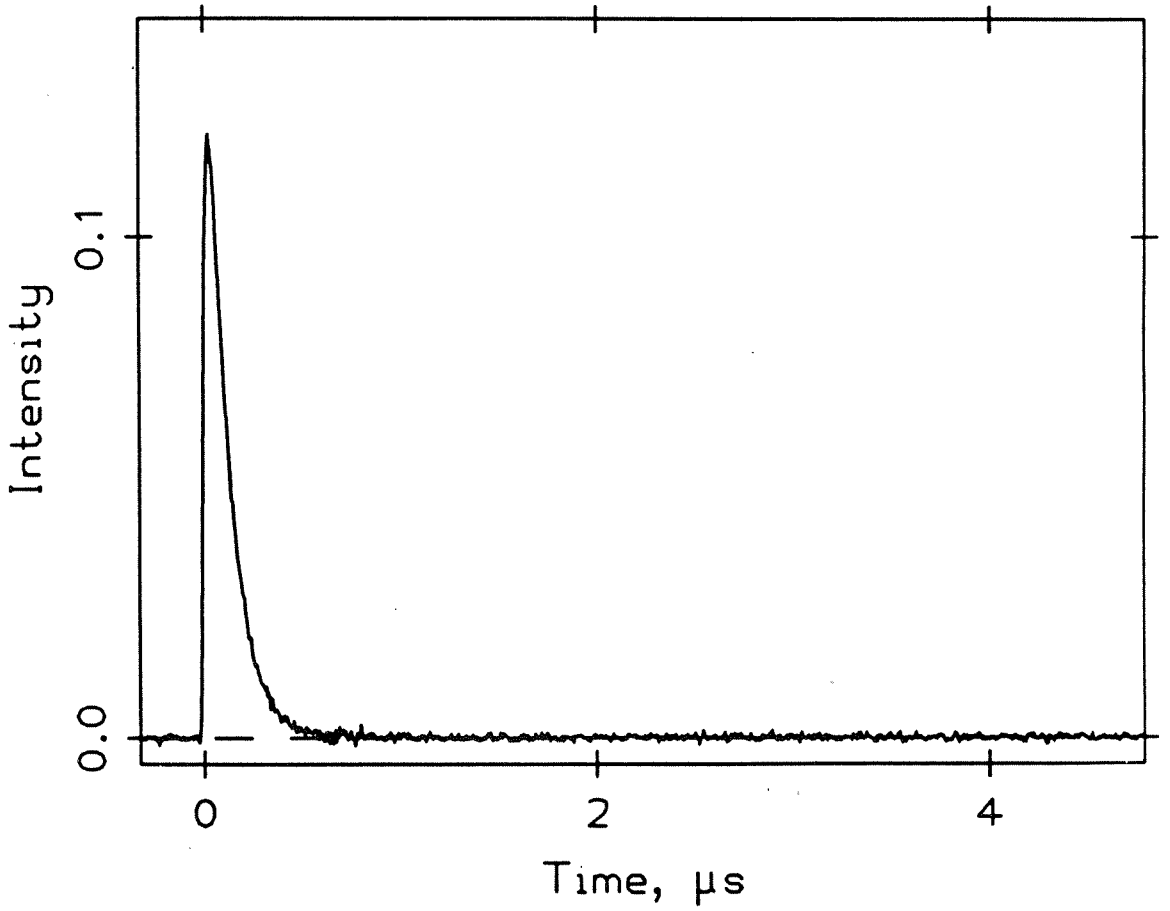
DATA FILE: 247-6.001 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 6.5mg q



DATA FILE: 247-6.002 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 500 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 06.5mgq



DATA FILE: 247-7.001 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: LUMINESCENCE DECAY
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 12.5mgq



DATA FILE: 247-7.003 USER:
TIME RANGE: 1.25us INPUT V RANGE: 0.250 V INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORPTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP MODE: QUASI-DIFFERENTIAL
SHOTS PER CYCLE: 100 CYCLES: 1
EXCITATION WAVELENGTH: 532 nm OBSERVATION WAVELENGTH: 690 nm
SAMPLE: ircodpz 2
SOLVENT: ch3cn
TEMPERATURE: rt
COMMENT:
COMMENT: 12.5mgq