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Los Angeles

Spectroscopic Studies of Ground and Excited State Mixed Valence

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of
Philosophy in Chemistry

by

Matthew Dean Kiesz

2014

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ABSTRACT OF THE DISSERTATION

Spectroscopic Studies of Ground and Excited State Mixed Valence

by

Matthew Dean Kiesz

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2014

Professor Jeffrey I. Zink, Chair

Mixed valence systems have two charge bearing units (M) that share a radical electron. Coupling between the sites is mediated by a covalent bridge (B). These systems have been extensively studied since the 1960's on account of their interesting electronic structure and as an ideal system for understanding intermolecular electron transfer. One of the characteristic

signatures of mixed valence is the intervalence charge transfer (IVCT): a low energy electronic absorption where the radical electron is formally transferred from one site to the other. However, this phenomenon is not unique to the ground state and has also been shown to occur in the excited state. In the electronic absorption spectrum excited state mixed valence manifests as a set of two transitions. The first three studies presented in this dissertation will focus on understanding the excited state geometric distortions upon photoexcitation of ground state and excited state mixed valence systems.

The first chapter of this dissertation is an introduction to the underlying principles and history of excited state mixed valence. Important tools to analyze and interpret mixed valence systems which are used throughout the remainder of this dissertation are presented including the neighboring orbital model and the time-dependent theory of spectroscopy. Several aspects of these tools as they apply to the coupling and transition dipole moments are presented through three historical models and additional pedagogical examples.

The following three chapters are fundamental studies of mixed valence systems. The first study investigates the relationship between ground and excited state mixed valence in the radical anion of 9,9-dimethyl-2,7-dinitrofluorene. Apparent similarities in the absorption spectrum are analyzed using time-dependent theory, the neighboring orbital model, and resonance Raman spectroscopy. The second study reviews the excited state mixed valence of diisopropyl ditolyl radical cation. This study presents an essential expansion of the transition dipole moment analysis that is typically applied to excited state mixed valence systems. The third mixed valence study examines the importance of coordinate dependent coupling in a dialkylaniline ether. The ground state geometry of this compound should forbid any coupling between the aniline moieties,

however, movement along a low frequency twisting coordinate facilitates coupling giving rise to mixed valence transitions.

The final two chapters of this thesis are applied spectroscopic studies. The first applied study characterizes the weak electronic interaction between iron and ruthenium in a ferrocene complex. This is achieved by combining electronic absorption spectroscopy with Raman spectroscopy in resonance with a near IR iron-ruthenium charge transfer. The profile of the iron-ruthenium Raman stretch aids in the assignment of the electronic transition. The second applied project studies the photoisomerization of an azobenzene based linker in a metal organic framework. Photophysical studies are presented to understand the dynamics of the linker and subsequently demonstrate the ability of the metal organic framework to store molecular cargo and release it on demand.

The dissertation of Matthew Dean Kiesz is approved.

Paula L. Diaconescu

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Jeffrey I. Zink, Committee Chair

University of California, Los Angeles

2014

This dissertation is dedicated to my parents, Darrel and Natalie Kiesz, and my wife Marisol
Madrigal Kiesz.

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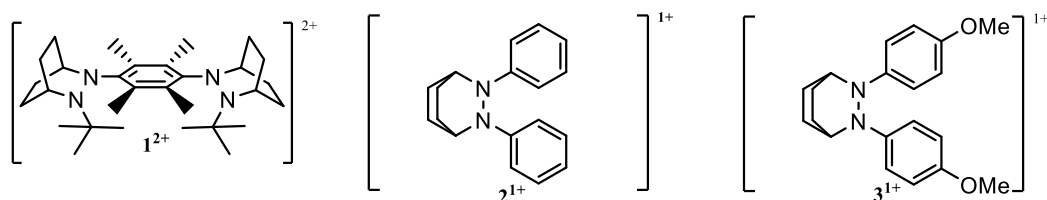
Chapter 1

Fundamental Aspects of Mixed Valence Excited States

1.1 Introduction

The interaction between donors and acceptors form a basis for interpreting low energy charge transfer (CT) features of absorption spectroscopy.^{1, 2} The absorption of a photon incites an electron to be transferred from a donor to an acceptor. This is commonly observed in organometallic complexes and assigned as either ligand to metal or metal to ligand CT. While the essential parameters for CT are well-studied and understood, the interaction of multiple equivalent CT transitions has not been considered until recently.³⁻⁵ Considering a metal complex with two equivalent ligands, how will the CT to either of these two ligands interact? Will the resulting transition be twice as intense or will there be no observable effect? Will the transition shift in energy?

This basic picture is the foundation of excited state mixed valence (ESMV): the transition of a charge (electron or a hole) in a symmetric ground state to two equivalent charge bearing units (CBUs). Scheme 1-1 displays the three molecular systems that have led to the understanding of ESMV and will serve as the basis within this review.



Scheme 1-1. Structure of studied ESMV compounds

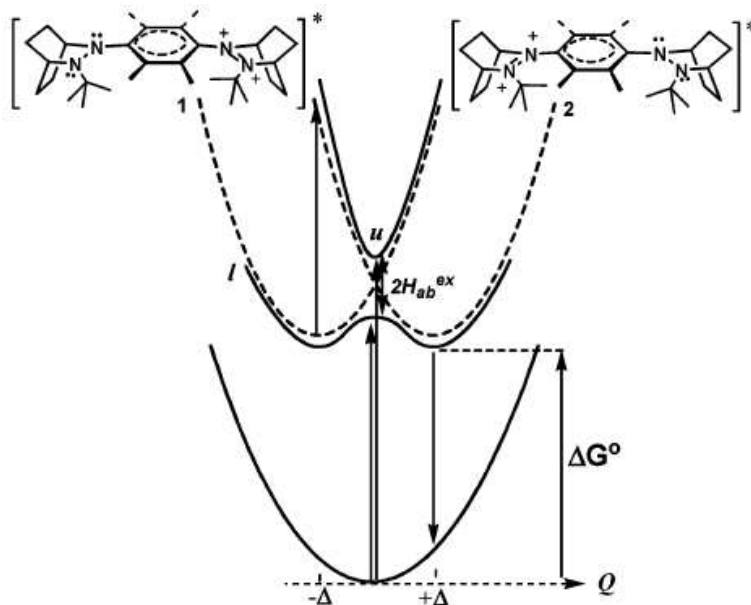


Figure 1-1. Three state model diagram of ESMV displaying a single ground state and a pair of diabatic (dashed) excited state surfaces that couple to form the adiabatic surfaces (solid).

In the ground state of 1^{2+} , the radical electrons are delocalized across either hydrazine π NN bond (Figure 1-1). The absorption of a photon induces a CT between the two hydrazine moieties resulting in two separate diabatic excited states that couple to form the familiar two-state model of ground state mixed valence (GSMV).³

The magnitude of coupling can be described in terms of the Robin-Day classifications⁶: Class I, weakly interacting centers, behave independently and would exhibit a single absorption for the two charge transfers. Class II and III compounds display moderate to high levels of electronic communication resulting in the clear separation of the two adiabatic surfaces and the presence of two bands in the absorption spectrum that are separated by approximately twice the coupling.

The sign and overall magnitude of the coupling play a significant role within ESMV.⁴ With normal through-space coupling the in-phase combination is lower in energy and the coupling is inherently negative. This is reminiscent of two hydrogen atoms forming a bond with the in-phase σ bonding orbital being lower in energy than the antibonding σ^* orbital. However, in through-bond coupling, the sign of the coupling is not inherently negative. It instead depends on the orbitals of a bridge connecting the CBUs. Hoffmann *et al* initially noted that the in-phase combination between the nitrogen lone pairs within a pyrazine molecule is strangely higher in energy than the out-of-phase combination.^{7, 8} This was explained by their through bond interaction with bridging orbitals. The same phenomenon may exist with coupled excited states and will be discussed as a topic within this review.

The wave functions associated with the coupled adiabatic states are essentially in-phase and out-of-phase combinations of the diabatic wave functions.⁹ A similar transformation for the transition dipoles results in an in-phase and out-of-phase combination. While the in-phase combinations results in an intense absorption band the out-of-phase combination of the transition dipoles does not vanish to zero. It instead leads to a vibronically allowed transition. Analyzing the diabatic to adiabatic transformation for the transition dipoles will explain these selection rules.

The main observable difference between GSMV and ESMV is the presence of two absorption bands in the latter corresponding to either adiabatic state. As will be discussed later, selection rules arise to give one allowed and one vibronic transition. However, the identity and energetic ordering of these transitions has an unexpected dependence on the sign of the coupling.⁴ This is in contrast to GSMV where the sign of the coupling has no effect.³

Calculating the resultant absorption spectrum for ESMV can be achieved by using the PKS theory,¹⁰ but requires a summation over states method that is computationally expensive. A more feasible alternative is the time-dependent theory of spectroscopy,^{11, 12} specifically with the split operator method of Feit and Fleck.^{13, 14} Within this review the details of mixed valence excited states will be explained in the context the time-dependent theory to explain its origins and spectral consequences.

1.2 Diabatic Coupling

A fundamental aspect of mixed valence is the off-diagonal coupling element. However, in contrast to the coupling between equivalent ground states, the sign of the coupling is important in coupled excited states. The energies of the orbitals involved in excited state mixed valence can be represented by the following matrix

$$\hat{V} = \begin{pmatrix} V_{GS} & 0 & 0 \\ 0 & V_1 & H_{AB} \\ 0 & H_{AB} & V_2 \end{pmatrix} \quad (1)$$

where V_{GS} , V_1 and V_2 are the potential energy operators for the symmetric ground state and charge localized excited states, respectively, and H_{AB} is the coupling. This matrix is diagonalized by the unitary transformation matrix

$$U^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix} \quad (2)$$

where

$$\tan 2\theta = \frac{2H_{AB}}{V_1 - V_2} \quad (3)$$

The diagonalization yields two adiabatic potential energy operators that are identical to those of ground state mixed valence

$$V_L = \frac{1}{2} \left\{ (V_1 + V_2) - \sqrt{(V_1 - V_2)^2 - H_{AB}^2} \right\} \quad (4)$$

$$V_U = \frac{1}{2} \left\{ (V_1 + V_2) + \sqrt{(V_1 - V_2)^2 - H_{AB}^2} \right\} \quad (5)$$

The lower energy surface, V_L , displays a double minimum for smaller H_{AB} values that merge to a single minimum for $H_{AB} > \frac{\lambda}{2}$. The higher energy surface has one minimum at the equilibrium configuration. Because these surfaces are dependent on H_{AB}^2 , the sign of H_{AB} has no influence on the topography of the surfaces. Similarly, the wave functions must undergo a transformation to the adiabatic basis. This results in in-phase $\Psi^+ = \Psi_1 \cos \theta + \Psi_2 \sin \theta$ and out-of-phase $\Psi^- = -\Psi_1 \sin \theta + \Psi_2 \cos \theta$ wave functions. The relative energy of these wave functions and the adiabatic surfaces they correspond to depend on the sign of H_{AB} .

For normal through-space coupling the in-phase combination is lower in energy than the out-of-phase combination and the coupling is inherently negative. In contrast, through-bond coupling can be either positive or negative, allowing either linear combination to be lower. Hoffmann *et al* pointed out that through-bond coupling *may* result in the counterintuitive case where an out-of-phase combination is lower in energy and coupling is thus positive. The nature of bridging orbitals that mediate the interaction of diabatic orbitals dictate the relative energies of the

two wave functions. By examining relevant orbitals of the coupled system the sign of the coupling can be determined through the neighboring orbital model (NOM).

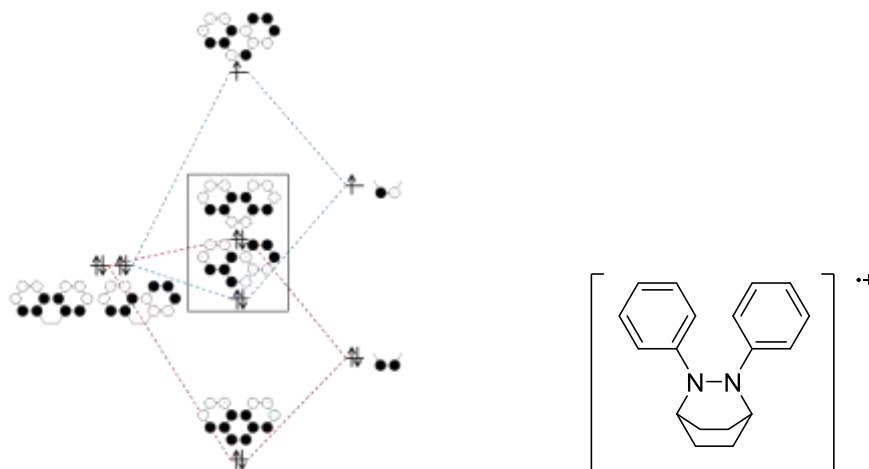


Figure 1-2. Neighboring orbital diagram for 2,3-diphenyl-2,3-diazabicyclo[2.2.2]octane. In C_{2v} symmetry, red and blue lines denote the combinations of b_2 and a_2 symmetry SALCs (symmetry adapted linear combinations). The pair of boxed orbitals are the adiabatic in-phase and out-of-phase molecular orbitals.

1.2.1 Neighboring Orbital Model

The NOM utilizes relevant orbitals of the bridge to couple diabatic orbitals of the CBUs and develop a partial molecular orbital diagram (Figure 1-2).¹⁵ A pair of symmetric and asymmetric bridge orbitals closest in energy to the diabatic CBU orbitals will experience the most mixing and will be the only ones considered for this model. The left and right sides of the diagram depict the diabatic π orbitals of CBUs and the bridge, respectively. Because the CBU orbitals are assumed to have negligible overlap, their uncoupled linear combinations are degenerate. Mixing these orbitals yields the symmetry adapted linear combinations shown in the center column of the diagram.

For the diphenyl hydrazine radical cation shown in figure 1-2 the relevant orbitals of the CBU and the bridge are the HOMOs and the HOMO and SOMO, respectively. The combinations of the diabatic orbitals can be determined from DFT calculation and their relative energies realized. For the molecular orbitals that have the most CBU character (boxed in figure 1-2), the out-of-phase combination is lower in energy than the in-phase combination, in contrast to through-space coupling (which is inherently negative), implying that the coupling must be positive. However, through-bond coupling is not guaranteed to be positive. By varying the relative energy of bridge orbitals, their symmetries, or their mixing with the CBU orbitals, the sign of the coupling may be either positive or negative. The spectral significance of the identity of the surfaces will be discussed more in relation to their selection rules in the following section on transitions dipoles.

1.2.2 Magnitude of Coupling

A second important aspect of the coupling is the magnitude. As in ground state mixed valence, the energy difference between the coupled diabatic orbitals is double the magnitude of the coupling. The spectral manifestation of this is that there are two transitions whose electronic origins are separated by double the coupling. Figure 1-3 shows the absorption and fluorescence spectrum of the diphenyl hydrazine cation. The absorption spectrum displays two transitions in the visible corresponding to the transitions to the lower and upper surfaces of the coupled mixed valence system at 17,900 and 25,900 cm^{-1} , respectively. This difference between these peaks is 8000 cm^{-1} yielding an approximate coupling of 4000 cm^{-1} . This effect of linearly increased separation between ESMV transitions with increased coupling is also exemplified in figure 1-9. In

General, figure 1-9 explores the effects of altering the coupling utilizing the parameters used to calculated spectra for a diradical cation. A calculation with the original coupling value ($H_{ab} = 2000 \text{ cm}^{-1}$) is shown in the middle and plots above and below demonstrate decreased and increased coupling.

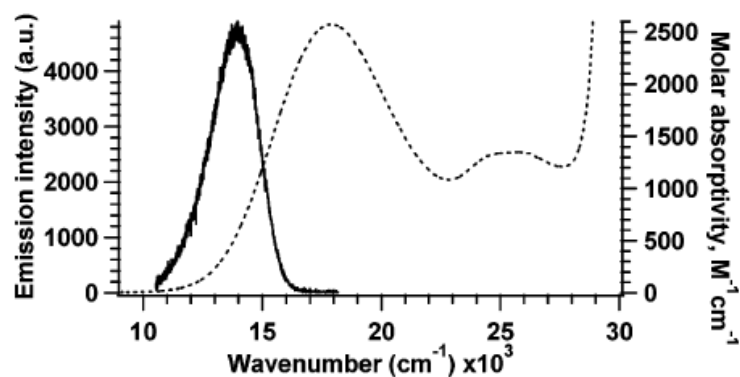


Figure 1-3. Absorption (dashed) and fluorescence (solid) spectra of 2,3-diphenyl-2,3-diazabicyclo[2.2.2]octane.

1.2.3 Coordinate Dependence of H_{ab}

For most molecular systems, the nuclear oscillation along any normal coordinate is small enough such that the change in the diabatic coupling is negligible and is approximately constant. However, significant distortions along normal coordinates that affect the coupling between two CBUs inherently have a coordinate dependent coupling between the diabatic states. Considering the 2,3-di-*p*-anisyl-2,3-diazabicyclo[2.2.2]octane radical cation, 3^{1+} , the symmetric C-N stretches perturb the overlap between the phenyl CBUs and the hydrazine bridge. Simultaneously decreasing the bond lengths increases the coupling between the phenyl units while moving to the opposite side of the coordinate increases the bond lengths and decreases coupling. In contrast, symmetric

stretches involving the C-C double bonds in the phenyl moieties do not affect the through-bond overlap between the phenyls and thereby do not display coordinate dependent coupling.⁴

$$H_{ab} = k * Q + C \quad (6)$$

The effect of coordinate dependent coupling on the ESMV transition can be observed in the bandwidth of the two components of the absorption spectrum. Along any symmetric coordinate the uncoupled diabatic surfaces are degenerate at all points. Coupling with a simple linear function (eq. 6) displaces the adiabatic surfaces to opposite sides of the diabatic surfaces (figure 1-4). The result is that the Franck-Condon region is now different for either adiabatic surface. The adiabatic surface that is more displaced yields a broader absorption band while the less displaced surface yields a narrower absorption band. In contrast, for a symmetric coordinate which does not display coordinate dependent coupling there will be little difference in the bandwidth of either absorption band.

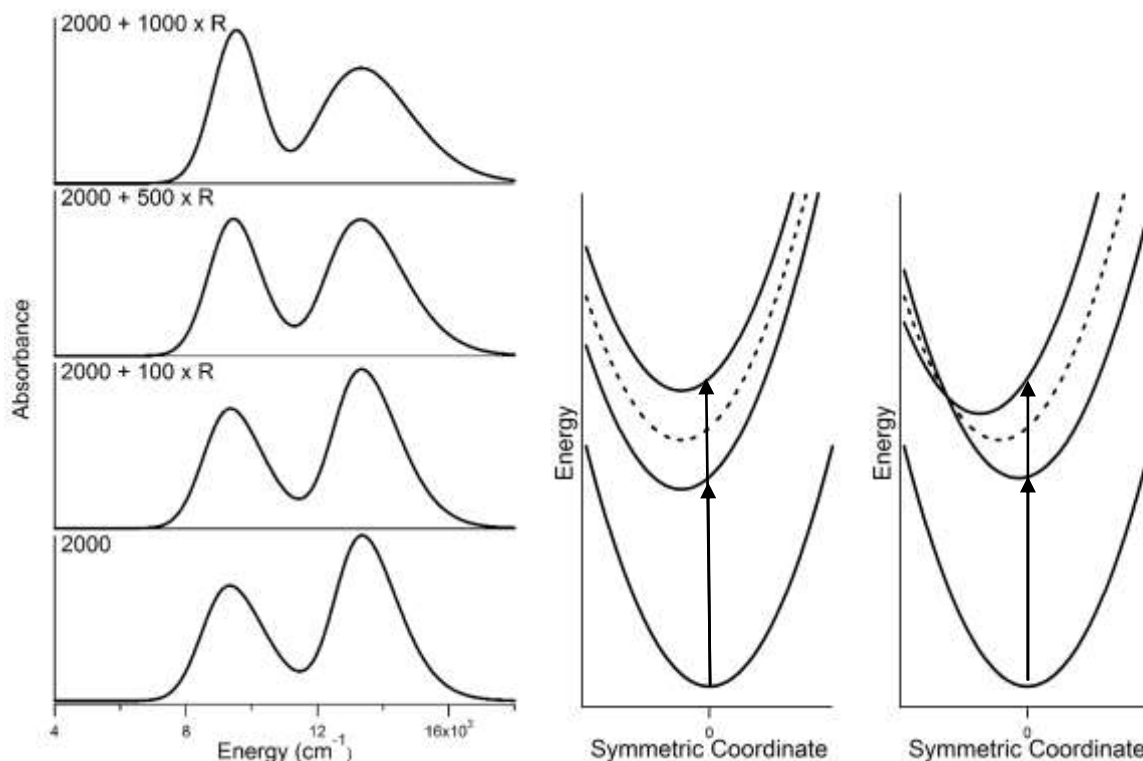


Figure 1-4. Left: Sequential calculated excited state mixed valence spectra demonstrating the effect on bandwidth of a coordinate dependent coupling along a symmetric coordinate. In these spectra, the coupling, H_{ab} , is in cm^{-1} and its dependence along the symmetric coordinate, R , has units $\frac{\text{cm}^{-1}}{0.1 \text{ \AA}}$. Cross-sectional views of two dimensional potential energy surfaces along the symmetric coordinate for the cases with 0 (middle) and 1000 coordinate dependence (right). The solid arrows represent vertical transitions and display the different slopes of the two adiabatic surfaces in the Franck-Condon region.

1.3 Transition Dipole Moment

The transition dipole promotes the wave function from an initial surface to a final surface. For a simple transition from one ground state to one excited state, the strength of the transition dipole moment only serves to change the magnitude of the overall absorption spectrum. However, in a mixed valence excited state we can consider two diabatic transition dipoles to either CBU that are coupled. How do the dipoles combine? Do they make simple linear combinations that result in

one transition being twice as intense and the other transition being forbidden or are the resulting selection rules more complex?

When considering the transition dipoles we must again undergo a transformation from the diabatic dipole matrix

$$\hat{\mu} = \begin{pmatrix} 0 & \pm\mu_1 & \mu_2 \\ \pm\mu_1 & 0 & 0 \\ \mu_2 & 0 & 0 \end{pmatrix} \quad (6)$$

where μ_1 and μ_2 are the transition dipoles to either diabatic surface and the sign indicates their spatial orientation. The positive sign applies to parallel transition dipoles and CBUs that have 0° separation while the negative sign applies to antiparallel transition dipoles where the CBUs are separated by 180° . Transforming to the adiabatic basis,

$$\mu = \begin{pmatrix} 0 & \pm\mu_1 \cos\theta + \mu_2 \sin\theta & \mp\mu_1 \sin\theta + \mu_2 \cos\theta \\ \pm\mu_1 \cos\theta + \mu_2 \sin\theta & 0 & 0 \\ \mp\mu_1 \sin\theta + \mu_2 \cos\theta & 0 & 0 \end{pmatrix} \quad (7)$$

The transition dipole to the in-phase wave functions, Ψ^+ , is $\pm\mu_1 \cos\theta + \mu_2 \sin\theta$, and to the out-of-phase combination wave function, Ψ^- , it is $\mp\mu_1 \sin\theta + \mu_2 \cos\theta$. For parallel transition dipoles, the transition to the in-phase state is allowed while the transition to the out-of-phase state is allowed for antiparallel transition dipoles. In both cases, the transition to the remaining state is vibronically allowed. The transition dipoles to the adiabatic states, their values along the coordinate, and the ensuing selection rules for all scenarios are summarized in Table 1-1.

Table 1-1. Tabulated transition dipoles in the adiabatic limit and corresponding selection rules for parallel and antiparallel oriented transitions.

	Transition to state	Dipole	Dipole value along Q	Selection rule
Parallel	Ψ^+	$\mu_1 \cos\theta + \mu_2 \sin\theta$	non-zero everywhere	Electric dipole allowed*
	Ψ^-	$-\mu_1 \sin\theta + \mu_2 \cos\theta$	zero at $Q = 0$ positive when $Q > 0$ negative when $Q < 0$	Dipole forbidden, but vibronically allowed
Antiparallel	Ψ^+	$-\mu_1 \cos\theta + \mu_2 \sin\theta$	zero at $Q = 0$ negative when $Q > 0$ positive when $Q < 0$	Dipole forbidden, but vibronically allowed
	Ψ^-	$\mu_1 \sin\theta + \mu_2 \cos\theta$	non-zero everywhere	Electric dipole allowed*

* In the adiabatic limit where $H_{ab}^{ex} \gg V_1(Q) - V_2(Q)$

A simple physical picture demonstrates that a transition from a symmetric ground state to a mixed valence excited yields these non-intuitive selection rules (figure 1-5). Overlap between the dipole promoted ground state and the out-of-phase excited state wave function is positive at all points along the asymmetric coordinate and is therefore an allowed transition. In contrast, the transition to the in-phase combination has net-zero overlap at the origin. However, overlap evolves upon movement to either side giving a vibronically allowed transition.

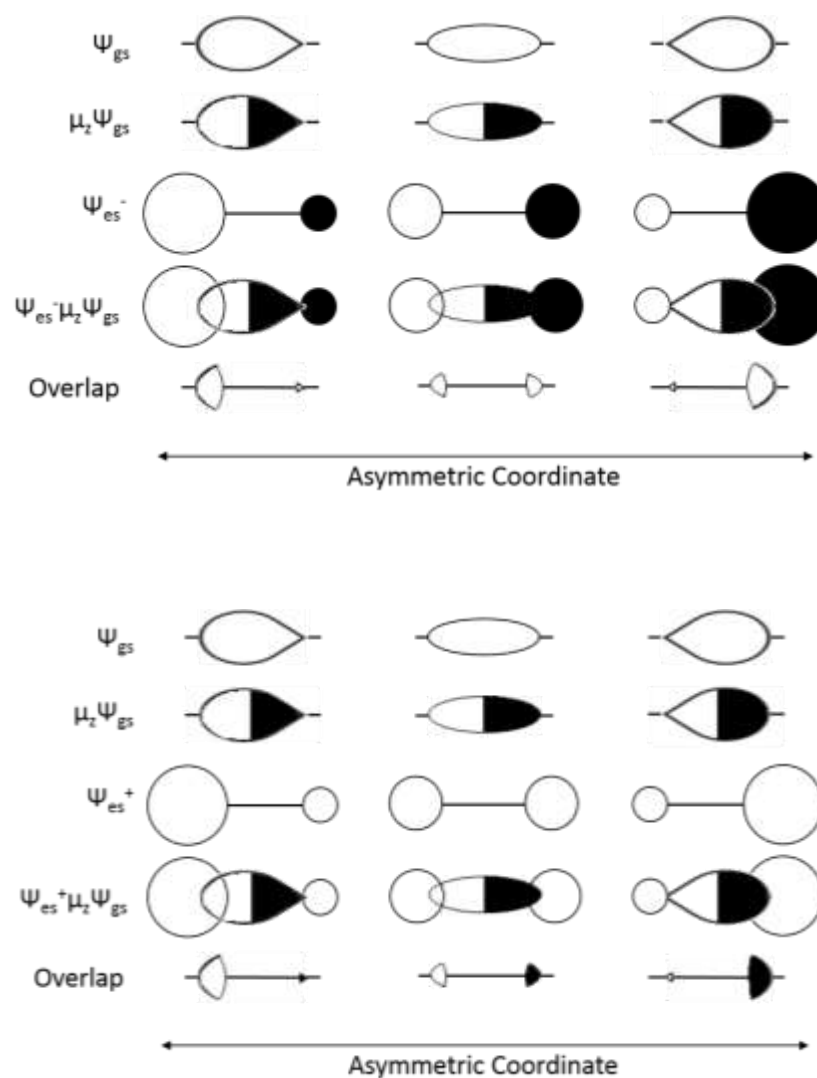


Figure 1-5. Pictorial depiction of overlap integral for transitions from a bridge centered symmetric ground state to out-of-phase (top) and in-phase (bottom) combinations. Left and right hand columns depict movement to either side of the nuclear coordinate. Line 1: Ground state wave function. Line 2: Ground state wave function multiplied by a dipole pointing along the molecular axis with a node placed at the center. Line 3: Excited state wave function. Line 4: Superposition of lines 2 and 3. Line 5: Overlap, where white and black denote positive and negative, respectively.

1.3.1 The Effect of the Angle of Interaction

One can see how the selection rules will determine the relative intensity of the absorption bands corresponding to the transitions to the two states. Examining the absorption spectrum and

geometry of 1^{2+} (figure 1-6), one can see that the antiparallel dipoles give rise to two transitions to the mixed valence excited state. The higher energy transition at $22,400\text{ cm}^{-1}$ is allowed while the shoulder at $17,200\text{ cm}^{-1}$ is vibronically allowed. This analysis assumes that CBUs are separated by either 0° or 180° and allows for facile calculation of their absorption spectra. But how can we analyze the absorption spectra of CBUs oriented at an intermediate angle? The absorption spectrum of the 1^+ (figure 1-6) displays strong absorptivity to either component of the coupled excited state. This can be analyzed by considering the absorption spectrum to be a trigonometric sum of spectra generated for parallel and antiparallel dipoles.⁴

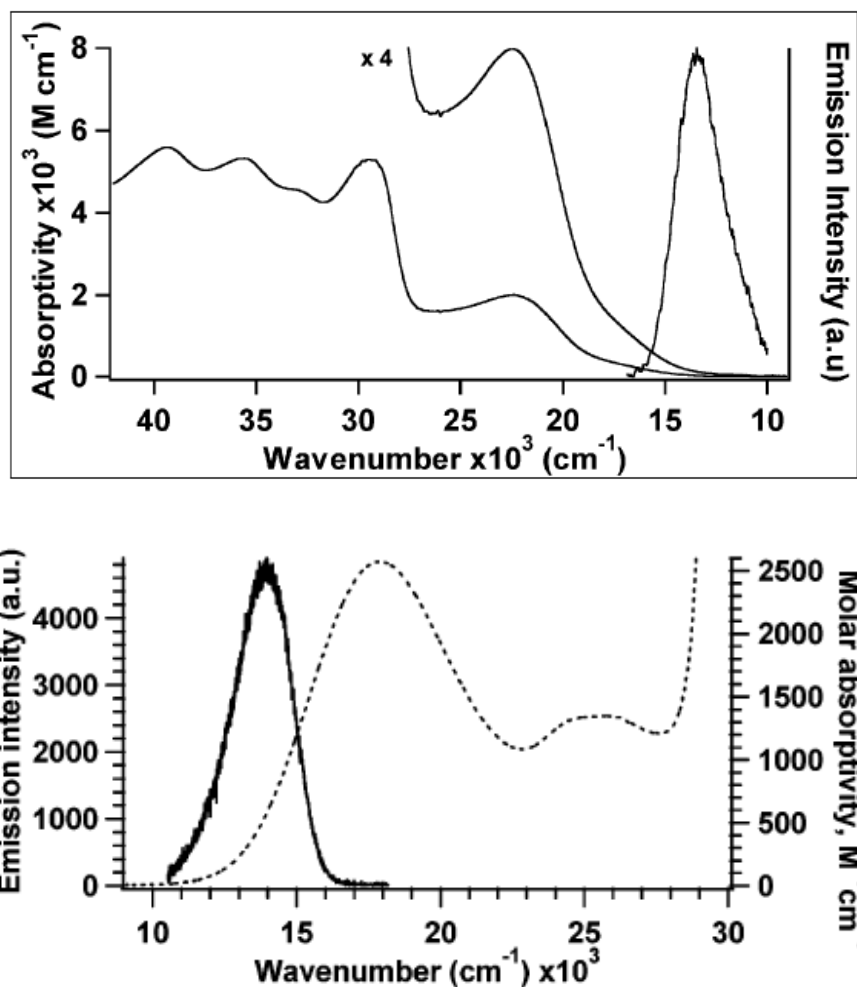


Figure 1-6. Experimental absorption and fluorescence spectra of 1,4-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-2,3,5,6-tetramethylbenzene-1,4-diyl dication.

A simple picture can determine the relative intensities of the two transition bands for chromophores that are neither parallel nor antiparallel (figure 1-7). In the case where β is between 0° and 180° , the orientation can be thought of as a superposition of the parallel and antiparallel dipoles:

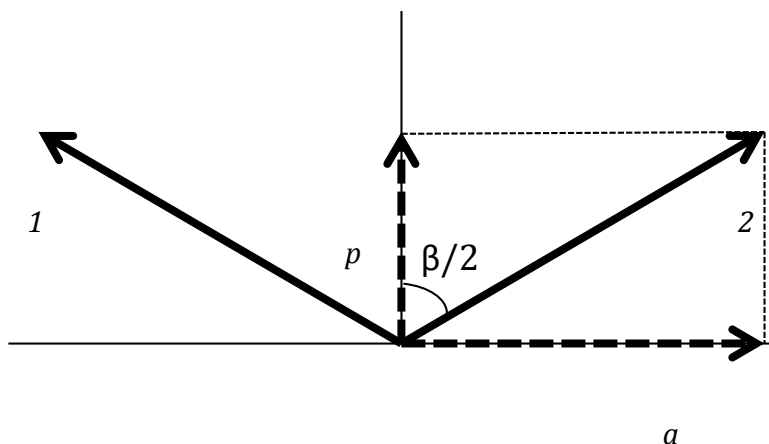


Figure 1-7. Cartoon of transition dipoles separated by an angle, β , being projected to a pair of orthogonal dipoles.

The projection of μ_1 and μ_2 on the bisecting axis correspond to the parallel dipole component μ_p , while their projections on the orthogonal axis will be in opposite directions and correspond to the antiparallel dipole component μ_a . The intensity ratio, being the square of the ratio of the antiparallel to parallel dipoles, is

$$\frac{f_a}{f_p} = \frac{\mu_a^2}{\mu_p^2} = \frac{\mu^2 \sin^2 \frac{\beta}{2}}{\mu^2 \cos^2 \frac{\beta}{2}} = \tan^2 \frac{\beta}{2} \quad (8)$$

This relation can also be derived by considering orientational averaging as presented in reference 5.

The spectral effect of the angle between two CBUs is the relative intensity of the two components of the absorption spectrum (Figure 1-8). For CBUs oriented 180° apart, the absorption spectrum consists almost entirely of one allowed transition and a weaker vibronically allowed transition. In this case the lower energy transition is allowed since the sign of the coupling is

negative. As the angle between the CBUs is decreased, a contribution from the parallel spectrum becomes apparent in a higher energy peak from the upper adiabatic surface.

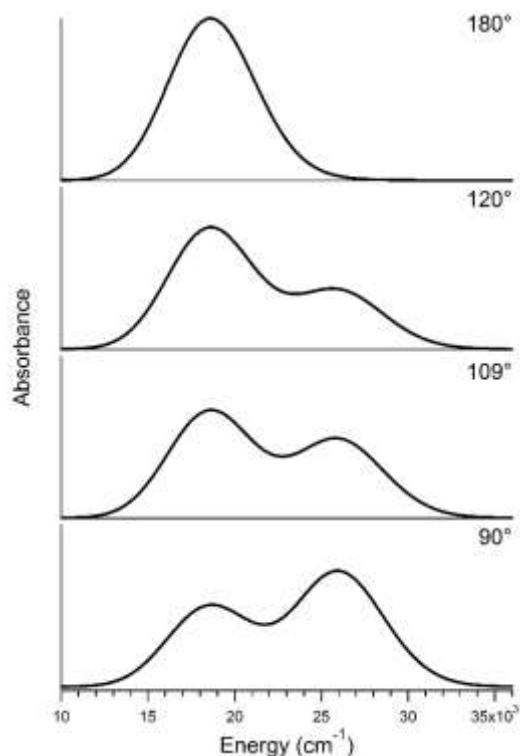


Figure 1-8. Calculated excited state mixed valence spectra for chromophores oriented at relevant angles generated from identical parameters used for 2,3-diphenyl-2,3-diazabicyclo[2.2.2]octane. The original spectra spectrum is shown an angle of 120°.

1.3.2 The Effect of Coupling on the Transition Dipole

How does the magnitude of the coupling affect the transitions to either state? The adiabatic forms of the transition dipoles, shown in table 1, have a trigonometric dependence on the coupling, H_{ab} . The right panel of figure 1-9 plots the transition dipoles to the upper and lower adiabatic surfaces for H_{ab} equal to 100, 1000, and 5000 cm^{-1} and the left panel displays corresponding absorption spectra (the lower energy transition is allowed since $H_{ab} < 0$ and $\mu_1 = -\mu_2$). For all

cases the transition to the lower surface is allowed since the transition dipole is non-zero at all points along the coordinate. However, the transition dipoles to the upper surfaces cross through zero at the ground state internuclear configuration and tend towards +1 and -1 at the extremes of the coordinate. This results in a vibronically allowed transition. For the case with $H_{ab} = 100 \text{ cm}^{-1}$, the sharp slope of the dipole near the origin requires minimal vibrational motion to yield an appreciable dipole and results in a more intense transition. In contrast, the case with $H_{ab} = 5000 \text{ cm}^{-1}$ displays very shallow changes in the dipole near the origin and the resulting transition is accordingly weak.

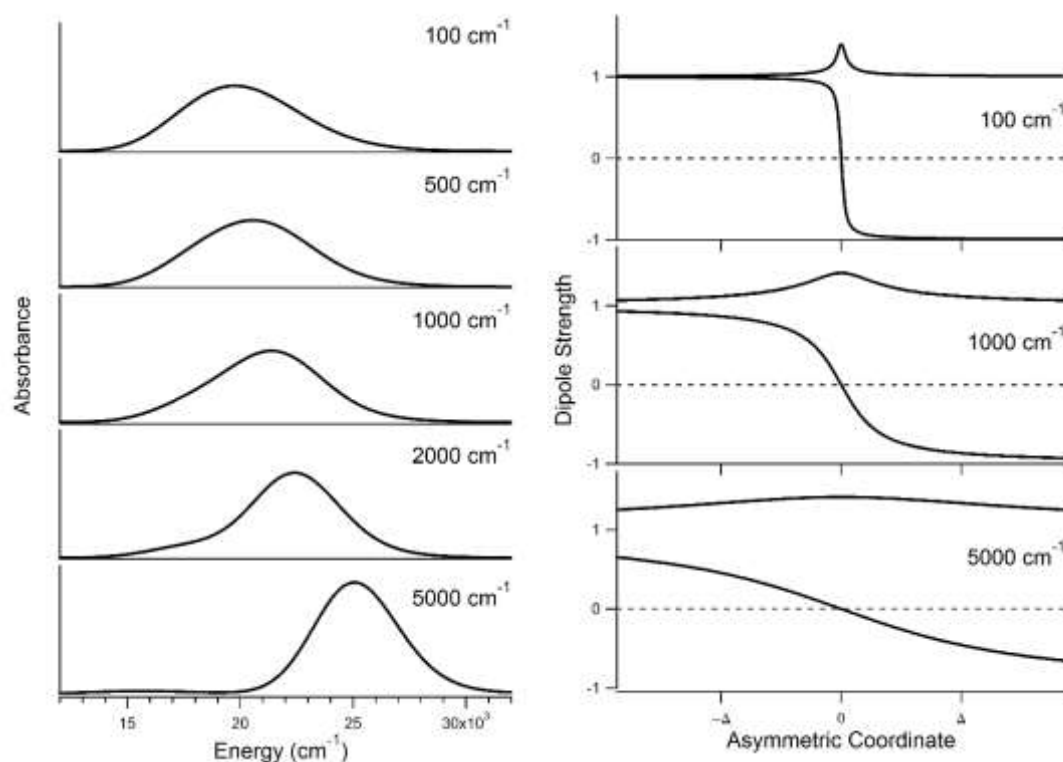


Figure 1-9. Left: Absorption spectra with varied degrees of coupling for 1,4-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-2,3,5,6-tetramethylbenzene-1,4-diyl dication. The original calculated absorption spectrum is in the middle with $H_{ab} = 1000 \text{ cm}^{-1}$. Right: Plots of transition dipoles to the upper and lower adiabatic states along an asymmetric normal coordinate for three coupling values.

1.4 Calculated Spectra

In order to calculate a best-fit absorption spectrum, a reasonable set of parameters must be chosen. Such parameters include the frequencies and distortions of the normal modes for the ground and excited states, sign and magnitude of coupling, dipole orientation, and electronic origin. These parameters can be estimated through examination of the absorption, resonance Raman, and IR spectra.⁵

Changes in the electron configuration upon absorption of a photon result in changes in bonding/antibonding character and correspond to geometrical distortions across the molecule. These distortions are a combination of the normal modes within the molecule, the most highly of which determine the features observed in the absorption spectrum. A normal mode corresponding to asymmetric distortions between the CBUs and the bridge will inherently have a large distortion since transferring an electron from a predominantly bridge orbital to either of the CBUs results in significant asymmetric bond length changes. However, symmetric modes exhibiting bond length changes in accordance with changes in electron density will also be significantly distorted and add to the overall breadth and structure of the absorption spectrum. While the relative distortions and frequencies for symmetric normal modes are determinable from resonance Raman, asymmetric modes are inactive in Raman and therefore their frequencies must be attained from the IR spectrum and their distortions approximated from similar symmetric modes.

1.4.1 Experimental Absorption Spectrum and Resonance Raman spectra

For a brief example of how to calculate ESMV absorption spectra, we will present the analysis of the absorption and resonance Raman spectra of 2,3-di-*p*-anisyl-2,3-diazabicyclo[2.2.2]octane radical cation. The experimental absorption and resonance Raman spectra of 3^+ are shown in figure 1-10. Primarily, the absorption spectrum displays two prominent peaks at 14,900 and 21,600 cm^{-1} in the solid state corresponding to the transitions to the lower and upper surfaces of the coupled system, respectively. The difference in energy between these two transitions yields a coupling of approximately 3350 cm^{-1} and an analysis of the neighboring orbitals identical to that presented in figure 1 reveals that the sign of the coupling is positive. The addition of *para* substituted methoxy groups to the diphenyl hydrazine shown in figure 1 (as in 3^+) only affects the magnitude of the coupling between the two CBUs, not the sign.

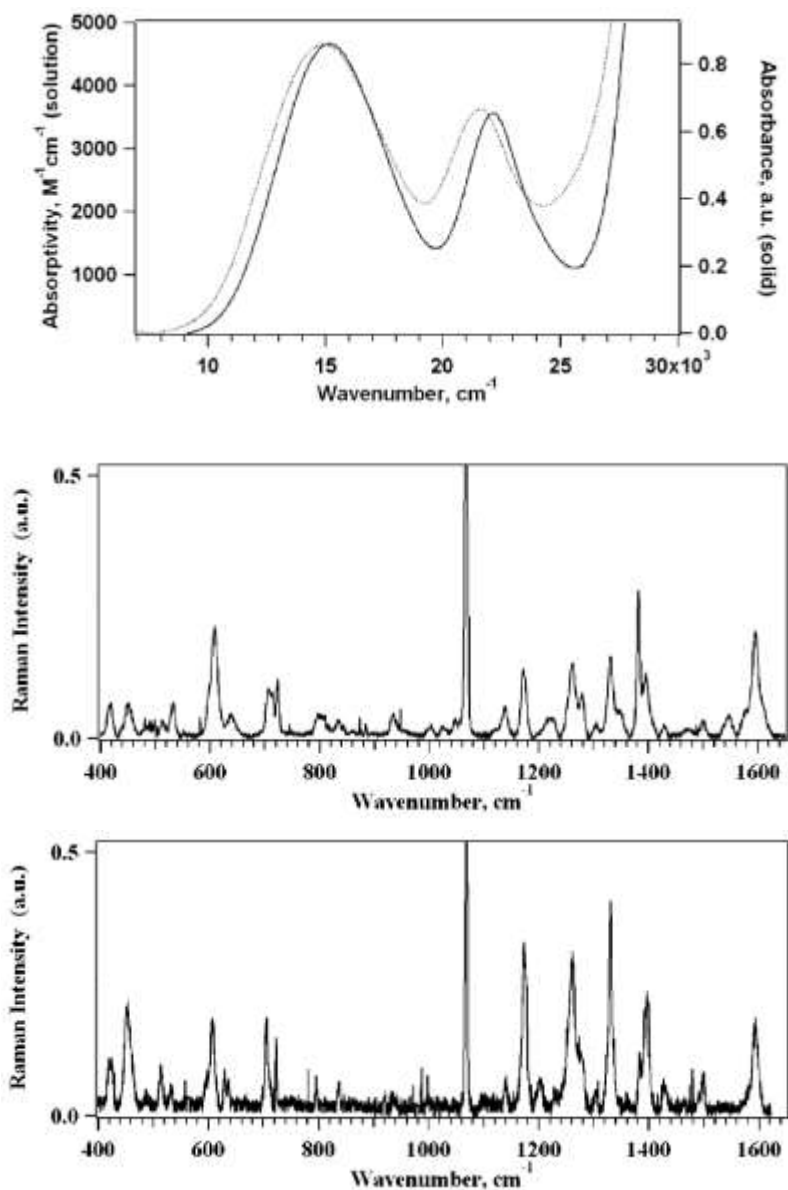


Figure 1-10. Top: Absorption spectrum of 2,3-di-*p*-anisyl-2,3-diazabicyclo[2.2.2]octane radical cation in acetonitrile solution (solid) and solid KBr pellet (dashed). Resonance Raman spectra of solid 3^+ using 476 nm (middle panel) and 676 nm (bottom panel) excitation sources.

Two Raman spectra were collected with excitation at 476 nm and 676 nm in resonance with either component of the ESMV. Several symmetric vibrations were observed and their

frequencies, relative intensities, distortions (as calculated by Savin's formula) and assignments are reported in table 2.

Table 1-2. Raman frequencies, intensities, absorptions and assignments for 2,3-di-*p*-anisyl-2,3-diazabicyclo[2.2.2]octane radical cation.

experimental frequency (cm ⁻¹)	$\lambda_{\text{ex}} = 676 \text{ nm}$		$\lambda_{\text{ex}} = 476 \text{ nm}$		calculated frequency (cm ⁻¹)	Assignment
	I_{676}	Δ_{676}	I_{476}	Δ_{476}		
418	0.527	1.71	0.150	0.787	426	Phenyl ring def.
450	1.38	2.56	0.202	0.848	486	C-N-N-C twist
532	0.240	0.904	0.127	0.569	542	C-N-N-C twist
608	0.980	1.60	0.768	1.22	611	C-N-N-C twist
707	0.639	1.11	0.201	0.538	715	C-N-N-C twist
1140	0.228	0.412	0.127	0.265	1165	N-N stretch
1174	1.37	0.977	0.207	0.329	1204	C-N stretch, Phenyl C-H
1264	1.85	1.06	0.359	0.402	1327	Phenyl ring def., C-O
1333	1.37	0.863	0.301	0.349	1381	Phenyl ring def., N-N
1397	0.954	0.686	0.213	0.280	1432	N-N stretch
1596	0.904	0.585	0.516	0.382	1661	Phenyl C=C stretch

1.4.2 Calculated Absorption Spectrum

Using the observed data from absorption and resonance Raman spectra, appropriate parameters can be chosen to define the ground and coupled excited states and calculate the absorption spectrum (figure 1-11). In the case of this molecule, there are eight significantly distorted symmetric modes and one asymmetric mode that contribute to the breadth of the absorption spectrum. However, due to the lack of any apparent vibronic structure in the absorption spectrum this can be simplified to a single symmetric and asymmetric coordinate. A vibration assigned as a C-N stretch with a frequency of 1174 cm⁻¹ is selected as a representative symmetric

coordinate. A large damping factor must also be used to effectively smooth out the absorption spectrum, accounting for the presence of large distortions along several other normal coordinates. A frequency of 487 cm^{-1} is employed along the asymmetric coordinate and corresponds to a C-N-N-C twist. A distortion of ± 1.5 is set for the displaced diabatic potentials along this coordinate with a coupling between the diabatic states of 3350 cm^{-1} .

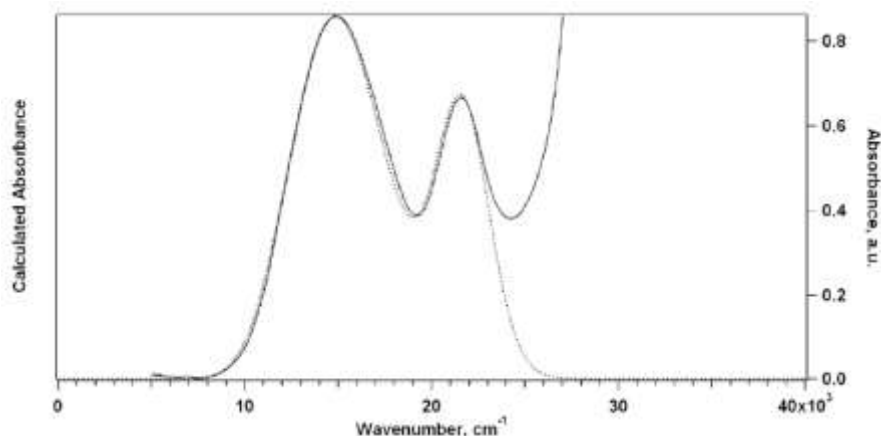


Figure 1-11. Calculated (dotted) and experimental (solid) absorption spectra for 2,3-di-*p*-anisyl-2,3-diazabicyclo[2.2.2]octane radical cation.

1.5 Conclusions

This chapter has outlined the background and foundation of excited state mixed valence. Specifically the combination of the time-dependent theory of spectroscopy and the neighboring orbital model provides a method to interpret ESMV and understand how the electronic interactions of the charge bearing units affect the geometric distortions. These analytical methods will be applied in the following three chapters and extend our understanding of coupled excited states.

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Chapter 2

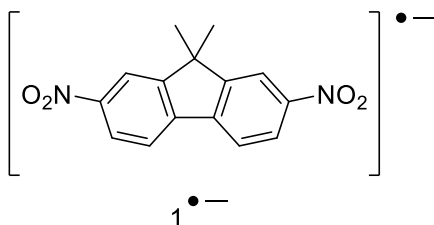
Coupled States in Dinitrofluorene: Relationships between Ground State and Excited State Mixed Valence

2.1 Introduction

Mixed valence occurs when a radical electron is shared between two equivalent charge bearing units and can occur in both ground and excited states. The theory of electron transfer in mixed valence systems was first developed in the 1960's and applied to transition metal complexes.^{1,2} Typical examples of ground state mixed valence contain two charge bearing units, M, and a bridge, B, that covalently links them leading to two unique configurations $[M^{\bullet}-B-M]$ and $[M-B-M^{\bullet}]$ where the radical charge is located on one metal or the other.³⁻⁵ Alternatively, a symmetric distribution of the radical charge in the ground state can result in a pair of degenerate yet displaced excited states that couple to produce a mixed valence excited state. The time-dependent theory of absorption,⁶ resonance Raman,^{7,8} and emission spectra has been established and used to interpret and calculate both types of mixed valence and to characterize the coupled states in terms of the distortions along normal coordinates.⁹⁻¹⁵ The relative magnitude of the distortions can be measured via a Raman spectrum in resonance with the mixed valence transition. However, in many cases ground state mixed valence absorption bands are low energy ($< 10,000\text{ cm}^{-1}$) and difficult to probe directly by resonance Raman spectroscopy.¹⁶⁻¹⁸

In this paper we examine both ground and excited state mixed valence transitions of 9,9-dimethyl-2,7-dinitrofluorene radical anion, $\mathbf{1}^{\bullet-}$ (scheme 1), and examine their spectroscopic and theoretical relationship. This compound exhibits a NIR ground state mixed valence band and an excited state mixed valence band in the visible region of the absorption spectrum.¹⁹ The excited state mixed valence transition is probed directly with resonance Raman spectroscopy in order to characterize the excited state in terms of the distortions along multiple normal coordinates.

However, the ground state mixed valence is too low in energy to conveniently examine by resonance Raman spectroscopy, but because these bands involve molecular orbitals that are common to both transitions, the ground state mixed valence can be indirectly probed and characterized.



Scheme 1.

2.2 Theoretical Methods

The theoretical framework for interpreting the vibrational spectrum and calculating the electronic absorption spectrum is provided by the time-dependent theory of molecular spectroscopy⁶ and is briefly presented here. This technique allows for a combination of multiple symmetric and asymmetric normal modes in calculating spectra along with an exact treatment of coupled electronic states.^{20, 21}

2.2.1 Absorption Spectroscopy

The primary equation for calculating absorption spectra within time-dependent theory is

$$I(\omega) = C\omega \int_{-\infty}^{\infty} \exp(i\omega t) \left\{ \langle \Phi | \Phi(t) \rangle \exp \left(-\Gamma^2 t^2 + \frac{iE_{00}}{h} t \right) \right\} dt \quad (1)$$

where $I(\omega)$ is the absorption intensity for a given frequency of light, E_{00} is the transition energy at the electronic origin, and Γ is a phenomenological damping factor. The damping accounts for the loss of the wave packet, Φ , to various modes and the bath, and it causes broadening of the absorption spectrum.

The most important component of equation 1 is the autocorrelation function, $\langle \Phi | \Phi(t) \rangle$, which determines the overlap of an initial wave packet with the time evolving wave packet as a function of time. Neglecting mixing of normal coordinates, the total autocorrelation function in a system with k normal coordinates is

$$\langle \Phi | \Phi(t) \rangle = \prod_k \langle \phi^k | \phi^k(t) \rangle \quad (2)$$

where ϕ^k is the wave packet propagating along the k^{th} normal coordinate. In the case of two coupled excited electronic states, ϕ^k bifurcates into two components associated with either state.

The initial wave packet, the eigenfunction of the ground state multiplied by the transition dipole, evolves on the excited surface. In the calculation of excited state mixed valence spectra, the transition dipole is

$$\mu_d = \begin{pmatrix} 0 & \pm\mu_1 & \mu_2 \\ \pm\mu_1 & 0 & 0 \\ \mu_2 & 0 & 0 \end{pmatrix} \quad (3)$$

where μ_i is the transition to either diabatic surface. The molecular structure dictates the relative sign of the transition dipole such that a positive sign implies parallel units whereas a negative sign implies antiparallel units that are oriented 180° apart from the linking bridge. Appropriate weighting of parallel and perpendicular spectra allow for calculation of spectra of molecules at intermediate angles:

$$\frac{I_a}{I_p} = \frac{\mu_a^2}{\mu_p^2} = \left(\tan \frac{\beta}{2} \right)^2 \quad (4)$$

where β is the angle between the charge bearing units. Alternatively, in calculating intervalence charge transfer (IVCT) spectra the transition dipole has the form

$$\mu_{d,IV} = \begin{pmatrix} 0 & \mu(Q) \\ \mu(Q) & 0 \end{pmatrix} \quad (5)$$

such that the components of the ground state eigenfunction associated with each diabatic surface are evolved on the other surface. The off-diagonal components may be a function of the configurational coordinate, Q , to reflect the selection rules of a given transition (e.g. vibronically allowed).

When a wave packet evolves on coupled excited states, the time evolved components on both surfaces must be determined. The time dependent wave packet is given by the time-dependent Schrödinger equation:

$$i \frac{\partial}{\partial t} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} H_1 & V_{12} \\ V_{21} & H_2 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} \quad (6)$$

where H_i move the wave packet along the coordinate and the off-diagonal V_{ij} transfer amplitude between the states. The diagonal components of the total Hamiltonian are

$$H_i = -\frac{1}{2M} \nabla^2 + V_i(Q) \quad (7)$$

The potential energy operators, $V_i(Q)$, are most often modeled as harmonic potentials which are displaced an equal amount in opposite directions along an asymmetric normal coordinate.

$$V_i(Q) = \frac{1}{2}k_i(Q \pm \Delta Q)^2 \quad (8)$$

The force constant is $k_i = 4\pi^2 M(\hbar\omega_i)^2$ and ω_i is frequency along the specified coordinate. The overlap is given by

$$\langle \phi | \phi(t) \rangle = \langle \phi_1 | \phi_1(t) \rangle + \langle \phi_2 | \phi_2(t) \rangle \quad (9)$$

Propagating wave packets and calculating spectra according to the equations and procedures outlined here provide a versatile framework that permits various functional forms of the off-diagonal diabatic coupling, V_{12} , the potential energy operator, and the transition dipole operator. Furthermore, the calculations carried out in this paper are carried out exactly according to the time-dependent Schrödinger equation where amplitude is transferred between potential surfaces at every time step, not in an adiabatic basis set where the potential energy Hamiltonian is diagonalized.

2.3 Results

2.3.1 Absorption Spectroscopy

The hexamethylphosphoramide (HMPA) solution absorption spectrum of **1**[•] in the visible and near IR wavelength region is shown in Figure 1. The low energy transition has a maximum at $6890 \pm 20 \text{ cm}^{-1}$ (1450 nm) and shoulders at $7930 \pm 100 \text{ cm}^{-1}$, $8500 \pm 100 \text{ cm}^{-1}$, and 10090 ± 100

cm^{-1} . The visible transition has a peak maximum at $18,980 \pm 50 \text{ cm}^{-1}$ (527 nm) and shoulders at $19,670 \pm 150 \text{ cm}^{-1}$, $20,660 \pm 100 \text{ cm}^{-1}$, and $22,150 \pm 200 \text{ cm}^{-1}$.

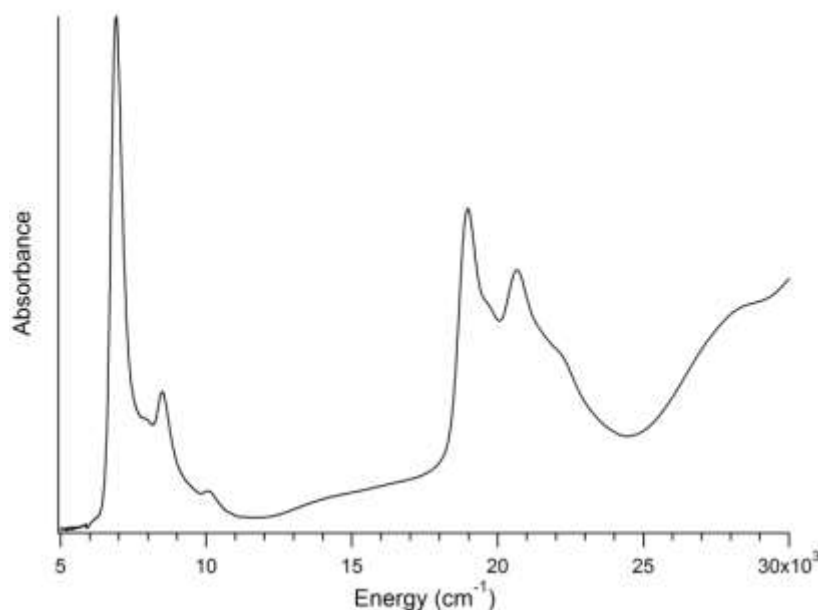


Figure 2-1. Absorption spectrum of **1*** in hexamethylphosphoramide

2.3.2 Resonance Raman Spectroscopy

Resonance Raman spectra were collected by a triple monochromator and detected with a CCD. Solutions of **1*** in HMPA were excited by argon and krypton ion lasers at wavelengths of 465, 476, 496, 514, and 530 nm. Peak intensities were numerically integrated and normalized to solvent peaks. The data obtained from 530.9 nm excitation are summarized in Table 1 including experimental and calculated frequencies, intensities, and assignments.

Table 2-1. Raman frequencies, intensities, distortions and assignments for vibrations observed upon 530 nm excitation of **1**⁺.

ω_{530} (cm ⁻¹)	relative intensity ^a	Δ_s	Δ_a	Assignment
229	5.11	1.20	1.20	Aryl-Aryl stretch
539	2.40	0.35	0.36	C-N wag
596	2.31	0.30	0.33	Aryl-Aryl rock
724	6.63	0.43	0.42	Aryl distortion, ONO bend
861	9.38	0.43	0.38	Aryl breathing
1028	1.14	0.12	0.16	Aryl distortion
1116	5.28	0.26	0.27	C-H wag, CN stretch
1328	12.49	0.32	0.33	CN stretch
1356	6.99	0.24	0.22	CN, CC stretch
1448	2.72	0.13	0.14	CN, CC stretch
1473	4.15	0.17	0.18	CN, CC stretch
1582	19.10	0.33	0.40	CC stretch

^aIntensities were scaled relative to a 630 cm⁻¹ vibration of the solvent, HMPA. ^bThe relative distortions, Δ_s , were calculated using Savin's formula. ^cThe distortions, Δ_a , were used to calculate the best fit absorption spectrum.

2.4 Discussion

2.4.1 Neighboring Orbital Model

The sign of the coupling is rarely considered for ground state mixed valence complexes since the adiabatic potential energy surfaces depend on the square of the coupling.^{2,22,23} Furthermore, since one of these two states is symmetric and the other is asymmetric, the transition between them is inherently Laporte allowed. However, the spectrum for a transition from a delocalized ground state to a mixed valence excited state has two bands (one to either adiabatic state) and only one will be allowed. The sign of the coupling has been evaluated in terms of how the excited state wave functions interact as interpreted by the neighboring orbital model.²² The

neighboring orbital model (NOM) considers how specific frontier orbitals of the charge bearing units interact.²³ For the majority of examples that have been studied the sign of the coupling was positive (i.e. the out-of-phase combination of the charge bearing units was more stable).^{22,24-28} This previously unexplained phenomenon results from the electronic interactions via the bridging unit – the orbitals on the bridge that are energetically the nearest neighbors to the orbitals on the charge bearing unit combined in such a way to stabilize the out-of-phase combination.²⁴⁻²⁸

In the case of **1**[•] the coupling is negative. The nitrobenzene π^* orbitals are the diabatic orbitals that interact to form the frontier molecular orbitals of **1**[•] are shown in the NOM diagram in Figure 2-2. The molecular orbitals were calculated in Gaussian 09 using the B3LYP/6-31G* method and the results were imaged by GaussView 5.²⁹ The coupling between the nitrobenzene charge bearing units occurs directly via the C-C bridging bond, and the in-phase combination is lower in energy as represented by the SOMO. Similarly, the higher energy out-of-phase combination of the diabatic orbitals forms the LUMO.

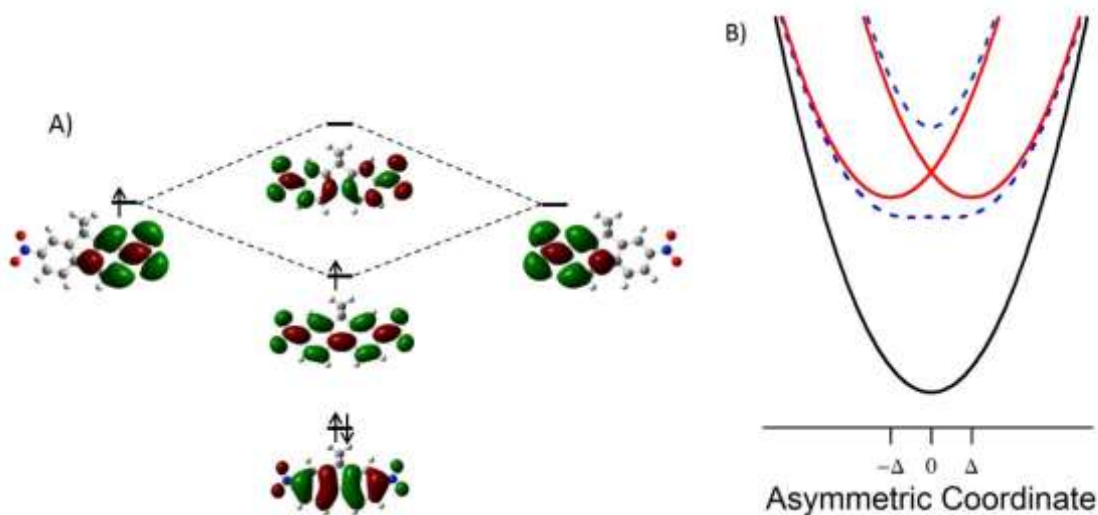


Figure 2-2. A) Neighboring orbital model diagram of **1**[•]. Left and right-hand sides depict diabatic orbitals of the two nitrobenzene charge bearing units. The center column displays the in-phase and out-of-phase combinations of the charge bearing units as well as the HOMO. B) Potential energy surfaces used to model electronic states.

In 1^* the nitrobenzene π^* in-phase and out-of-phase combinations are represented by the SOMO and LUMO, respectively, indicating that the coupling is negative. This implies that in a two-state model the lower surface corresponds to an in-phase combination while the upper surface corresponds to an out-of-phase combination. Since the HOMO is asymmetric with respect to the interchange of the two charge bearing units, the transition to the symmetric in-phase combination (the SOMO) is allowed while the transition to the asymmetric higher energy out-of-phase combination is forbidden.

The preponderance of positive coupling in previously analyzed systems has led to confusion with a different type of coupling, through space dipole coupling such as exciton coupling.^{24, 25, 30} In the molecular exciton model, neighboring transition dipole within dimers couple, forming a new set of electronic transitions that are similarly in-phase and out-of-phase combinations of the monomer's transitions.^{31, 32} The resulting states and their corresponding selection rules have been summarized by Kasha for the possible arrangements of dimers. The case of two molecules with collinear dipoles is similar to the arrangement of the nitrobenzenes in 1^* , Figure 2-3. The electronic transition of the monomer is shown on the left-hand side of the diagram. In a dimer the transition dipoles couple to form the two states E' and E'' . The identity of these states can be determined by considering the electrostatic interaction of the transition dipoles in this collinear arrangement. The two unique combinations are a head-to-head and a head-to-tail combination. Because the head-to-tail combination has an attractive coulombic interaction it is the lowest energy state, E' . The transition dipoles constructively add to produce an allowed transition with approximately double the intensity. In contrast, the head-to-head combination has

a repulsive interaction which leads to the higher energy state E'' , and this arrangement of the transition dipoles cancels out leading to an electric dipole forbidden transition.³²

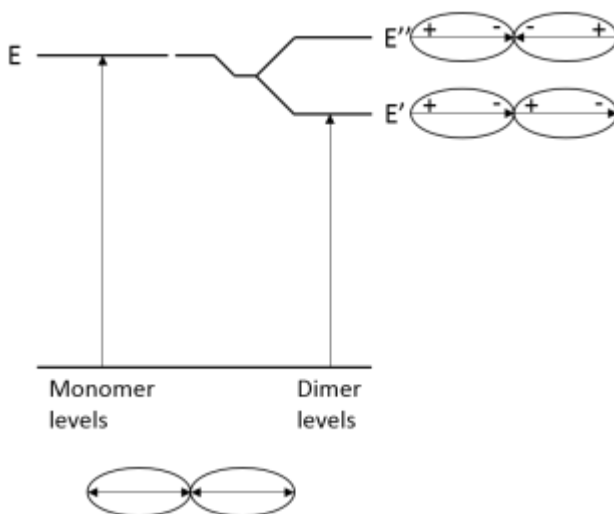


Figure 2-3. Energy level diagram for coupled excitons in a dimer.

There are two significant differences between the neighboring orbital model and the molecular exciton model. Primarily, the molecular exciton model is coupling between the transition dipoles and requires that the “*electron overlap between the light absorbing units must be small*”.³² In contrast the NOM specifically couples the electronic wave functions of the light absorbing units since the electron overlap is large. Secondly, for molecules in a collinear arrangement the molecular exciton model requires that the sign of the coupling is positive while the sign of the coupling from the NOM is dictated by the interaction of the individual orbitals of the covalent bridge and the charge bearing units. In the case of $\mathbf{1}^{\bullet-}$, the NOM indicates that the sign of the coupling is negative demonstrating a difference from the molecular exciton model.

2.4.2 Absorption Spectrum Assignment

The electronic absorption spectrum of $1^{\bullet}$ displays two intense transitions at 6894 and 18,975 cm^{-1} . The lowest energy transition is assigned as the IVCT where the lone electron is formally transferred from one nitrobenzene unit to the other. In the NOM this corresponds to moving the electron from the SOMO to the LUMO. The higher energy transition is assigned as the excited state mixed valence charge transfer where an electron is removed from the HOMO and placed in either the SOMO or the LUMO.

Two aspects of the HOMO to LUMO and SOMO to LUMO absorptions are a result of these assignments. First, the similarities in the vibronic spacing of these transitions are not accidental. Because both of these transitions involve the same diabatic orbitals, it is expected that the absorption spectra will show similar progressions. Second, the pattern for the relative intensity of the vibronic peaks are similar and support the hypothesis that the same molecular orbitals are involved in both transitions.

2.4.3 Important Symmetric Modes

The presense of highly distorted symmetric modes in electronic transitions add width and vibronic structure to the abosrption spectrum.³³ In contrast to a mode with a small distortion that will produce a very sharp spectrum, a highly distorted mode will give a significantly larger bandwidth. In the case of small distortion, only the lowest energy vibrational level has any significant overlap and a sharp absorption is observed; highly distorted modes display much larger

overlap for higher vibrational levels yielding a broadened spectrum. These highly distorted modes can be observed and their relative distortions calculated from the resonance Raman spectrum.

Raman spectra collected in resonance with the excited state mixed valence HOMO to SOMO transition displayed many enhanced vibrational modes. The vibrations that were enhanced greater than 5% of the most intense vibration were chosen for further analysis. From the relative intensities, relative dimensionless distortions can be calculated via Savin's formula^{34, 35} (Table 1). These distortions correspond to the geometrical changes that occur in the molecule when it is excited from the ground to an excited state. The specific coordinates that are most distorted will correspond to regions that have changes in electron density or changes in the bonding/antibonding interactions. These changes in the bonding interactions will cause geometrical distortions such as bond length or angle changes which are distortions along one or more normal coordinates.

How can we interpret from the molecular orbitals specifically which normal modes are enhanced in the resonance Raman spectrum of 1⁺? In promoting an electron from the HOMO to the SOMO level, an electron is moved from an out-of-phase combination of nitrobenzene orbitals to the in-phase combination of the diabatic nitrobenzene π^* orbitals (Figure 2-4). Analyzing the specific changes in nodal structure and electron density will dictate which normal coordinates will be distorted in the excited electronic state.

The HOMO has significant antibonding character of the π system along three vertical nodes. There is one node within the ring of both nitrobenzene charge bearing units and a third node between the two charge bearing units. While the SOMO is similarly an antibonding orbital of the π system, the specifics of the nodal structure change as individual bonds change from bonding to

antibonding and *vice versa*. Most importantly the interaction between the two charge bearing units changes from antibonding to bonding and the N-C bond becomes more strongly bonding.

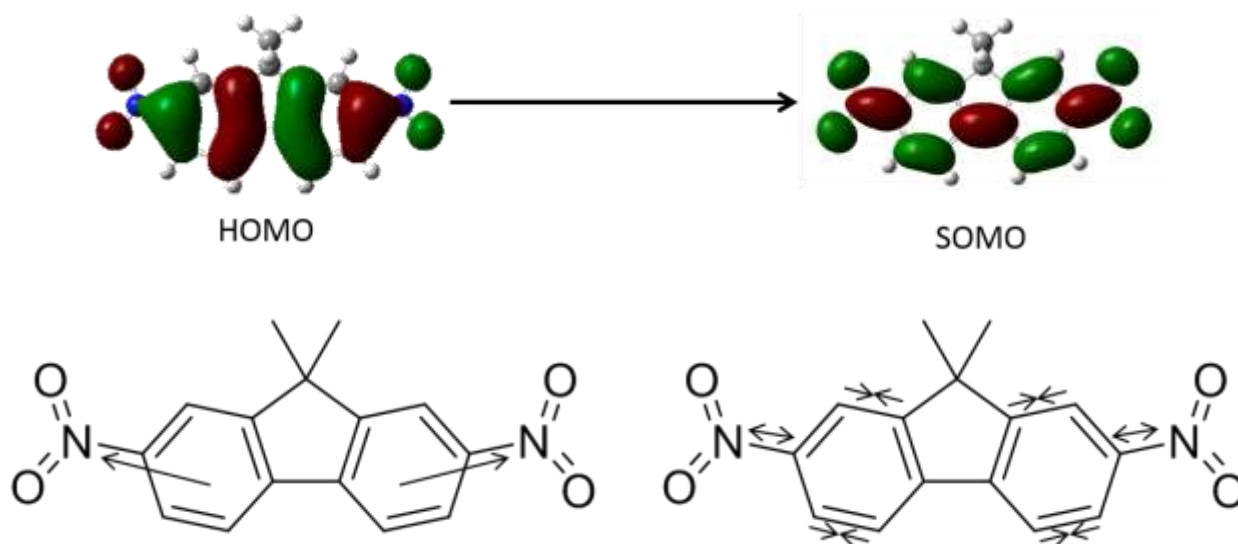


Figure 2-4. Top: HOMO and SOMO orbitals of 1^+ . Bottom: Representative displacement vectors for a 229 cm^{-1} (left) and 1582 cm^{-1} (right) normal modes of 1^+ .

By identifying the changes in electron density, it is expected that the most enhanced modes in the resonance Raman spectrum will have large distortions along the carbon-carbon double bonds in the rings and the C-C bond connecting the nitrobenzene units. The phases of the displacements can also be rationalized from this picture. Since all the carbon-carbon double bonds change strength in the HOMO-SOMO transition, one of the highly distorted modes should display simultaneous in-phase contractions along these bonds. Modes showing large distortions along the nitrogen-carbon bonds should also be distorted and enhanced in the Raman spectrum. DFT calculations of 1^+ predict a normal mode at 1624 cm^{-1} consistent with in-phase contractions along the carbon-carbon double bonds and the carbon-nitrogen bonds as expected. Accordingly, there is an intense vibration in the resonance Raman spectrum at 1582 cm^{-1} that is assigned to this normal

mode. The other most enhanced normal mode of $\mathbf{1}^{\bullet-}$ is observed at 229 cm^{-1} and assigned to a normal mode in which the two nitrobenzene units rock towards and away from each other. This motion is driven by the increased bonding interaction between the two phenyl rings but is more difficult to interpret since the distortion is not occurring directly along the bond axes.

2.4.4 Calculating the Absorption Spectrum

The band shape of the absorption spectra for the transitions involving the mixed valence system of $\mathbf{1}^{\bullet-}$ can be calculated using eq. 1 and the distortion data derived from the resonance Raman spectra. However, the enhanced vibrations observed in the resonance Raman spectrum are all symmetric. Calculating a spectrum using only these normal coordinates neglects the asymmetric coordinate of the mixed valence system. Since the system is highly delocalized, the vibronic structure is a result of the progression of the symmetric modes and the asymmetric coordinate does not contribute to the band shape.²⁷

The visible region of the absorption spectrum includes at least two prominent transitions. The more dominant transition that peaks near $18,980\text{ cm}^{-1}$ is assigned to the HOMO to SOMO transition. However, the breadth and intensity on the high energy side of the visible band cannot be accounted for by a single electronic transition. Calculating both the absorption spectrum and the resonance Raman profiles will demonstrate the presence of a second electronic transition near $20,000\text{ cm}^{-1}$. Since the SOMO $\rightarrow$ LUMO transition is near $7,000\text{ cm}^{-1}$, the HOMO $\rightarrow$ LUMO transition should similarly be found approximately $7,000\text{ cm}^{-1}$ above the HOMO $\rightarrow$ SOMO transition. This is far beyond the visible region of the absorption spectrum and indicates that other

orbitals must be involved. The second electronic transition therefore most likely originates from an orbital that is more stabilized than the HOMO and places an electron in the SOMO. The HOMO-3 orbital contains significant electron density on the benzene rings and is a likely candidate for the origin of a second electronic transition.

The distortions for the most intense Raman vibration modes collected in resonance with the visible band were calculated using Savin's formula. Using the relative distortions calculated from Savin's formula, Δ_s , a good fit can be produced for the low energy IVCT. Optimizing the magnitude of the distortions within the experimental error of the Raman intensity improves the overall quality of the calculated absorption spectrum. The dimensionless distortions, Δ_a , were utilized to calculate the IVCT shown in Figure 2-4 ($E_{00} = 6840 \text{ cm}^{-1}$, $\Gamma = 90 \text{ cm}^{-1}$).

The same Δ_a values can be used to calculate the primary component of the visible absorption by shifting the electronic origin to $18,920 \text{ cm}^{-1}$ (Figure 2-4). While this calculated absorption spectrum displays some of the vibronic features of the experimental spectrum, the intensity on the higher energy side of the spectrum is not reproduced. Some of the intensity in this region is due to the tail of an intense UV transition not shown in this Figure, although this cannot account for all of the excess intensity in this region.

A second problem with the fit is the large vibronic feature that appears near 1685 cm^{-1} from the E_{00} . The presence of this vibronic feature cannot be easily explained since there was no observed Raman vibrational mode at that frequency and the nearest enhanced mode is at 1582 cm^{-1} . While decreases in frequency between the ground and excited state are common, a 100 cm^{-1} increase in the vibrational frequency is unusual. Excited state vibrations are often at lower frequencies than ground state vibrations since ground to excited state transitions normally remove

an electron from a bonding orbital and place it in an antibonding orbital. However, the assigned HOMO $\rightarrow$ SOMO transition significantly changes the π structure from antibonding to bonding along several bonds. Specifically, all of the bonds that change from π^* to π have significant distortion in the 1582 cm^{-1} mode justifying a large increase in the vibrational frequency of the 1582 cm^{-1} mode. Yet even a large adjustment of this vibrational frequency does not produce a satisfactory fit of the experimental absorption spectrum in this region.

In order to produce a quality best fit absorption spectrum a second electronic transition must be included in the calculated absorption spectrum corresponding to the HOMO-3 to SOMO transition. Including a second transition accounts for the vibronic feature at 1685 cm^{-1} from E_{00} and account for the intensity on the high energy side of the spectrum. However, the interference of the Raman scattering in the region where the two visible transitions overlap prevents the calculation of distortions that correspond to the second transition. These effects of a second state on the Raman signal will be explained further in the following section. The inclusion of a second transition with a progression in a single normal coordinate ($\omega = 860 \text{ cm}^{-1}$, $\Delta = 1.7$, $E_{00} = 19920$, $\Gamma = 275 \text{ cm}^{-1}$) approximated the total absorption spectrum as shown in Figure 2-5.

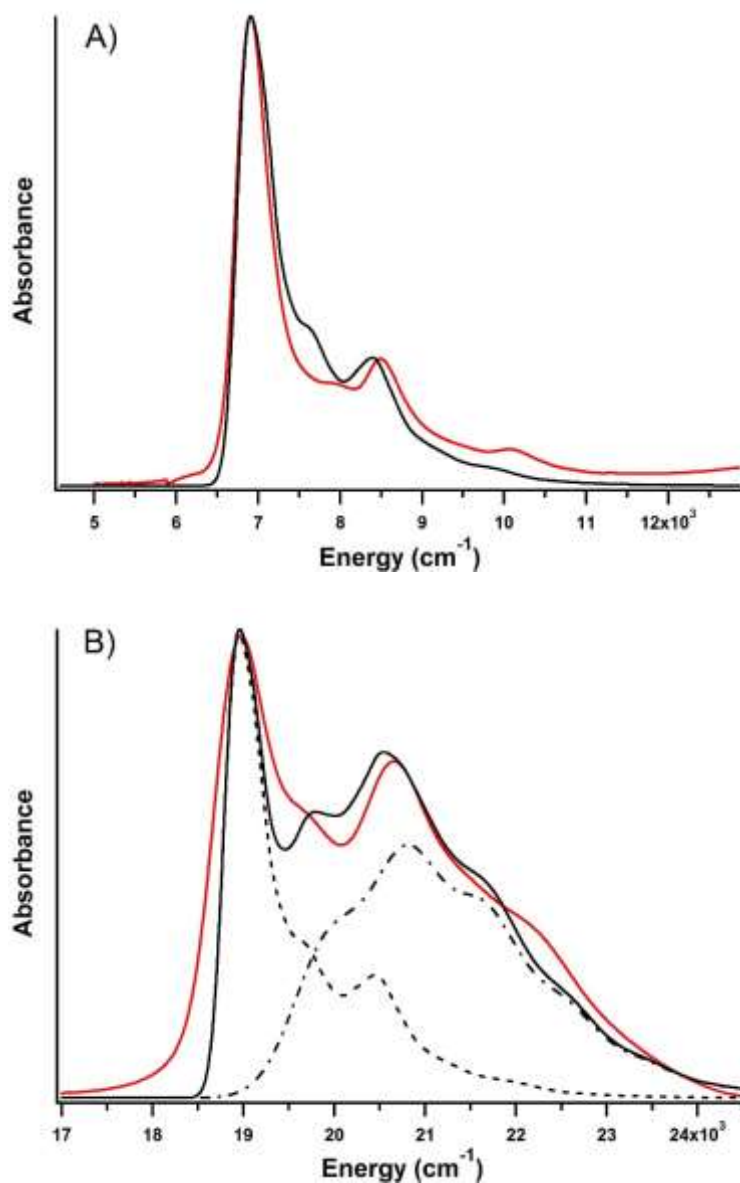


Figure 2-5. A) Experimental (red) and calculated (black) absorption spectra of the low energy band of 1^+ . B) Baseline subtracted experimental (red) absorption spectrum of visible region of 1^+ . The $\text{HOMO} \rightarrow \text{SOMO}$ (---) and $\text{HOMO-3} \rightarrow \text{SOMO}$ (- · - · - ·) were added to produce the calculated visible spectrum (black).

2.4.5 Interference Effects on Resonance Raman Profiles

The Raman profiles of 1^+ across the visible region provide additional evidence for the presence of a second excited state. Figure 2-6a shows three Raman spectrum of 1^+ excited at 530, 496, and 465 nm (normalized to the 630 cm^{-1} HMPA peak) and Figures 2-6b and 2-6c show the Raman profiles of the 229 and 1582 cm^{-1} modes respectively. Examining the resonance Raman spectra there is a noticeable decrease in the relative scattering intensity as the excitation wavelength decreases. The Raman profiles plot the Raman scattering intensity of the peak as a function of excitation wavelength and demonstrate that the relative Raman intensities do not follow the contour of the absorption spectrum.

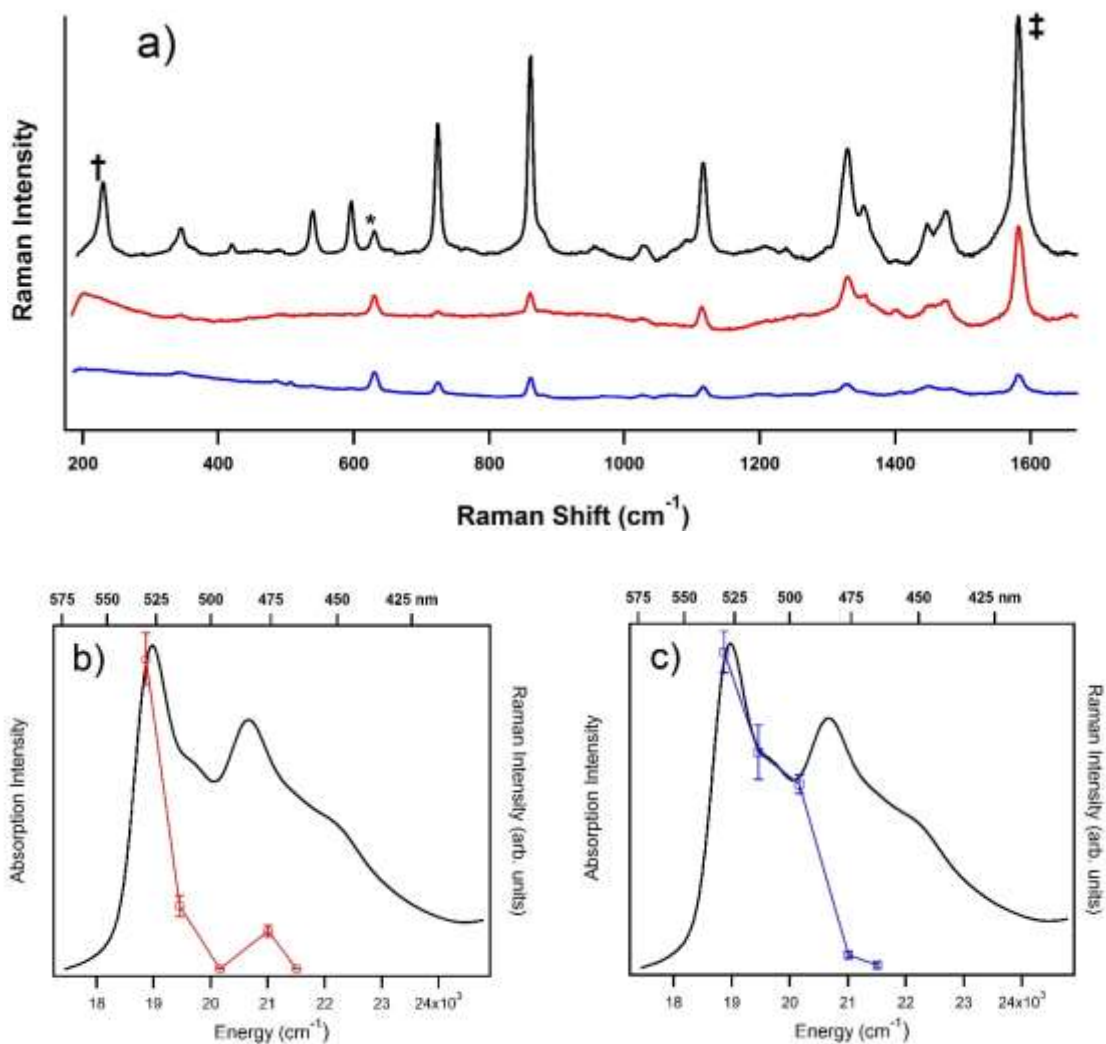


Figure 2-6. Top: Raman spectra excited at 530 nm (black), 496 nm (red) and 465 nm (blue). All spectra are normalized to the 630 cm^{-1} solvent peak (*). The 229 cm^{-1} peak (†) and 1582 cm^{-1} peak (‡) are denoted. Bottom: Raman profiles of 229 cm^{-1} (left) and 1582 cm^{-1} (right) modes of 1^* . The experimental intensities are marked by circles and squares for the 229 and 1582 cm^{-1} modes, respectively.

In contrast to the absorption spectrum that is the sum of the intensities of multiple overlapping excited states, Raman scattering squares the sum of the polarizabilities of the of excited states.^{36, 37} The effect of this produces an interference between neighboring excited states and thus the Raman profile may not mimic the shape of the absorption spectrum. Instead, the real

and imaginary components of the polarizability from the nearby states can effectively cancel out causing a Raman deenhancement.³⁸ This has previously been demonstrated in organometallic sandwich complexes and complexes displaying mixed valence excited states.^{36, 39-41}

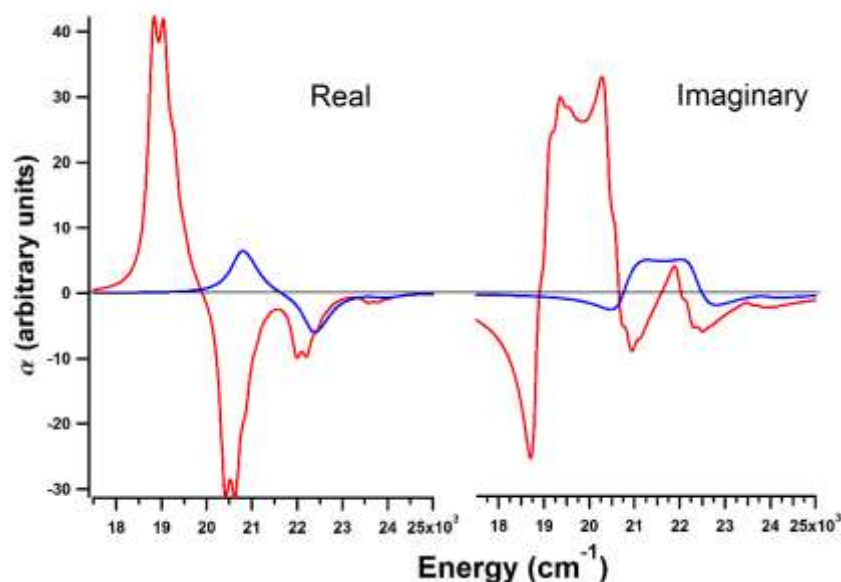


Figure 2-7. Left: Real components of the polarizability for state 1 (red) and state 2 (blue). Right: Imaginary components of the polarizability.

The presence of a second excited state within the visible region can be inferred by the de-enhancement of the intensities in the Raman profiles. The Raman profiles of the 229 and 1582 cm^{-1} modes of 1^+ demonstrate the presence of the second excited state. The experimental Raman profile of the 229 cm^{-1} mode has a maximum at 18,868 cm^{-1} excitation and decreases rapidly as the excitation energy is increased but has a slight increase in the scattering intensity near 21,000 cm^{-1} . Similarly, the Raman profile of the 1582 cm^{-1} mode closely follows the absorption spectrum at lower energies with a maximum intensity near 18,868 cm^{-1} . However, the scattering intensity of the 1582 cm^{-1} sharply drops off and has a minimum and does not regain its intensity at higher

energy. The loss of Raman intensity, which does not follow the absorption spectrum, is a result of the Raman deenhancement induced by the presence of a nearby excited state.

The potential of neighboring excited states to cause Raman deenhancement can be demonstrated via a pedagogical example to demonstrate how the polarizabilities from neighboring states can cancel out (Figure 2-7). Examining plots of the polarizabilities for the 1582 cm^{-1} mode shown in Figure 2-6 demonstrates the origin of the Raman deenhancement. Between $21,000$ and $21,500\text{ cm}^{-1}$, near the electronic origin of the second excited state, both the real components and imaginary components of each state are opposite in sign. Adding them thus diminishes the intensity of either one alone producing the observed deenhancement in the Raman profile.

2.5 Conclusion

The electronic absorption spectrum of 1^* contains two bands that are characteristic of ground state and excited state mixed valence. The NIR transition corresponds to the IVCT associated with ground state mixed valence while the energy of the transition to the mixed valence excited state is in the visible region. The similar vibronic progressions in both of these bands is a result of the molecular orbitals that are in common with these transitions.

The neighboring orbital model of 1^* demonstrates that a set of orbitals localized on the nitrobenzene units combine in-phase and out-of-phase to form the SOMO and LUMO molecular orbitals respectively. Furthermore, the in-phase combination, the SOMO, is lower in energy than the out-of-phase combination implying that the coupling between the nitrobenzene is negative. The molecular exciton model predicts that chromophores interacting in this geometry will result

in positive coupling. This difference in the sign of the coupling for 1^* demonstrates how the excited state mixed valence model is distinct from the molecular exciton model.

Raman spectra collected in resonance with the transition to the mixed valence excited state were used to determine the distortions along symmetric normal coordinates of 1^* . In particular, the 229 cm^{-1} and 1582 cm^{-1} vibrations were the most intense in the resonance Raman spectrum and therefore the most distorted coordinates in the excited state. However, as the excitation wavelength was decreased, the Raman intensity of several vibrations decreased significantly due to Raman deenhancement. The interaction between nearby excited states caused the polarizability terms to cancel and greatly reduced the Raman scattering.

Fitting both of the transitions that correspond to the ground state and excited state mixed valence showed that the 229 cm^{-1} and 1582 cm^{-1} vibrations contributed significantly to the overall width and vibronic progression of both bands. This relationship in the normal coordinate distortions and electronic absorption spectra of the two transitions is not coincidental. It is a result of the fact that both transitions change the population of the SOMO leading to similar geometric distortions as a relationship between ground state mixed valence and excited state mixed valence.

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Chapter 3

Molecular Distortions and Selection Rules in the Mixed Valence Excited States of Diisopropyl Ditolyhydrazine

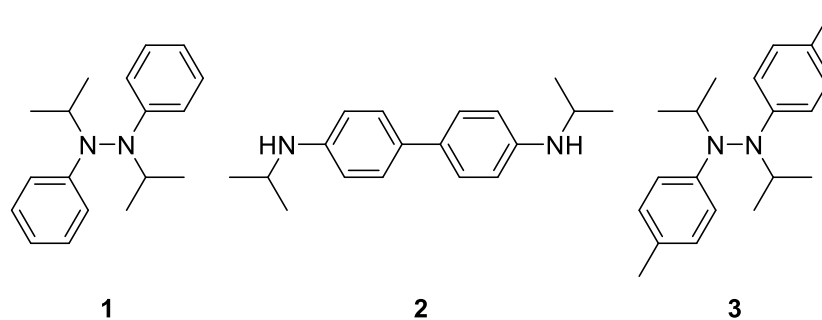
3.1 Introduction

The donor-acceptor nature of charge transfer optical absorptions are well known principles of molecular spectroscopy.¹⁻⁴ A photon excites an electron to transfer between relatively molecular orbitals (MOs) that are separated by a distance, such as metal to ligand charge transfers, formally changing the oxidation state at both sites.² The changes in the oxidation states and the bond order between the sites induce large nuclear distortions in the molecule as it rearranges in the excited state.⁵⁻⁷ The dynamics of this process and the resultant absorption spectra that result from the interaction of a single donor-acceptor pair are understood in terms of PKS⁸ and the time-dependent theory of spectroscopy;⁹⁻¹² but how do these aspects differ when a second equivalent donor or acceptor is added to the molecular mixture?

Excited state mixed valence (ESMV) exists when molecules possess a second donor or acceptor resulting in two possible charge transfer transitions.¹³⁻¹⁵ How do a pair of equivalent charge transfer transitions in a single molecule interact? In the null case of insignificant electronic coupling, nothing happens. However, if the pair of electronic transitions can be electronically coupled they combine to produce in-phase and out-of-phase combinations.¹⁶ The spectral effects of coupling charge transfer transitions to yield mixed valence excited states have been previously established by Lockard *et. al*, detailing the origin of the coupling in terms of MOs,¹³ the sign of the coupling,¹⁴ and the dependence on the spatial orientation¹⁴ of the transitions.

The presence of an extra equivalent site that can participate in charge transfer paints a picture that is reminiscent of the familiar ground state mixed valence. Ground state mixed valence (GSMV) is characterized by two interchangeably equivalent charge bearing units (M) that share

an excess charge and are covalently linked either directly or through a bridge (B) yielding the diabatic states $M^{+/-}-B-M$ and $M-B-M^{+/-}$.^{2, 3, 17, 18} Many studies have focused on the magnitude of coupling,^{2, 17, 19} the rate of electron transfer,²⁰⁻²⁴ and the origin of the coupling¹⁶ for a variety of mixed valence complexes. In contrast, ESMV has a charge distribution that is symmetric in the ground state yet becomes isolated on either M in the excited state. The two charge localized states couple producing a pair of adiabatic states that are identical to those of GSMV. Naturally, the wave packet dynamics within this coupled system is the same for both phenomenon. However the spectra that result from ESMV display two bands: one corresponding to the transition to each surface.¹³⁻¹⁵



Scheme 3-1. Molecular structure of ESMV compounds studied.

Lockard *et al.* previously presented the absorption and resonance Raman spectra of 1,2-diphenyl-1,2-diisopropyl hydrazine radical cation (1^+) and explained the absorption spectra in terms of ESMV.²⁵ Thomas Bally later pointed out that the reported absorption spectrum was not typical of diphenyl hydrazine radical cations. Further investigation revealed that at room temperature 1^+ readily undergoes a benzidine rearrangement to form 2^+ . Therefore, the spectra and analysis originally reported are actually of 2^+ , not 1^+ . Fortunately, this does not nullify the validity

or usefulness of ESMV as an interpretation of absorption spectra since 2^+ is similarly expected to demonstrate ESMV.

Herein we report the absorption and resonance Raman spectra of 1,2-ditolyl-1,2-diisopropyl hydrazine radical cation (3^+), a compound that is structurally similar to 1^+ yet is thermally stable. The absorption spectrum of 3^+ is interpreted in terms of ESMV utilizing the typical tools of the neighboring orbital model (NOM), an analysis of the transition dipoles, and the resonance Raman spectrum. The non-trivial differences between the absorption spectra of 2^+ and 3^+ are also explained.

3.2 Theoretical Methods

The time-dependent theory of molecular spectroscopy outlines the calculation of absorption spectra utilizing normal coordinate distortions as experimentally observed in vibrational spectra.²⁶ This theory can be applied to molecular systems exhibiting excited state mixed valence.¹³ Here, we present a brief background of this theory:

Absorption spectra are calculated according to Eq. 1:

$$I(\omega) = C\omega \int_{-\infty}^{\infty} \exp(i\omega t) \left\{ \langle \Phi | \Phi(t) \rangle \exp\left(-\Gamma^2 t^2 + \frac{iE_{00}}{\hbar} t\right) \right\} dt \quad (1)$$

where the absorption, $I(\omega)$, is absorption as a function of frequency, Γ is a phenomenological damping function and E_{00} is the energy difference between the ground and excited electronic state of interest. Essentially, the calculated absorption spectrum is the Fourier transform of the time-dependent overlap, $\langle \Phi | \Phi(t) \rangle$. This is the autocorrelation function and it corresponds to the

overlap of the evolving wavepacket, $\Phi(t)$, with the initial wave packet, Φ . When n uncoupled normal coordinates exist, the autocorrelation may be calculated by:

$$\langle \Phi | \Phi(t) \rangle = \prod_n \langle \Phi^n | \Phi^n(t) \rangle \quad (2)$$

where Φ^n is the n^{th} individual wave packet associated with the n^{th} coordinate of which there are N . Wave packets are propagated on harmonic surfaces that are displaced from the ground state. In conjunction with resonance Raman data, the relative displacements of individual vibrational modes may be calculated according to Savin's formula and the corresponding absorption spectrum may be calculated.

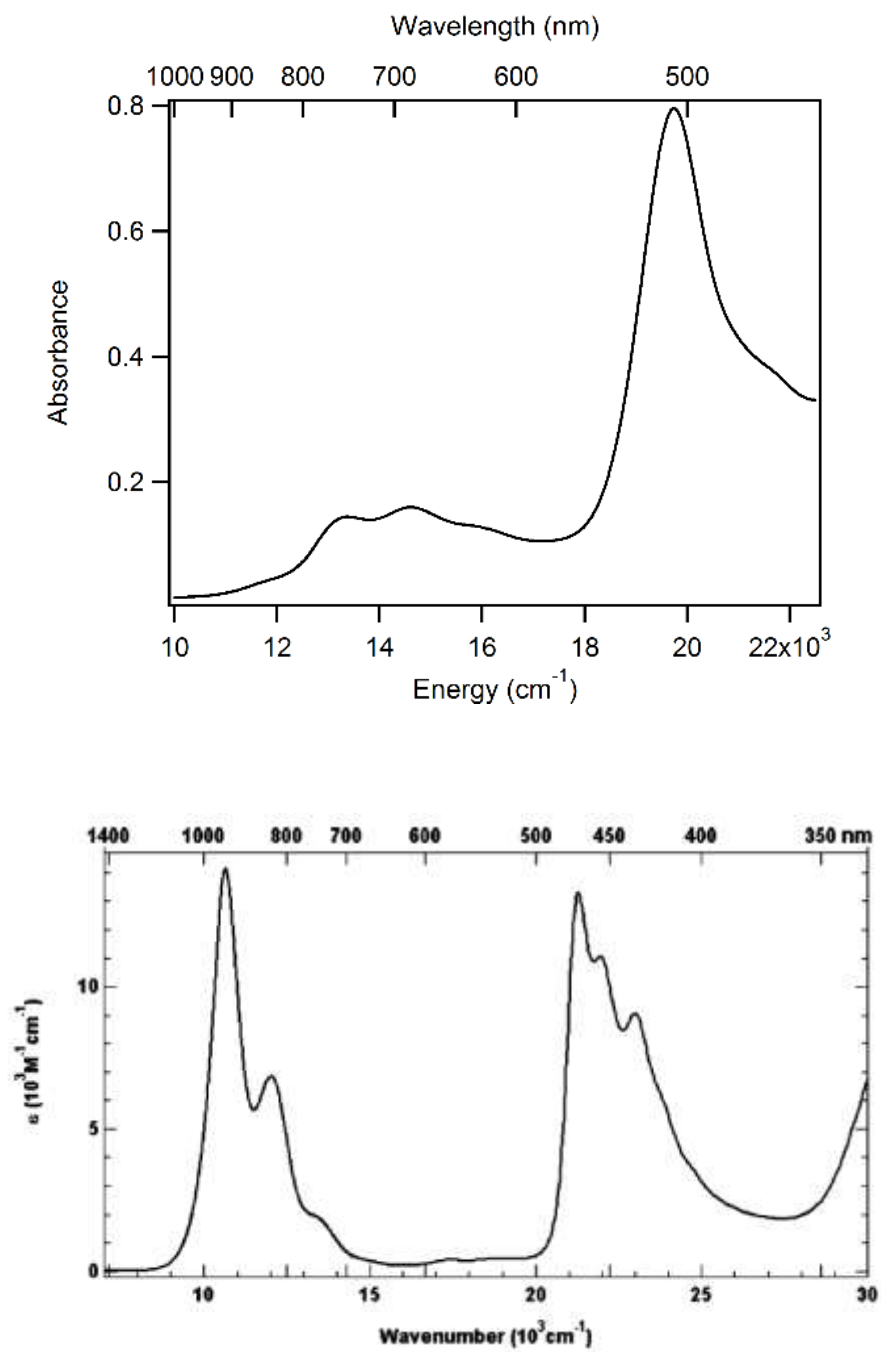


Figure 3-1. Absorption spectrum of 3^+ (top) and 2^+ (bottom)

3.3 Results

The absorption spectrum of 3^+ was acquired at room temperature in methylenechloride, see figure 9. Both the lower energy absorption and the higher energy absorption with maxima at $14,600\text{ cm}^{-1}$ and $19,720\text{ cm}^{-1}$, respectively, appear to display a vibronic progression. The lower energy transition has a peak spacing of $\sim 1210\text{ cm}^{-1}$. Any vibronic progression for the higher energy transition is not resolvable.

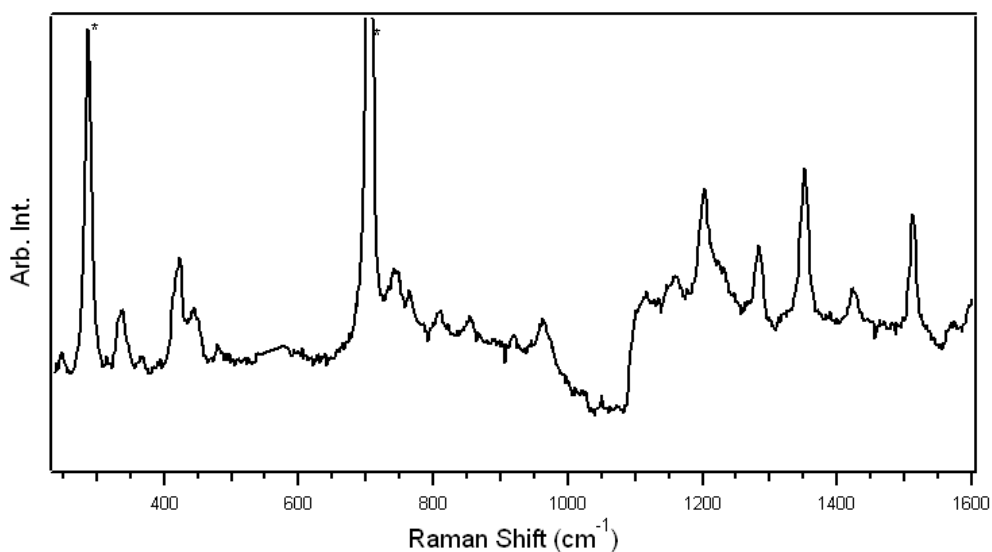


Figure 3-2. Resonance Raman spectrum of 3^+ obtained using 514 nm excitation. The stars indicate the methylenechloride solvent peaks.

The Resonance Raman spectrum of 3^+ (Figure 3-2) was collected using 514 nm excitation which is in resonance with the higher energy absorption band of the compound. Due to the thermal stability of 3^+ , it was not possible to acquire multiple Raman spectra from one sample. The observed frequencies along with their intensities, distortions, and assignments are presented in Table 3-1.

Table 3-1. Resonance Raman data including experimental and calculated frequencies, intensities, displacement and assignments for observed vibrational modes of 3^+ . ^a Intensities are scaled to the the most intense vibration at 1351 cm^{-1} . ^b Displacements are obtained using Savin's formula.

Experimental Frequency (cm^{-1})	Calculated Frequency (cm^{-1})	I/I'_{514} nm^a	$\Delta_{514 \text{ nm}}^b$	Δ Low Energy	Δ High Energy	Assignment
337	341	0.40	2.52		0.81	N-Ph wag
420	417	0.84	2.95		0.94	Ph out-of-plane
444	445	0.46	2.06		0.66	N twist
766		0.05	0.41		0.13	
809	814	0.06	0.41		0.13	Ph breathing
854		0.10	0.50		0.16	
964	990	0.87	1.31	1.32	0.42	NN str. + Ph breathing
1158	1196	0.20	0.52		0.16	ⁱ Pr bend
1201	1236	0.59	0.87	0.88	0.28	NN str.
1221	1243	0.91	1.05	1.07	0.34	Ph-Me str.
1283	1301	0.35	0.62		0.20	NN stretch + N-Ph str.
1351	1349	1.00	1.00	1.01	0.32	Ph deformation
1425	1460	0.23	0.45		0.14	CC stretch
1512	1540	0.68	0.74		0.24	Ph-Me + C-N str.
1571	1606	0.06	0.21	0.21	0.07	CC str.
1607	1644	0.82	0.76		0.24	CC str.

3.4 Discussion

3.4.1 Excited State Mixed Valence

Similar to ground-state mixed valence, excited state mixed valence can be modeled by coupling harmonic potential energy surfaces (Figure 3-3). A single harmonic potential models the ground state, which is not displaced along the nuclear coordinate, represents the positive charge as being localized on the nitrogen atoms. Upon excitation, the positive charge can be transferred to either of the two phenyl substituents. Both of these states are modeled by harmonic potentials that are equally displaced in the opposite direction from the equilibrium position of the nuclear coordinate. This pair of degenerate excited states is coupled yielding two non-degenerate adiabatic

surfaces centered at the zero of the nuclear coordinate where the splitting between the states $\Delta E = 2H_{ab}$. The presence and height of an energy barrier in the lower adiabatic state is determined by the ratio of the coupling, H_{ab} , and λ ; a barrier is present if $H_{ab} < \lambda/2$, resulting in a system that is partially localized. A larger coupling constant results in a delocalized charge.

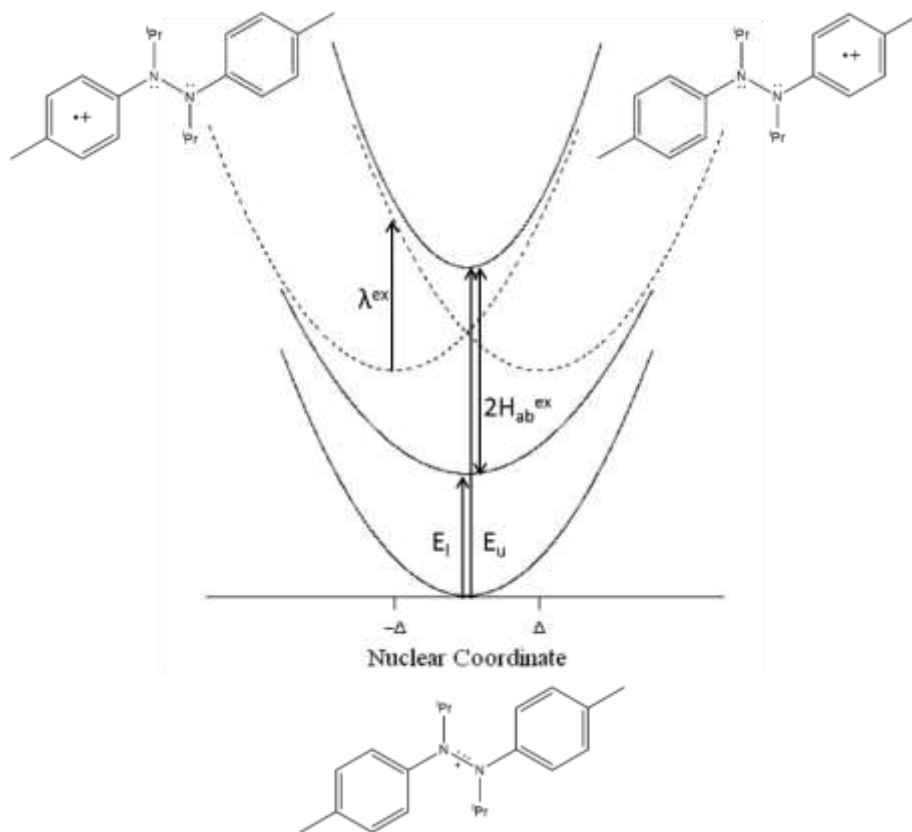


Figure 3-3. Excited-state mixed valence diagram of 3^+ depicting the potential energy surfaces of the ground state, degenerate diabatic excited states (dashed lines), and coupled adiabatic excited states (solid lines).

The effects of excited state mixed valence can be observed in the absorption spectrum of 3^+ . The two transitions at $14,600\text{ cm}^{-1}$ and $19,720\text{ cm}^{-1}$ are the transitions to the lower and upper coupled surfaces. Since the energy difference between these states is twice the coupling, the coupling is approximately 2500 cm^{-1} .

3.4.2 Neighboring Orbital Analysis

An analysis of specific frontier molecular orbitals of a molecule exhibiting mixed valence can provide insightful information in determining the sign of the coupling,¹⁴ identifying the adiabatic states, and ultimately determining the selection rules. While through space coupling is intrinsically negative, coupling that is mediated by a bridge may be either positive or negative.

The neighboring orbital model of 3^+ depicts a degenerate set of diabatic phenyl π orbitals on the left (Figure 3-4). Similarly, a pair of nitrogen diabatic p orbitals are shown on right. These orbitals from the bridge and the charge bearing unit. Mixing the orbitals of the same symmetry to generate in-phase and out-of-phase combinations yields the four molecular orbitals shown in the center of the diagram. The adiabatic molecular orbitals used in Figure 3-4 were calculated by DFT methods using Gaussian 09 and B3LYP/6-31G*.

Within the neighboring orbitals of 3^+ there are seven electrons. Therefore, the ground state electron configuration $\Psi_B^- = (\psi_B^+)^2(\psi_M^-)^2(\psi_M^+)^2(\psi_B^-)^1$ and the charge resides on the nitrogen bridge. The lowest energy transition promotes an electron from ψ_M^+ to ψ_B^- (this is equivalent to moving a positive charge from the nitrogen bridge to either phenyl substituent); the resulting electron configuration is $\Psi_M^+ = (\psi_B^+)^2(\psi_M^-)^2(\psi_M^+)^1(\psi_B^-)^2$. This excited state is represented by the lower adiabatic surface shown in Figure 3. Similarly, promotion of an electron from ψ_M^- to ψ_B^- yields an electron configuration $\Psi_M^- = (\psi_B^+)^2(\psi_M^-)^1(\psi_M^+)^2(\psi_B^-)^2$ and this state is represented by the upper adiabatic surface. Examining the two states corresponding to the hole being in the coupled phenyl system, Ψ_M^+ and Ψ_M^- , the transition to the in-phase combination of the phenyl π orbitals is

lower in energy than the out-of-phase combination implying that the coupling is negative. The difference in energy between Ψ_M^+ and Ψ_M^- equals the energy difference of the upper and lower adiabatic states and therefore is also $2H_{ab}$.

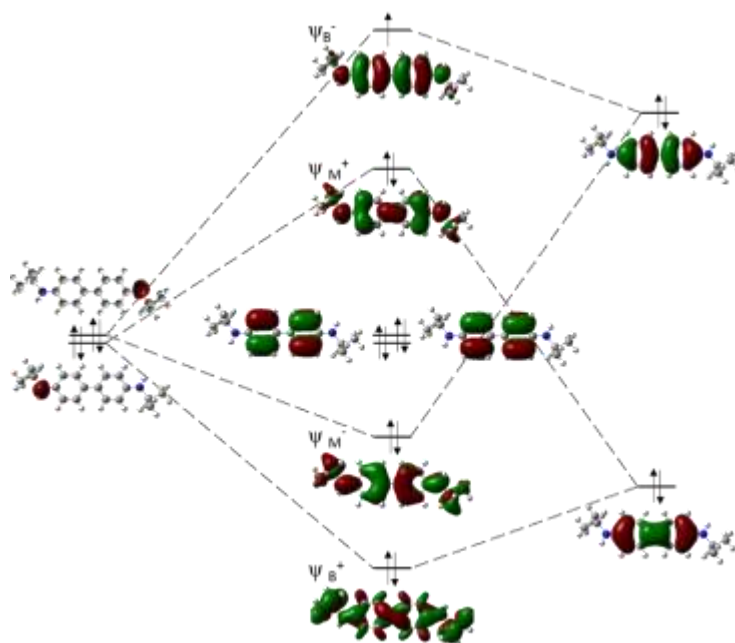
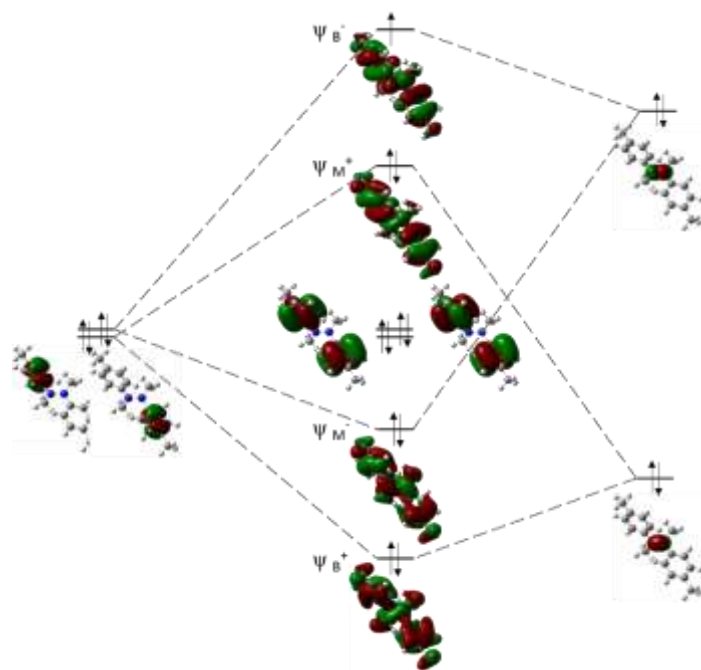


Figure 3-4. Neighboring orbital diagram of 3^+ (top) and 2^+ (bottom)

3.4.3 Transition Dipole

The symmetry of the transition dipole determines the selection rules for a given transition. Some transitions may be non-zero at all points along a vibrational coordinate and are therefore allowed, while other transitions may be zero at the origin and non-zero as the molecule vibrates to either side (vibronically allowed). Within the molecule 3^+ , both of the charge transfer transitions from the bridge π^* orbital, ψ_B^- , to either benzene π orbital alone are allowed. However, within the excited state the orbitals couple producing linear combinations; similarly their transition dipoles must be transformed to reveal the selection rules for this molecule.

A simple starting point for the diabatic orbitals of this system employs four states: a set of π bonding orbitals on both benzene rings, and a π orbital on both nitrogen atoms (figure 5). A simple Hamiltonian for this system is

$$\hat{H}_{Diabat} = \begin{pmatrix} Ph & H_{Ph} & 0 & 0 \\ H_{Ph} & Ph & 0 & 0 \\ 0 & 0 & N & H_N \\ 0 & 0 & H_N & N \end{pmatrix} \quad (3)$$

where Ph and N represent the Hamiltonian operators for the phenyl and nitrogen sets, respectively, and H is the coupling between either set. This diabatic matrix can be diagonalized by the unitary transformation matrix

$$U = \begin{pmatrix} \cos\theta & \sin\theta & 0 & 0 \\ -\sin\theta & \cos\theta & 0 & 0 \\ 0 & 0 & \cos\varphi & \sin\varphi \\ 0 & 0 & -\sin\varphi & \cos\varphi \end{pmatrix} \quad (4)$$

where $2\theta = \frac{2H_{Ph}}{V_{PhL}-V_{PhR}}$, $Tan2\varphi = \frac{2H_N}{V_{NL}-V_{NR}}$ and the L and R differentiate phenyl/nitrogen that is

located on either the left or right hand side of the molecule. Undergoing the same transformation

for wave functions, $\psi_{Adiabatic} = U^{-1} \cdot \psi_{Diabat} \cdot U$, produces four adiabatic wave functions:

$$\psi_B^+ = \psi_{BL} \cos\theta + \psi_{BR} \sin\theta \quad (5)$$

$$\psi_B^- = \psi_{BR} \cos\theta - \psi_{BL} \sin\theta \quad (6)$$

$$\psi_M^+ = \psi_{ML} \cos\varphi + \psi_{MR} \sin\varphi \quad (7)$$

$$\psi_M^- = \psi_{MR} \cos\varphi - \psi_{ML} \sin\varphi \quad (8)$$

which are shown in the center column of Figure 3-5. This model inherently produces wave functions that neglect mixing between the bridge and phenyl moieties. However, the coupling between the nitrogen atoms is through space and inherently much larger since they are close while the through-bond coupling of the phenyls is much weaker. This produces the adiabatic orbitals ψ_B^+ and ψ_B^- which are predominantly nitrogen and ψ_M^- and ψ_M^+ which place most of the electron density on the phenyl moieties.

The transition dipole operator for this model is

$$\hat{\mu}_{diabat} = \begin{pmatrix} 0 & 0 & \mu_\alpha & \mu_\beta \\ 0 & 0 & -\mu_\beta & -\mu_\alpha \\ \mu_\alpha & -\mu_\beta & 0 & 0 \\ \mu_\beta & -\mu_\alpha & 0 & 0 \end{pmatrix} \quad (9)$$

where μ_α is a transition dipole from a nitrogen to the nearer phenyl and μ_β is the transition dipole to the farther phenyl. The positive and negative signs indicate the spatial directionality.

Transforming to the adiabatic basis yields the matrix

$$\hat{\mu}_a = \begin{pmatrix} 0 & 0 & \mu_{\psi_B^+ \rightarrow \psi_M^+} & \mu_{\psi_B^+ \rightarrow \psi_M^-} \\ 0 & 0 & \mu_{\psi_B^- \rightarrow \psi_M^+} & \mu_{\psi_B^- \rightarrow \psi_M^-} \\ \mu_{\psi_B^+ \rightarrow \psi_M^+} & \mu_{\psi_B^- \rightarrow \psi_M^+} & 0 & 0 \\ \mu_{\psi_B^+ \rightarrow \psi_M^-} & \mu_{\psi_B^- \rightarrow \psi_M^-} & 0 & 0 \end{pmatrix} \quad (10)$$

$$\mu_{\psi_B^+ \rightarrow \psi_M^+} = \text{Cos}[\theta + \varphi]\mu_\alpha - \text{Sin}[\theta - \varphi]\mu_\beta \quad (11)$$

$$\mu_{\psi_B^+ \rightarrow \psi_M^-} = -\text{Sin}[\theta + \varphi]\mu_\alpha + \text{Cos}[\theta - \varphi]\mu_\beta \quad (12)$$

$$\mu_{\psi_B^- \rightarrow \psi_M^+} = -\text{Sin}[\theta + \varphi]\mu_\alpha - \text{Cos}[\theta - \varphi]\mu_\beta \quad (13)$$

$$\mu_{\psi_B^- \rightarrow \psi_M^-} = -\text{Cos}[\theta + \varphi]\mu_\alpha - \text{Sin}[\theta - \varphi]\mu_\beta \quad (14)$$

The two transitions of interest are the transitions from ψ_M^+ and ψ_M^- to ψ_B^- . The transition from ψ_M^+ to ψ_B^- , the lowest energy transition, has the corresponding transition dipole $\mu_{\psi_B^- \rightarrow \psi_M^+}$. Since the potential energy operators are equal at the origin, $\text{Tan}2\theta = \text{Tan}2\varphi = \infty$ at the origin. It follows that $\theta = \varphi = 45^\circ$. Thus $\mu_{\psi_B^- \rightarrow \psi_M^+}$ equals $-\mu_\alpha - \mu_\beta$ at the origin which is non-zero since $\mu_\alpha \neq \mu_\beta$ producing an allowed transition. The transition from ψ_M^- to ψ_B^- has the transition dipole $\mu_{\psi_B^- \rightarrow \psi_M^-}$. In contrast this transition dipole is zero at the origin. However, movement to either side of the origin along an asymmetric coordinate produces a non-zero transition dipole yielding a vibronically allowed transition.

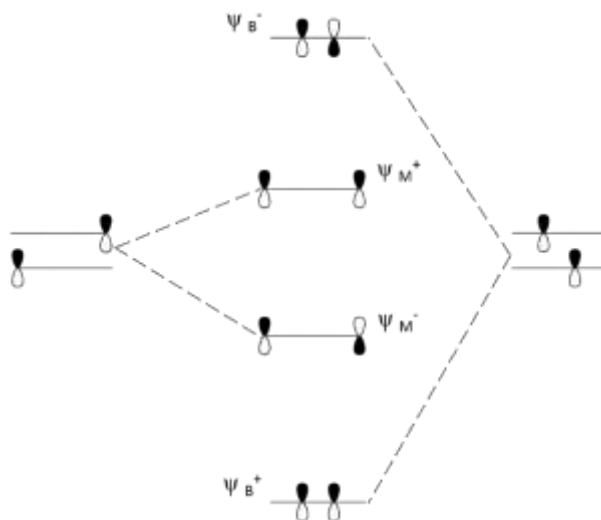


Figure 3-5. Simplified NOM for 3^+

These selection rules are also in agreement with group theory and TD-DFT calculations for this and similar compounds. Neglecting significant twisting, 3^+ belongs to the point group C_{2h} and the ground state is B_g . The transition to the lowest energy excited state, A_u , is allowed while the transition to the next lowest state, B_g , is Laporte forbidden. Similarly, the transition from the lowest orbital in the NOM, ψ_B^+ , to ψ_B^- is allowed since this excited state is also A_u .

3.4.4 Absorption Spectra

The absorption spectrum for 3^+ agrees with these various approaches and displays a broad low energy absorption with vibronic structure at $14,600\text{ cm}^{-1}$ that corresponds to the lowest energy transition in the NOM, Ψ_M^+ to Ψ_B^- . The intense peak at $19,720\text{ cm}^{-1}$ is assigned as the transition from Ψ_B^+ to Ψ_B^- . The vibronically allowed transition to the mixed valence excited state, Ψ_M^- to Ψ_B^-

, is not observable in this spectrum due to either the strength of the coupling or the overlap with other transitions.

The selection rules that can be determined for 2^+ are identical to those for 3^+ . Despite structural differences, the symmetry and energetic ordering of the NOM for 2^+ is identical to that of 3^+ yielding identical selection rules. The absorption spectrum displays a similar pattern of an allowed peak at $10,650\text{ cm}^{-1}$, a vibronically allowed peak near $\sim 17,500\text{ cm}^{-1}$, followed by an allowed peak at $21,280\text{ cm}^{-1}$ that correspond to the same transitions discussed for 3^+ .

The major discrepancy between the absorption spectra of 3^+ and 2^+ is the shape of the lowest energy transitions in either one. The spectrum of 2^+ displays a sharp intense peak in contrast to the much broader absorption of 3^+ . This difference can be explained by the geometry of these two compounds. The planarity of 2^+ allows for greater overlap and stronger coupling within the extended π system. The primary effect is a larger separation of the adiabatic states; the separation of the mixed valence excited states for 2^+ is $\sim 7000\text{ cm}^{-1}$ compared to $\sim 4000\text{ cm}^{-1}$ for 3^+ . A significantly larger coupling that is present in 2^+ results in a Robin-Day class III system that is characterized by complete delocalization of the electron. In a one dimensional picture of coupled states (Figure 3), Class III produces two adiabatic states that have a single minimum centered at the equilibrium internuclear configuration. Because there is no distortion, a transition from the ground state to either adiabatic state will only overlap with the lowest energy vibrational level producing a sharp absorption.

In contrast, the steric interactions of 3^+ cause significant twisting, a deviation from planarity, decreasing the coupling of the π system. The transition to these excited states are much less separated in 3^+ such that the vibronically allowed is not even resolvable between the allowed

transitions. The weaker coupling of this molecule is typical of a Robin-Day Class II system where the lower adiabatic state has a double minimum that partially localizes the electron (Figure 3-3). In the Franck-Condon region, a vertical transition to this state will overlap with many individual vibrational levels producing a broadened absorption spectrum.

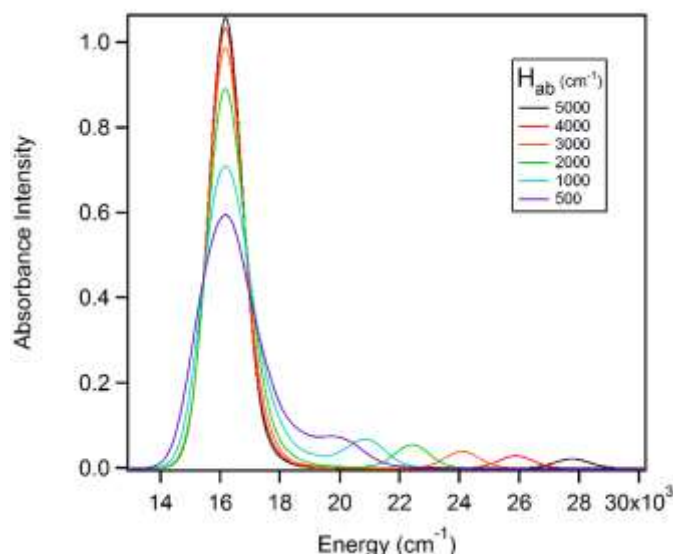


Figure 3-6. Calculated absorption spectra as H_{ab} is sequentially changed from 500 to 5000 cm^{-1} .

To the author's knowledge, the spectral effect of changing the coupling and transitioning between a class II and a class III system has not been explored. A pedagogical example will be presented to demonstrate the relevant aspects of this change. Using a time-dependent wave packet evolution method, absorption spectra were calculated for as coupling slowly increased from 500 cm^{-1} to 5000 cm^{-1} (Figure 3-6). These calculations were carried out in one-dimension along an asymmetric coordinate. Harmonic potential energy operators were used for the diabatic states, which had a frequency of 1000 cm^{-1} and the displaced excited diabatic states had a displacement

$\Delta=1.8$. The calculated spectra have a phenomenological damping factor $\Gamma=400\text{ cm}^{-1}$ and have been shifted along the energy axis such that the electronic origins are aligned for facile comparison.

The two most obvious effects are the increasing separation of the two bands and the increasing intensity and broadening of the lower energy band. As the coupling increases, the adiabatic surfaces become farther separated. Similar to a two-state model for mixed valence, the separation between the adiabatic states is $2H_{ab}$, which is approximately the separation between the two bands in the excited state mixed valence spectrum. The increasing intensity and broadening in the class II/III transition is reminiscent of the same effects observed for ground state mixed valence. Transitions involving the lower surface of a class II system are broadened and weaker because Franck-Condon region has a non-zero slope. Pass the limit of delocalization, the same transition for class III systems are sharper and more intense since the slope is zero in the Franck-Condon region. The calculated absorption spectra exemplify these trends smoothly as they transition from localized to delocalized when $H_{ab}=3193\text{ cm}^{-1}$.

3.4.5 Calculated Absorption Spectrum

The absorption spectra of compounds provide a window through which a chemist can view the molecular distortions of between the ground and excited states of a molecule. This is a simple yet powerful tool for understanding the changes in geometry and electronic configuration for many compounds. In well resolved spectra with highly distorted modes, a vibronic progression may be visible showing the successive absorption to individual vibrational levels of the excited state and indicating a large distortion along that particular normal coordinate. Unfortunately, in most cases

an absorption spectrum becomes a smooth band under normal conditions and all the vibronic information is hidden underneath a broad gaussian envelope.

However, resonance Raman spectroscopy provides an even more informative looking glass to view molecular distortions. In resonance Raman scattering, vibrational modes that are distorted between ground and excited electronic states become enhanced. The enhancement factor of a vibration scales quantitatively with its distortion according to Savin's formula. Using the time dependent theory of spectroscopy, the frequencies and distortions of the enhanced normal modes can be used to calculate a best-fit absorption spectrum. Combining these calculations with insight provided by DFT calculations the vibrations can be assigned and the electronic transition can also be assigned in terms of the molecular orbitals. The final picture describes both the changes in electron density and the molecular geometry that occur between the ground and excited states.

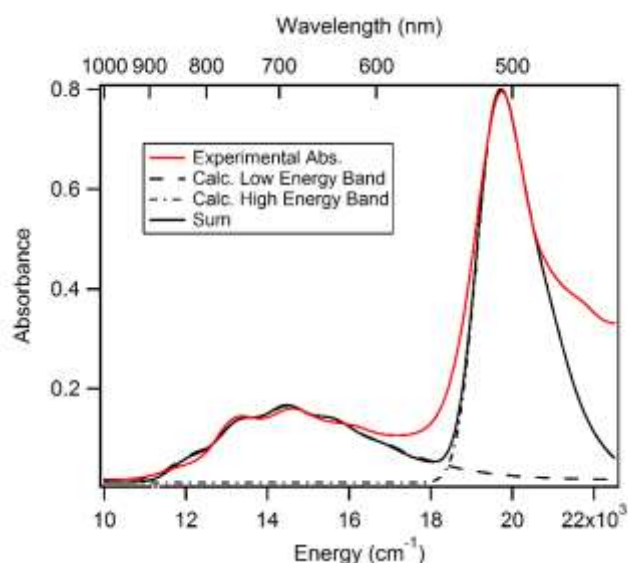


Figure 7. Calculated absorption spectrum of 3^+ .

The vibrational frequencies and their Raman intensities for 3^+ are summarized in Table 3-1. This data was used to calculate a best fit absorption spectrum according to equations 1 and 2 (Figure 3-7). The Raman spectra were collected in resonance with the high energy band and all of the vibrations observed in the spectrum were used in the calculation for the high energy band. However, resonance Raman spectroscopy only enhances symmetric vibrational modes, inherently omitting the characteristic asymmetric coordinate of electron transfer for mixed valence systems. Asymmetric normal modes are subsequently omitted from calculated absorption spectra. The symmetric distortions were scaled to give a best fit and are summarized in Table 1. A damping factor $\Gamma=300\text{ cm}^{-1}$ and an electronic origin $E_{00}=19350\text{ cm}^{-1}$ were applied. The low energy excited state mixed valence band was fit by selecting vibrations that are near the frequency of the observed vibronic progression: 964, 1201, 1221, 1351, and 1571 cm^{-1} . Using a slightly larger damping factor $\Gamma=340\text{ cm}^{-1}$ and an electronic origin $E_{00}=12,100\text{ cm}^{-1}$, the low energy best fit was calculated. These two components corresponding to the $\Psi_M^+ \rightarrow \Psi_B^-$ and $\Psi_B^+ \rightarrow \Psi_B^-$ were added together to give yield the solid black trace shown in Figure 3-7.

There are two regions centered at $18,000$ and $22,000\text{ cm}^{-1}$ where the calculated spectrum deviates from the experimental absorption spectrum. The difference is due to the involvement of other states that were left out of the calculation. The missing intensity near $18,000\text{ cm}^{-1}$ is mostly accounted for by the electric dipole forbidden $\Psi_M^- \rightarrow \Psi_B^-$. However, uncertainties in the separation of the coupled mixed valence excited states and the overlap with neighboring transitions make it difficult to acquire a fit with meaningful distortions. The gap at $22,000\text{ cm}^{-1}$ is credited to a series of higher energy transitions with larger extinction coefficients.

The normal modes that are significantly enhanced when in resonance with a particular transition should correspond to the regions of the molecule that have significant changes in electron density. Accordingly, several of the most distorted modes for both the $\Psi_M^+ \rightarrow \Psi_B^-$ and $\Psi_B^+ \rightarrow \Psi_B^-$ transitions display a component along the N=N axis. This is expected since both of these transitions move an electron from a molecular orbital that contains N=N π to one that has N=N π^* . This change from bonding to anti-bonding along the N=N axis thereby induces displacement along that axis and vibrations with movement also along that axis are enhanced. Vibrations with frequencies at 964, 1201, and 1283 cm^{-1} are assigned from DFT calculations to have a contribution from the N=N stretch. Within both portions of the calculated absorption spectrum all of these vibrations are significantly enhanced as expected. In the higher energy $\Psi_B^+ \rightarrow \Psi_B^-$ transition, several other distortions broaden the band filling it in with no resolvable vibronic structure. This is understandable since the change in the electronic structure of the molecular orbitals is more convoluted. However, because the $\Psi_M^+ \rightarrow \Psi_B^-$ solely changes the nitrogen's bond from π to π^* , only those characteristic vibrations are significantly distorted to produce the observed progression.

3.5 Conclusion

The near IR and visible regions of the absorption spectrum of 3^+ contains three components, two of which are electric dipole allowed and one is forbidden. The lowest energy vibronically resolved peak corresponds to the dipole allowed transition from the in-phase phenyl orbital to the mixed valence excited state. The other allowed transition corresponds to the π to π^*

transition for the N=N bond. The transition to the other component of the mixed valence system is vibronically allowed with antiparallel transition dipoles and contributes a small amount of intensity to the absorption spectrum between the two electric dipole allowed transitions. The energetic ordering of the coupled phenyl π excited states is a result of the sign of the coupling. Since the transition that removes an electron from the in-phase phenyl orbital is lower in energy, the sign of the coupling is positive for the mixed valence excited states. This is demonstrated in the neighboring orbital model and manifested in the absorption spectrum since the allowed transition is lower in energy than the forbidden one. Raman spectra were collected in resonance with the visible π to π^* transition and the vibrational frequencies and distortions were applied with the time-dependent theory of spectroscopy to calculate a best-fit absorption spectrum. The dimensionless distortions from the best-fit indicate that several normal modes containing displacement along the N=N bond axis are enhanced. This is in agreement with the NOM since both of the allowed transitions place an electron in the N=N π^* orbital, increasing the bond distance. Similarly, in the lowest energy absorption band, the vibronic spacing is close to 1200 cm^{-1} which corresponds to several normal modes with significant N=N stretching.

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Chapter 4

Twist Coordinate-Dependent Electronic Coupling in a Dialylniline Radical Cation

4.1 Introduction

Since the 1960's there has been a profusion of research of mixed valence systems.¹⁻⁴ Symmetric mixed valence compounds typically have two charge bearing units, M, which are covalently linked by a bridge, B, and a radical charge that can localize on either charge bearing unit. This produces two states: $M^{+/-}-B-M$ and $M-B-M^{+/-}$ that are interchangeably equivalent. These systems have attracted a lot of interest as simple systems for electron transfer and their unique electronic structure. Studies of mixed valence systems have focused on absorption,^{2, 3, 5, 6} resonance Raman,⁷ NMR,⁸ and EPR⁹⁻¹¹ experiments. Resonance Raman spectroscopy in conjunction with the time-dependent theory of spectroscopy is particularly useful to examine the geometric distortions of excited states.^{12, 13}

A signature characteristic of mixed valence compounds is the intervalence charge transfer (IVCT), a lower energy electronic absorption that transitions the molecule between the two states.⁴ The Marcus-Hush two state model is commonly employed to model the dynamics of mixed valence systems and calculate the IVCT.^{4, 14} A physical model that accompanies the two state model is the neighboring orbital model (NOM) which pictographically demonstrates how the diabatic orbitals of the charge bearing units couple to form the adiabatic molecular orbitals.¹⁵ A crucial component to the two state model and the NOM is the coupling element, H_{ab} , which adds the charge isolated states to form in-phase and out-of-phase combinations. The through-bond coupling of the charge bearing units typically occurs via π symmetry orbitals. This aspect of mixed valence imposes a mutually planar geometry on the π system of the charge bearing units.

A dialkylaniline ether radical cation, 1^+ , was recently reported to display an IVCT in the NIR region corresponding to electron transfer between the aniline charge units (Figure 4-1).¹⁶ This is surprising since the expected ground state geometry specifies a dihedral angle of nearly 90° between the anilines which should forbid any electron transfer. However, calculations demonstrated that twisting of the aniline units is energetically feasible and would allow electron transfer. In this paper we explore NOM and the resonance Raman spectroscopy of 1^+ to determine how the charge bearing units couple and which vibrational coordinates are significant to the electron transfer process.

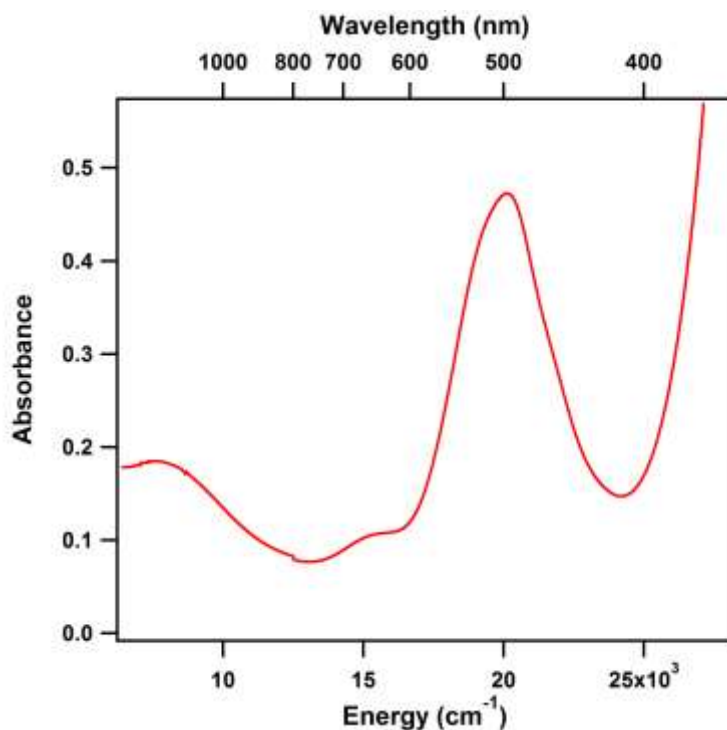


Figure 4-1. Absorption spectrum of 1^+ in MeCl_2

4.2 Results

4.2.1 Absorption Spectroscopy

The UV-Vis-NIR absorption spectrum of **1**⁺ in dichloromethane is shown in Figure 4-1. The spectrum displays a broad low energy peak in the NIR with a maximum at 7700 cm⁻¹ (1300 nm). The visible portion of the spectrum contains an intense peak with a maximum at 20,140 cm⁻¹ (497 nm) and a lower energy shoulder with a maximum near 15,500 cm⁻¹ (645 nm).

4.2.2 Resonance Raman Spectroscopy

The Raman spectrum of **1**⁺ in dichloromethane was acquired with 514.5 nm Ar⁺ laser excitation from 200 to 2400 cm⁻¹ (Figure 4-2). The observed vibrational intensities are normalized to the most intense peak and reported in Table 1. Bands that have an intensity of at least 10% of the most intense band are reported.

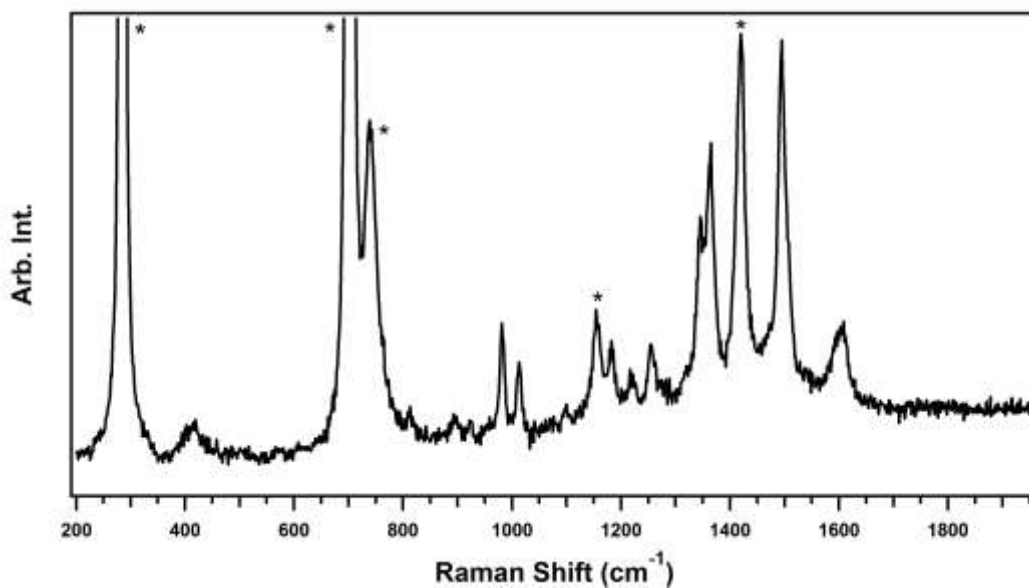


Figure 4-2. Resonance Raman spectrum of **1⁺** in dichloromethane. Solvent peaks are denoted by an asterisk.

Table 4-1. Experimental and calculated frequencies, Raman intensities, distortions, and assignment for observed Raman vibrations of **1⁺**.

Experimental frequency (cm ⁻¹)	Calculated frequency (cm ⁻¹)	Relative Intensity	Δ (dimensionless)	Assignment
419	429	0.12	1.26	Out-of-plane Aryl distortion
811	822	0.03	0.32	Aryl breathing
891	914	0.04	0.31	Aryl breathing
980	982	0.61	0.61	Aryl breathing
1013	1013	0.48	0.48	In-plane Aryl bending
1182	1202	0.15	0.47	Aryl-H wag
1217	1206	0.04	0.24	Aryl-H wag
1255	1273	0.14	0.33	Aryl-O-Aryl + C=C stretch
1265		0.02	0.18	
1345	1350	0.31	0.57	Aryl-N wag
1365	1381	0.54	0.79	
1495	1503	0.79	0.81	C=N stretch
1508		0.12	0.33	C=N stretch
1590		0.02	0.13	C=C stretch
1608	1663	0.41	0.46	C=C stretch

4.3 Discussion

4.3.1 Neighboring Orbital Model

The neighboring orbital model considers the interaction of diabatic orbitals of charge bearing units to yield the adiabatic molecular orbitals involved in an electronic transition of interest.¹⁵ This model has proven useful at determining the sign of the coupling between charge bearing units and assigning the electronic absorption spectrum.¹⁷⁻¹⁹

The identity of the charge bearing units and where the radical charge is localized remains an important aspect to understanding and interpreting mixed valence systems.⁶ Constructing a NOM requires careful attention in selecting charge bearing units that accurately reflect the most significant electronic characteristics of the ground and excited electronic states. In the resonance Raman spectrum the most intense modes correspond to regions of the molecule that have large changes in electron density between the ground and excited state.^{13, 20} Since several of the most intense normal modes are assigned to the aniline moieties, it is reasonable to assign them as the diabatic charge bearing units. In this process of building up the NOM, there are now aniline charge bearing units on either side of the molecule. However, the charge bearing units are separated by a bridging oxygen and must combine by a through-bond coupling in contrast to the through space coupling that is normally described.^{17, 21, 22}

Next, consider the frontier orbitals of the charge bearing units. The HOMO-2 of the Aryl-N moiety is a π symmetry orbital with a single node perpendicular to the N-Aryl-O axis. While the HOMO of the Aryl-N also has the single node, it has an additional node between the Aryl and the

N. In contrast, the HOMO-1 does have a node that runs parallel to the N-Aryl-O axis, making through bond coupling of the HOMO-1 impossible since there is zero electron density on the carbons that immediately bond to the oxygen bridge. The oxygen p_z and p_y orbitals are of correct symmetry to couple both sets of diabatic orbitals. Coupling the HOMO-2 diabatic orbitals yields the E_1 and E_2 orbitals of 1^+ , shown in the center column of Figure 4-3. Similarly coupling the HOMO diabatic orbitals yields the E_3 and E_4 orbitals of 1^+ .

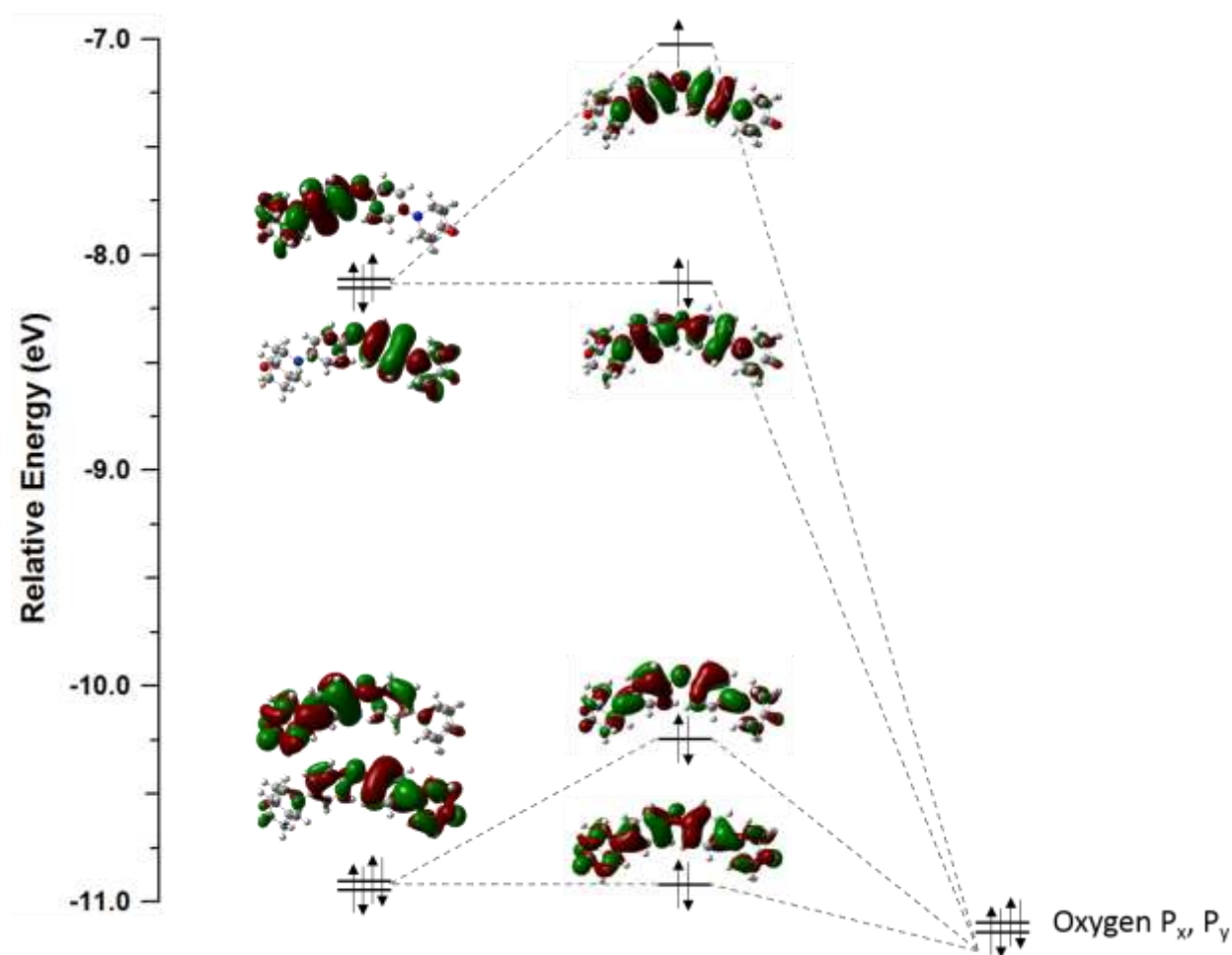


Figure 4-3. Neighboring orbital model for 1^+ .

Filling the diagram with 7 electrons gives a ground state electron configuration of $\Psi_1 = (E_1)^2(E_2)^2(E_3)^2(E_4)^1$. Three possible electronic transitions move the hole from the highest energy orbital to either of E_1 , E_2 , or E_3 and place the corresponding electron in E_4 (the selection rules for these transitions will be discussed in the following section). The lowest energy transition is to the state $\Psi_2 = (E_1)^2(E_2)^2(E_3)^1(E_4)^2$ and is the familiar intervalence charge transfer between coupled states. The higher energy transitions to either E_1 or E_2 place the hole in a second pair of coupled states creating mixed valence excited state. The two coupled excited states place the hole in the diabatic HOMO-2 of the N-Aryl moiety and in the excited state the electron can formally reside on left or the right-hand side of the molecule. The electron configurations corresponding to the adiabatic states are $\Psi_3 = (E_1)^2(E_2)^1(E_3)^2(E_4)^2$ and $\Psi_4 = (E_1)^1(E_2)^2(E_3)^2(E_4)^2$ where Ψ_3 and Ψ_4 place the hole in the in-phase combination and the out-of-phase combination of the HOMO-2 diabatic orbitals, respectively. Since the state Ψ_3 occupying the in-phase combination is lower in energy than the state occupying the out-of-phase combination, the sign of the coupling is negative. By similar logic, the coupling that gives rise to the adiabatic states Ψ_1 and Ψ_2 is also negative since the state which occupies the in-phase combination is the ground state.

This result of negative coupling for the through-bond interaction of two charge bearing units may seem trivial since it is the same as the normal interpretation for through bond coupling.¹⁷ However, the sign of the coupling for ESMV compounds is not inherently negative. Instead, it is a result of how the charge bearing units' diabatic orbitals interact with each other through a bridge. The symmetry and relative energies of the bridge orbitals that facilitate coupling ultimately determine the relative energy of the adiabatic orbitals. In both the GSMV (Ψ_1 and Ψ_2) and the ESMV (Ψ_3 and Ψ_4) of $\mathbf{1}^+$, the out-of-phase combination of the diabatic orbitals is higher in energy

than the in-phase combination. The only oxygen orbital that is the correct symmetry to couple either of the sets of the diabatic Aryl-N orbitals is the p_y orbital. The p_y orbital only interacts with the out-of-phase combination of the diabatic orbitals yielding the antibonding orbitals E_2 and E_4 . In contrast, the in-phase combinations have no oxygen orbital to interact with and remain non-bonding.

$$\Phi_+ = \frac{1}{\sqrt{1 + \zeta^2}} [\zeta \varphi(E_A) + \varphi(E_B)] \quad (1)$$

$$\Phi_- = \frac{1}{\sqrt{1 + \zeta^2}} [\varphi(E_A) - \zeta \varphi(E_B)] \quad (2)$$

Since the two pairs of mixed valence adiabatic orbitals are proposed to be a combination of two diabatic orbitals, it is expected that forming linear combinations of the adiabatic orbitals will yield the diabatic orbitals (equations 1 and 2).²³ Normalizing the in-phase and out-of-phase combinations of adiabatic orbitals, E_A and E_B , respectively, where ζ is the overlap produce the diabatic orbitals, Φ_+ and Φ_- . This *diabatization* process was applied to the adiabatic orbitals in the center of the Figure 3 to produce the diabatic orbitals on the left-hand side. The calculated diabatic orbitals correctly demonstrate the localized nature of the electron on either of side of the molecule. Furthermore, this suggests that the aryl-amine units are the charge bearing units.

4.3.2 Electronic Transition Assignments

From the neighboring orbital model there are three possible electronic transitions of interest originating from each of the filled orbitals to the SOMO. The lowest energy HOMO $\rightarrow$ SOMO transition is assigned as the IVCT. Together the pair of higher energy transitions, HOMO-3 $\rightarrow$ SOMO and HOMO-6 $\rightarrow$ SOMO, comprise the transition to the mixed valence excited state. In the absorption spectrum these three transitions are assigned in order of increasing energy. The IVCT corresponds to the NIR transition at 7700 cm^{-1} while the excited state mixed valence transitions occur at $15,500\text{ cm}^{-1}$ and $20,140\text{ cm}^{-1}$.

An apparent difference between the transitions to the mixed valence excited state is the large difference in intensity. The higher energy HOMO-6 $\rightarrow$ SOMO transition is nearly four times as intense as the HOMO-3 $\rightarrow$ SOMO transition. The large difference is mainly due to the symmetries of the molecular orbitals. Since the HOMO-3 and the SOMO are both totally symmetric, the electronic transition between them is Laporte forbidden. However, movement along the asymmetric electron transfer coordinate yields a vibronically allowed transition. In contrast, the HOMO-6 is not totally symmetric and thus produces an allowed transition. A more rigorous explanation of these selection rules utilizing the coupling of the transition dipole moments to each of the charge bearing units is presented in the introduction. These derivations also account for the relative orientation of the charge bearing units within the mixed valence system.

4.3.3 Calculated Absorption Spectrum

The absorption spectrum can be calculated according to the equations for time-dependent theory of spectroscopy outlined in the introduction (Figure 4-4). The relative normal coordinate distortions between the ground and excited state are calculated from the resonance Raman intensities. The distortions are scaled to match the total bandwidth with a particular excited state. A phenomenological damping factor, $\Gamma = 500 \text{ cm}^{-1}$, is applied to account for inhomogeneous broadening observed in the experimental absorption spectrum.

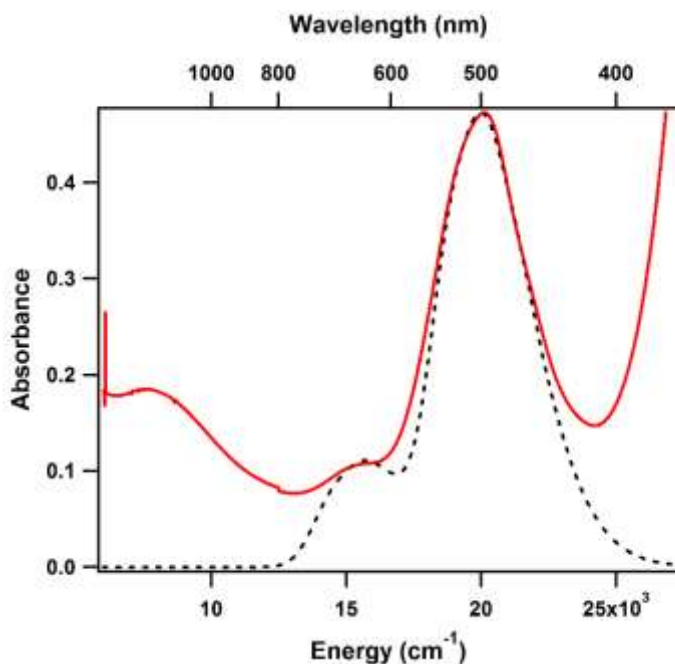


Figure 4-4. Experimental (red) and calculated (black) absorption spectrum of **1⁺**.

The large coupling present in the mixed valence excited states produces a large splitting between the bands ($>4500 \text{ cm}^{-1}$). Furthermore, there is a lack of resolved vibronic structure in the absorption spectrum. These diminish the observable effect of asymmetric modes in the absorption

spectrum and permit it to be omitted from the calculated absorption spectrum. The oblique angle between the charge bearing units implies that we must calculate spectra corresponding to both the parallel (0°) and anti-parallel (180°) orientations and weight them appropriately. Since an asymmetric coordinate is not being used, only the symmetric coordinates are being used to calculate the two transitions. The parallel transition corresponds to the higher energy allowed transition while the anti-parallel transition corresponds to the lower energy vibronically allowed transition. To produce the calculated absorption spectrum E_{00} of 14,250 and 18,600 cm^{-1} were used for either transition and they were weighted with a relative factor of 1 : 2.56 corresponding to an angular separation of 122° between the charge bearing units. This geometry closely corresponds to the expected geometry as predicted by DFT calculations.

4.3.4 Vibrational Analysis

It is well known that the most intense modes in a resonance Raman spectrum correspond to coordinates that have large changes in electron density. For instance, changing an individual bond axis from bonding to anti-bonding extends the bond length resulting in a distorted excited state and an increase in the Raman signal for vibrations with movement along that bond axis. This effect has been applied to assign transitions in the absorption spectrum and interpret which coordinates are most distorted.

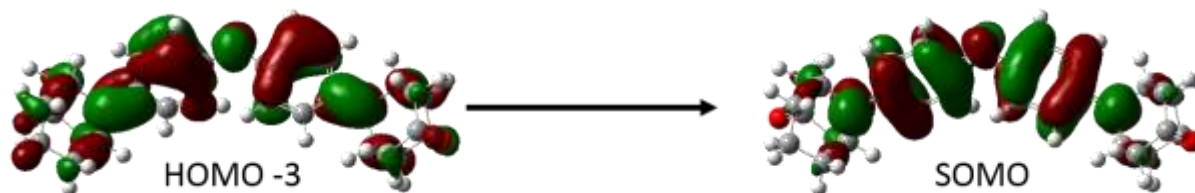
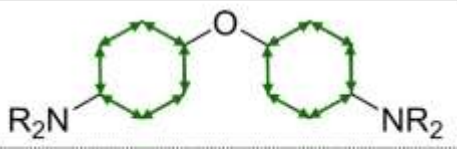
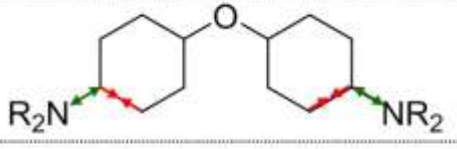
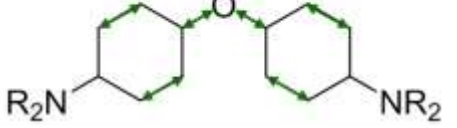


Figure 4-5. Change in electronic structure from HOMO-3 to SOMO.

The MOs for the HOMO-3 $\rightarrow$ SOMO transition are shown in Figure 4-5. In both MOs most of the electron density is delocalized across the aryl-amine moieties and the transition only changes the nodal structure. As a result the most intense Raman vibrations will display significant distortion within those moieties.

As discussed earlier, the HOMO-3 is an in-phase combination of a single node π -symmetry benzene orbital with a nitrogen p orbital. In contrast, the SOMO is π anti-bonding between the nitrogen and the ring. Furthermore, while the benzene electron density of the SOMO still retains a single node it is rotate slightly, lying across different axes. The largest changes in geometry from this change in electronic structure should correspond to a lengthening of the N-C bond and similar bond length increases of CC double bonds within the ring. The top and bottom CC double bonds in the ring have $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ changes in structure respectively and result in the largest CC bond length increases within the ring.

Table 4-2. Displacement vectors for most distorted vibrations of **1⁺**.

Experimental frequency (cm ⁻¹)	Δ (dimensionless)	Displacement Vectors
981	0.61	
1365	0.79	
1495	0.81	

The observed Raman frequencies, distortions, and displacement vectors are drawn for the three most distorted vibrational modes of **1⁺** in Table 4-2. The displacement vectors were determined from a Gaussian09 frequency calculation and the vibrations were visualized with GaussView. The 1495 cm⁻¹ vibration is the most intense vibration in the resonance Raman spectrum of **1⁺** and is similarly the most distorted. Along this normal coordinate there are in-phase changes of the top and bottom C=C bonds of both rings along with the C-O-C bond. As expected, the displaced bonds within this most distorted vibration correspond to regions that display significant change in electronic structure upon excitation. Similarly, the 1365 cm⁻¹ vibrational mode has significant displacement along the N-C bond axis and along a single C=C axis. However, in contrast to the 1495 cm⁻¹ mode these two displacement vectors are out-of-phase. Along this vibrational coordinate the N-C bond expands while the C=C bond contracts. This relative phasing

of the two motions matches the changes in the electronic structure where the N-C bond goes from bonding to anti-bonding while the C=C bond transitions from non-bonding to bonding. The 1365 cm^{-1} mode is a ring breathing mode and shows simultaneous lengthening of all the C=C bonds. This vibrational mode is highly distorted since the SOMO has more electron density on the rings than the HOMO-3.

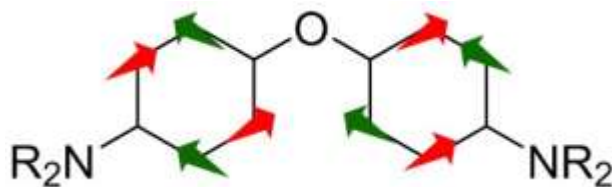


Figure 4-6. Displacement vectors for 413 cm^{-1} mode.

The most distorted Raman mode is a low frequency 413 cm^{-1} out-of-plane ring distortion with alternating carbon atoms twisting into and out of the plane (Figure 4-6). Since resonance Raman spectroscopy only enhances totally symmetric vibrations, this vibration is symmetric with respect to the C_2 rotational axis. While resonance Raman does not enhance non-totally symmetric modes it is hypothesized that the asymmetric coordinate involved in mixed valence electron transfer is related to the most distorted symmetric coordinate. The asymmetric analogue of the out-of-plane distortion is expected to be important in the electron transfer process of $\mathbf{1}^+$. Furthermore, since equilibrium inter-nuclear geometry rotates the aryl rings both the symmetric and asymmetric out-of-plane distortions increase the π overlap between both aryl rings and the bridging oxygen atom. This implies that the coupling between the charge bearing units of $\mathbf{1}^+$ has a coordinate dependence on the twisting of the aryl rings.

4.4 Conclusion

The electronic absorption spectrum of 1^+ displays an IVCT in the NIR region that has been assigned as the HOMO $\rightarrow$ SOMO transition in the. The HOMO and SOMO of 1^+ are combinations of a pair diabatic orbitals localized on aniline charge bearing units. Similarly, a second set of diabatic aniline orbitals form the HOMO-6 and HOMO-3. Electronic transition originating from these orbitals result in a mixed valence excited state that manifests as two bands in the visible region.

A Raman spectrum was collected in resonance with the allowed transition to the mixed valence excited state, HOMO-6 $\rightarrow$ SOMO. Analysis of the 1495 cm^{-1} vibration, which was the second most distorted vibration, showed significant bond length changes of C=C and C-O bonds in both rings. These distortions matched the changes in electron density and nodal structure expected from the NOM. Additional highly distorted ring modes also correlated to the change in electronic structure. These vibrational assignments support the assignment of the electronic transitions as well as the assignment of the aniline moieties as the charge bearing units. The most distorted resonance Raman active vibration is the 413 cm^{-1} vibration which is an out-of-plane ring twisting. Movement along this twisting coordinate strongly affects the π overlap and overall coupling between the aniline charge bearing units. This demonstrates how the coupling has a strong coordinate dependence that facilitates the coupling giving rise to the intervalence charge transfer and the mixed valence excited state.

4.5 References

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Chapter 5

Characterization of an Iron-Ruthenium Interaction in a Ferrocene Diamide Complex

Adapted from recently published Green, A. G.; Kiesz, M. D.; Oria, J. V.; Elliott, A. G.; Buechler, A. K.; Hohenberger, J.; Meyer, K.; Zink, J. I.; Diaconescu, P. L., Characterization of an Iron-Ruthenium Interaction in a Ferrocene Diamide Complex. *Inorganic Chemistry* 2013, 52, 5603-5610

5.1 Introduction

Metal-metal bonds have been the subject of intense research and discussion.¹ Specifically, interactions between metal centers in bimetallic complexes can give rise to interesting electronic and magnetic properties²⁻¹³ and novel reactivity.¹⁴⁻²⁰ Ferrocene derivatives²¹ have seen widespread use as ancillary ligands for metal complexes,²¹⁻²⁴ largely due to the unique steric and electronic properties of the flexible and redox-active^{25, 26} ferrocene backbone. Metal complexes supported by chelating 1,1'-ferrocenediyl derivatives are particularly interesting and may allow a direct interaction between iron and the metal center.²⁷⁻²⁹

Weak interactions between the ferrocene iron with both early and late transition metals have been reported;³⁰⁻³⁷ however, the nature of these interactions has been controversial. For example, the Seyferth group found that upon the oxidative addition of 1,2,3-trithia[3]ferrocene to Pd(PPh₃)₄, a four-coordinate palladium complex was formed, featuring an iron-palladium bond.³² Sato and coworkers also synthesized a variety of late transition metal complexes that showed an interaction between the iron and the metal; that interaction was characterized by X-ray crystallography, NMR and absorption spectroscopy.^{38, 39}

For group 4 metals, complexes supported by 1,1'-ferrocene diamide ligands were initially reported by Arnold *et. al.*, who showed that a highly reactive cationic titanium(IV) species was stabilized by an interaction with iron.³¹ Recently, the Stephan group reported that ferrocene can stabilize cyclopentadienyl zirconium alkyl cations through an iron-zirconium interaction.³⁰ In both cases, the iron-metal interactions were based on structural parameters obtained from X-ray crystallography.

Weak metal-metal bonding was reviewed by Braunschweig, et al. from the perspective of Lewis pairs.⁴⁰ X-Ray crystallography, Mössbauer, X-ray absorption spectroscopy, and computational methods were listed as methods used to determine the nature of weak metal-metal interactions. The authors also noted that it was especially difficult to assign the Lewis base and the Lewis acid in the case of 1,1'-ferrocenediyl (fc) complexes of middle-to-late transition metals. Such an assignment is important in expanding the concept of transition metal Lewis basicity, which is of fundamental interest in understanding the reactivity of the corresponding metal complexes.⁴⁰ This concept is difficult to grasp since most transition metals are viewed as Lewis acids. Herein, we report the characterization of $[\text{fc}(\text{NH})_2]\text{Ru}(\text{PPh}_3)_2$ (fc = 1,1'-ferrocenylene),⁴¹ a complex that features a short Fe-Ru distance, consistent with an iron-ruthenium donor-acceptor interaction. This interaction was characterized by electronic absorption, Mössbauer, and, for the first time, resonance Raman spectroscopy in conjunction with DFT calculations. Resonance Raman studies were also carried out on previously published palladium complexes that feature an iron-palladium interaction in order to validate the method. Aside from the importance of understanding the role played by the Lewis basicity of metal ions in organic reactions (for example, oxidative addition processes),⁴⁰ the present article shows that it is possible to characterize donor-acceptor interactions between two metals with a similar Lewis acid/base character, even when such a characterization becomes dependent on their chemical environment.

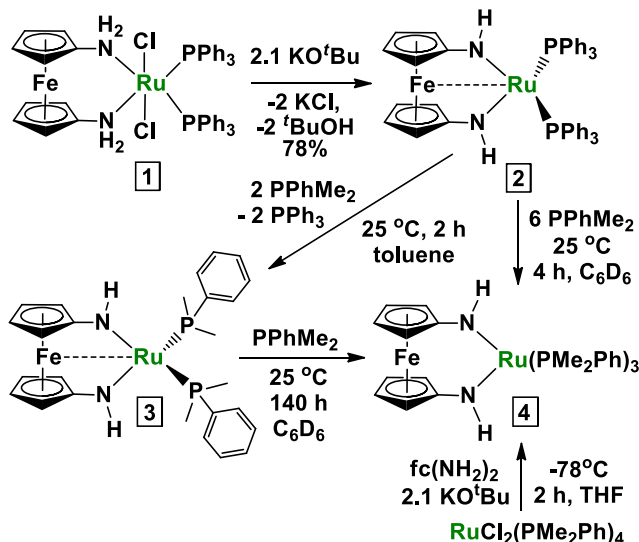
5.2 Results and Discussion

5.2.1 Synthesis and structural characterization

We have been interested in the chemistry of substituted 1,1'-ferrocene diamides as ancillary ligands for group 3 metals, lanthanides, and uranium.^{27, 28} In certain instances, we observed short iron-metal distances and proposed that the ferrocene diamide supporting ligand was instrumental in stabilizing certain bonding motifs.^{42, 43} In order to differentiate between the influence of the nitrogen substituent and that of the ferrocene diamide core, we chose the parent 1,1'-ferrocene diamine, (fc(NH₂)₂), as a platform to study metal-metal bonding. Inspired by Seyferth's and Sato's pioneering work with late transition metals, and because of numerous reports of stable amine⁴⁴⁻⁵⁰ and amide⁵⁰⁻⁵³ ruthenium compounds, we chose to investigate ruthenium complexes. Additionally, the syntheses of the dichloride [fc(NH₂)₂]RuCl₂(PPh₃)₂ (**1**) and of the diamide [fc(NH)₂]Ru(PPh₃)₂ (**2**) species were recently reported by us.⁴¹

Compound **2** was prepared by the reaction of **1** with KO^tBu (Scheme 3-1).⁴¹ Interestingly, **2** was found to be remarkably resistant to σ donors. No reactions were observed in the presence of THF, MeCN, or aniline. When two equivalents of PMe₂Ph were added to **2**, however, a new bisphosphine complex [fc(NH)₂]Ru(PMe₂Ph)₂, **3**, was formed (Scheme 1). This complex was isolated as black crystals, which decomposed slowly at room temperature in the absence of PMe₂Ph to form 1,1'-ferrocene diamine. Addition of a third equivalent of phosphine to this complex resulted in the formation of the trisphosphine species [fc(NH)₂]Ru(PMe₂Ph)₃, **4**, as determined by ¹H and ³¹P NMR spectroscopy. The formation of **4** could also be observed by the

direct addition of 6 equivalents of PPhMe_2 to **2**, or by the addition of 1 equivalent of $\text{fc}(\text{NH}_2)_2$ to $\text{RuCl}_2(\text{PPhMe}_2)_4$ ⁵⁴ at -78°C followed by the addition of 2.1 equivalents of KO^tBu . Compound **4** could not be isolated since it rapidly decomposed to form $\text{fc}(\text{NH}_2)_2$ and an intractable mixture containing phosphorous species.



Scheme 5-1. Syntheses of complexes 1-4.

Compounds **1**, **2**, and **3** were characterized by X-ray crystallography. The solid-state molecular structure of **1** (Figure 5-1) exhibits a distorted octahedral ruthenium complex with chloride ligands in the axial positions and a Cl-Ru-Cl angle of 165° . The Ru-N distances were 2.24 Å and 2.27 Å, while the Ru-P distances were 2.31 Å and 2.32 Å. In addition, the Cp-ring twist angle was 1.7° and the Cp-Cp tilt angle was 102.9° (see Figure 5-2 for an explanation of twist and tilt).

The X-ray crystal structure of **2** (Figure 5-3) shows the ruthenium center in a distorted trigonal bipyramidal geometry with an N1-Ru-N2 angle of 159° and a Ru-N distance of 2.16 Å.

The Ru-P distances decreased to 2.20 Å. More importantly, a drastic decrease in the iron-ruthenium distance in **2** (2.80 Å) compared to **1** (4.20 Å) was observed. The Fe-Ru distance in **2** is only 0.02 Å greater than the sum of the covalent radii (2.78 Å),⁵⁵ indicating that a metal-metal interaction may be present. The Cp-ring twist angle was 10.61° and the Cp-Cp tilt angle was 121.63° (for comparison, the Cp-Cp tilt angle in ferrocene is 107.4°) indicating appreciable distortion of the ferrocene ligand relative to **1**. The solid-state molecular structure of **3** (Figure 5-4) exhibits similar features to complex **2** with a notably short Fe-Ru distance of 2.77 Å, a Cp-ring twist angle of 0.1° and a Cp-Cp tilt angle of 118.7°.

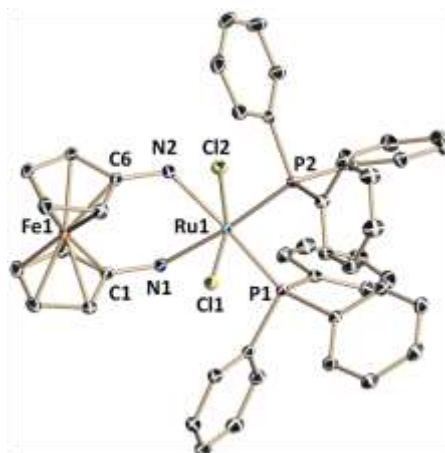


Figure 5-1. Thermal-ellipsoid (50% probability) representation of **1**. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Ru1-Cl1 2.3948(5), Ru1-Cl2 2.4427(4), Ru1-P1 2.3150(5), Ru1-P2 2.3205(4), Ru1-N1 2.2669(11), Ru1-N2 2.2407(12); Cl1-Ru1-Cl2 164.96(1), Cl1-Ru1-P1 91.71(1), Cl1-Ru1-P2 93.60(2), Cl1-Ru1-N1 92.36(3), Cl1-Ru1-N2 89.36(3), Cl2-Ru1-P1 100.57(1), Cl2-Ru1-P2 93.91(2), Cl2-Ru1-N1 79.43(3), Cl2-Ru1-N2 77.69(3), P1-Ru1-P2 95.13(1), P1-Ru1-N1 88.51(3), P1-Ru1-N2 175.04(3), P2-Ru1-N1 172.93(3), P2-Ru1-N2 89.64(3), N1-Ru1-N2 86.61(4), Fe1-C1-N1 127.48(8), Fe1-C6-N2 126.78(9), twist 1.66, tilt 102.90.

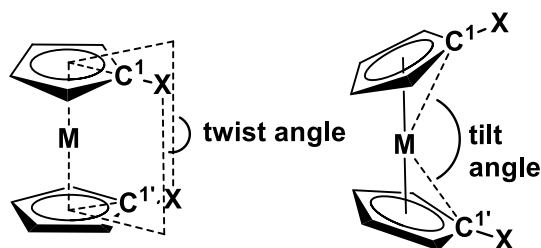


Figure 5-2. Description of twist and tilt angle for 1,1'-ferrocenediyl ligands. Twist angles were calculated by measuring the angle between the two planes formed by C¹ and the centroids of the two Cp rings, and C^{1'} and the centroids of the two Cp rings. The Cp tilt angle is C¹-Fe-C^{1'}; the Cp-Cp tilt angle in ferrocene is 107.4°.

The ¹H NMR spectra of **2** and **3** in C₆D₆ exhibit a large splitting between the signals for the α (4.10 and 4.21 ppm, respectively) and β (2.20 and 2.08 ppm, respectively) Cp protons (Δδ = 1.9 and 2.1 ppm, respectively). Splitting of the α and β proton peaks of the Cp rings has been previously explained by the anisotropic effect of the iron-metal bond providing a shielding effect on the α protons, while the β protons are less affected because they are further away.³⁵⁻³⁹

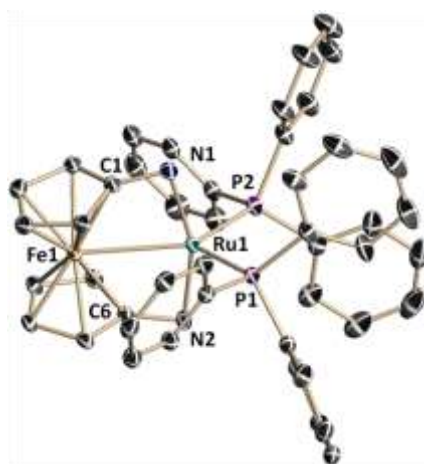


Figure 5-3. Thermal-ellipsoid (50% probability) representation of one of the two independent molecules in the unit cell of **2**. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Ru1-Fe1 2.7996(6), Ru1-P1 2.2031(8), Ru-P2 2.2023(7), Ru1-N1 2.1583(23), Ru1-N2 2.1582(23); Fe1-Ru1-P1 130.02(2), Fe1-Ru1-P2 131.62(2), Fe1-Ru1-N1 79.67(6), Fe1-Ru1-N2 79.76(2), P1-Ru1-P2 98.36(3), P1-Ru1-N1 93.66(7), P1-Ru1-N2 99.98(7), P2-Ru1-N1 99.54(7), P2-Ru1-N2 93.68(7), N1-Ru1-N2 159.42(9), Ru1-N1-C1 90.82(16), Ru1-N2-C6 90.94(16), Fe1-C1-N1 128.59(19), Fe1-C6-N2 128.33(19), Cp-Fe1-Cp 170.2, twist 10.31, tilt 121.63.

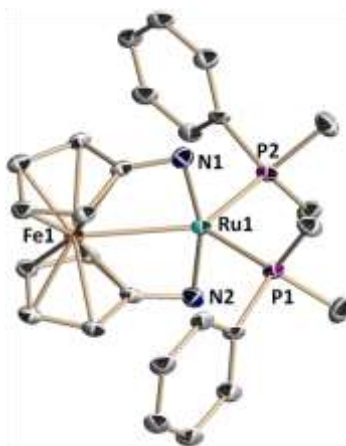


Figure 5-4. Thermal-ellipsoid (50% probability) representation of **3**. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Ru1-Fe1 2.768(2), Ru1-P1 2.192(1), Ru1-N1 2.163(4); Fe1-Ru1-P1 133.40(3), Fe1-Ru1-N1 82.20(10), P1-Ru1-P2 93.20(6), P1-Ru1-N1 93.07(11), N1-Ru1-N1 164.39(20), Ru1-N1-C9 87.75(26), Cp-Fe1-Cp 173.09, twist 0.06, tilt 118.71.

5.2.2 Mössbauer spectroscopy

In order to probe the electronic structure of iron in complexes **1** and **2**, Mössbauer spectroscopy studies were carried out. The Mössbauer spectrum of **1** (Figure 5-5) exhibits a doublet at $0.53(1) \text{ mm s}^{-1}$, consistent with an Fe(II) center. The Mössbauer spectrum obtained for **2** (Figure 5) also exhibits a doublet, at $\delta = 0.56(1)$, indicating an Fe(II) center. For comparison, Mössbauer spectroscopic studies were also carried out (Figure 5-5) on $[(\text{dppf})\text{Pd}(\text{PPh}_3)][\text{BF}_4]_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene), **5**, and $[(\text{dppf})\text{Pd}(4\text{-picoline})_2][\text{BF}_4]_2$, **6**.³⁹ These measurements resulted in data that are consistent with Fe(II) centers. The results obtained for **1**, **2**, **5**, and **6** are expected since the ^1H NMR spectra for these complexes exhibit diamagnetic characteristics.

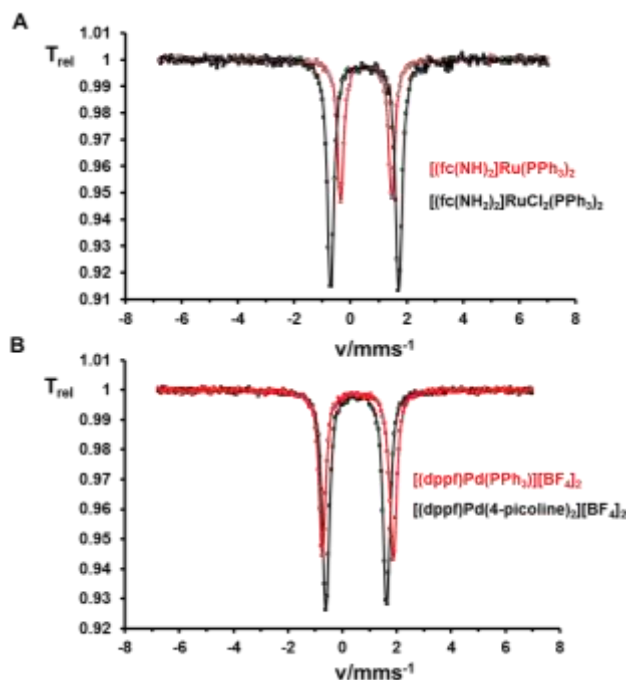


Figure 5-5. A) Overlaid Mössbauer spectra of **1** and **2**. B) Overlaid Mössbauer spectra of **5** and **6**.

5.2.3 DFT calculations

DFT geometry optimizations were carried out with ADF2012.01 on the full molecules of **1**, **2**, and **3**. For **2**, calculations were performed at the LDA⁵⁶ and PW91⁵⁷ theory levels, with full electron (no frozen cores) triple-zeta-potential (TZP) basis sets, and using the relativistic scalar ZORA approximation. The values for the calculated Fe-Ru distance in **2**, 2.76 Å (LDA) and 2.87 Å (PW91), match well the experimental distance determined by X-ray crystallography (2.80 Å, see above). In accord with the short Fe-Ru distance, HOMO-6 of **2** shows a σ interaction between the two metals (Figure 5-6). The calculated Mayer bond order^{58, 59} for the iron-ruthenium interaction for **2** and **3** is 0.28 (PW91) and 0.26, respectively. For comparison, the Mayer bond

orders for the single Ru-Ru bond in $[\text{Ru}(\text{CO})_4]_8$ and $\text{Ru}_3(\text{CO})_{12}$ were found to be 0.70 and 0.62, respectively,⁶⁰ indicating that the Fe-Ru bonds of **2** and **3** are weaker than metal-metal single bonds.

The optimized coordinates were used for further analysis with NBO 5.0⁶¹ and Bader's atoms in molecules (AIM) methods.^{62, 63} Analysis of the natural bond orbitals (NBOs) generated shows overlap from two occupied valence orbitals centered on Fe and Ru (Figure 5-7). Natural localized molecular orbitals (NLMOs) generated from these NBOs show a significant contribution from Fe and a small total (7.15%) contribution from Ru (Figure 5-7). Conversely, three NLMOs centered on Ru only have a 0.39% contribution from Fe. These data indicate that there is donation from iron to ruthenium. Natural population analysis shows that there is a net linear overlap of 0.29 (both LDA and PW91 calculations gave the same value) between the metal centers.

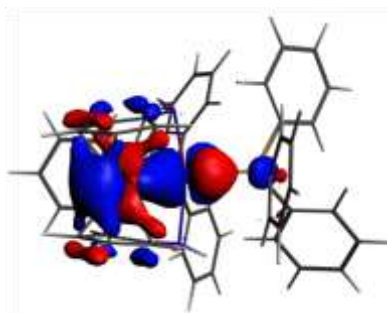


Figure 5-6. HOMO-6 for **2**. Orbitals are similar for the LDA and PW91 calculations.

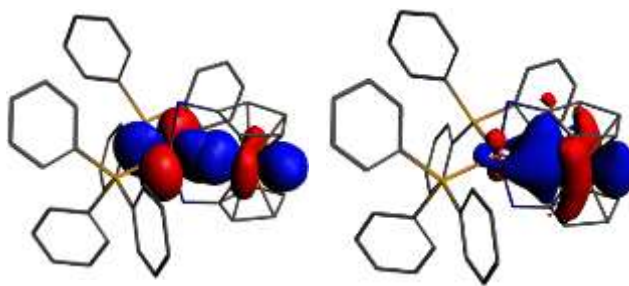


Figure 5-7. Left: Overlap between NBOs 209 (Ru) and 211 (Fe); right: NLMO 211.

Additionally, an NBO second order perturbation theory analysis of the donor-acceptor data shows stabilizing interactions (10.1 kcal/mol total energy) from occupied valence orbitals on iron to empty orbitals on ruthenium. The reverse, i.e stabilizing interactions from occupied valence orbitals on ruthenium to empty orbitals on iron, was not found, consistent with a donor-acceptor interaction between iron and ruthenium with iron functioning as the donor.

Topological analysis of electron density was carried out using Bader's atoms in molecule (AIM) theory. This module is provided as a subroutine in ADF2012. AIM identifies any type of bond by calculating a (3, -1) critical point, and it differentiates between covalent bonds, on one hand, and weak interactions such as hydrogen bonds, van der Waals, and donor-acceptor, on the other, by the value of the Laplacian (∇^2_{ρ}). If $\nabla^2_{\rho} < 0$, the interaction is considered covalent. If $\nabla^2_{\rho} > 0$, the interaction is a weak interaction. AIM has been used to calculate bond critical points between two metal centers⁶⁴ and in ferrocene complexes.⁶⁵ A (3, -1) critical point was found in **2** at 1.43 Å (PW91), the midpoint of the Fe-Ru distance, supporting the presence of a weak interaction between the two metal centers. Calculation of the Laplacian for **2** shows greater electron density surrounding iron than ruthenium, consistent with the NBO findings of electron donation from iron to ruthenium. The contour plot of the Laplacian in the plane of iron, ruthenium,

and one of the amide nitrogen atoms (Figure 5-8) shows low electron density between the two metal centers, with the gradient consistent with a weak interaction. For comparison, a significant gradient is found between the amide nitrogens and carbons, indicative of a covalent bond. Combined with the short distances determined experimentally and the spectroscopic data discussed above, the results of DFT calculations support the existence of a weak interaction between iron and ruthenium in **2**, consistent with electron donation from iron to ruthenium.

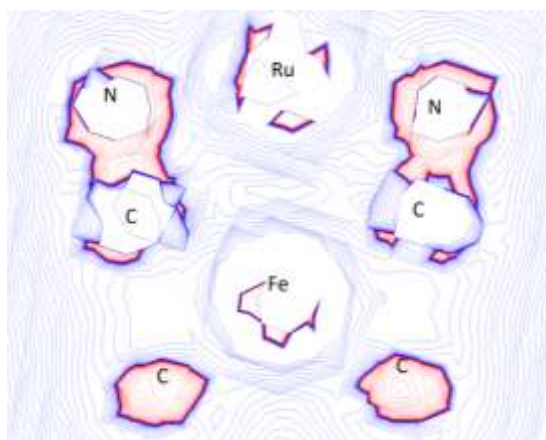


Figure 5-8. Contour plot of the Laplacian $\nabla^2\rho$ in the plane of iron, ruthenium, and one of the amide nitrogen atoms for **2**. Red lines indicate areas of high charge $\nabla^2\rho < 0$, blue lines indicate depletion of charge $\nabla^2\rho > 0$.

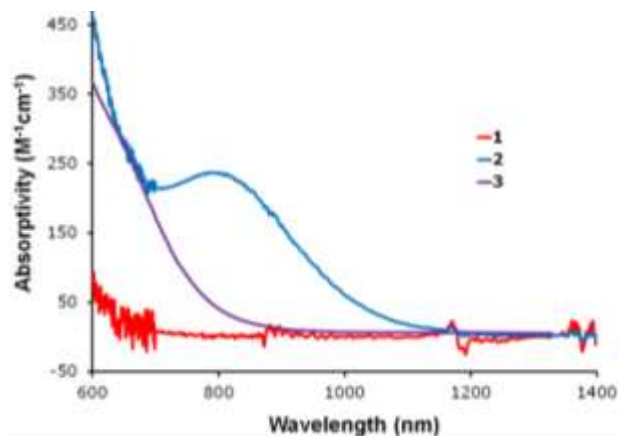


Figure 5-9. Near-infrared spectra in THF of **1** (2.5 mM), **2** (0.8 mM), and **3** (0.8 mM).

5.2.4 Electronic absorption spectroscopy

The UV-Vis and NIR (near infrared) spectra of **1** and **2** (Figure 5-9) show remarkable differences. The dichloride complex exhibits peaks at 320 nm ($\epsilon = 5784 \text{ M}^{-1}\text{cm}^{-1}$) and 500 nm ($\epsilon = 578 \text{ M}^{-1}\text{cm}^{-1}$), which were assigned to Fe-Cp charge transfer and Fe d-d transitions. Similarly, the diamide complexes **2** and **3** (Figure 5-9) exhibit peaks at 360 ($\epsilon = 9647 \text{ M}^{-1}\text{cm}^{-1}$) and 352 ($\epsilon = 6258 \text{ M}^{-1}\text{cm}^{-1}$) nm, 530 ($\epsilon = 1214 \text{ M}^{-1}\text{cm}^{-1}$) and 454 ($\epsilon = 1427 \text{ M}^{-1}\text{cm}^{-1}$) nm. In addition to those peaks, an absorption at 798 ($\epsilon = 236 \text{ M}^{-1}\text{cm}^{-1}$) and 663 ($\epsilon = 261 \text{ M}^{-1}\text{cm}^{-1}$) nm, respectively, is observed for these two complexes. As for **1**, the first two peaks in the UV-Vis spectra of **2** and **3** were assigned to Fe-Cp and d-d. By comparison to Sato's previous observations, the third, weakly absorbing peak, was assigned to an iron-ruthenium charge transfer band.³⁹ The increase in energy of the iron-ruthenium charge transfer band from **2** to **3** can be expected since PMe_2Ph is a stronger σ -donor than PPh_3 .

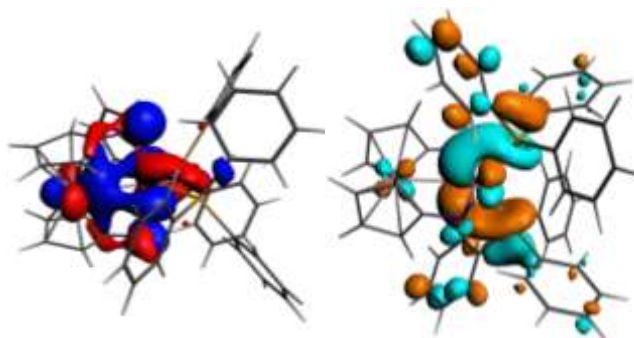


Figure 10. HOMO (left) and LUMO (right) of **2** (isosurface value = 0.03).

The time-dependent DFT calculated excitation spectrum of **2** matches the UV-Vis and NIR spectra obtained experimentally, with an offset of -350 nm. These calculations show a low energy transition corresponding to the IVCT band, calculated at 768 nm (corresponding to the 798 nm absorption found experimentally); this transition arises from promoting an electron from the HOMO to the LUMO. The HOMO of **2** (Figure 5-10) was found to consist of mainly ruthenium d orbitals (31% total contribution) and iron d orbitals (22% total contribution) in addition to contributions from nitrogen p orbitals (19% total contribution). In contrast, the LUMO of **2** (Figure 5-10) is primarily ruthenium based with some contribution from the phosphorous atoms. Neither molecular orbital shows contributions from the phosphine ligands or the ferrocene Cp rings. The HOMO shows antibonding interactions between the ruthenium and nitrogen, with a nonbonding interaction between the ruthenium and iron. The LUMO shows no contribution from the nitrogen; this indicates that promotion of an electron from HOMO to LUMO weakens the Ru-Fe bond while strengthening the Ru-N bond. Therefore, the change in bond order of the iron-ruthenium interaction may be probed by resonance Raman spectroscopy (see below).

5.2.5 Resonance Raman spectroscopy

Resonance Raman spectroscopy utilizes photons that are in resonance with an electronic transition of interest. When an electronic transition occurs, the electron density of the molecule shifts relative to the ground state. Normal modes with nuclear motion corresponding to the changes in electron density in the excited state are displaced relative to the ground state, enhancing the Raman signal. Symmetric transitions are resonantly enhanced most strongly since the intensity of scattering scales with the square of the distortion.^{66, 67} The ability to amplify the intensity of vibrations when in resonance with an electronic transition enables resonance Raman spectroscopy to assist in the assignment of these specific electronic transitions.⁶⁷ This technique,^{68, 69} as well as regular Raman spectroscopy,^{70, 71} has been used previously to establish electronic communication within bimetallic complexes. However, the present study represents the first instance when resonance Raman spectroscopy is used to investigate the nature of weak metal-metal interactions. Here we will demonstrate the resonance enhancement of a Raman active iron-metal (Pd or Ru) stretch when in resonance with the charge transfer electronic transition (Figure 5-11). This resonance enhancement, in conjunction with the results of DFT calculations, supports the assignment of weak metal-metal interactions.

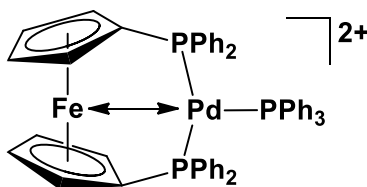


Figure 5-11. Displacement vectors for the normal metal-metal stretching mode of 5. Displacement occurs primarily along the iron-palladium axis.

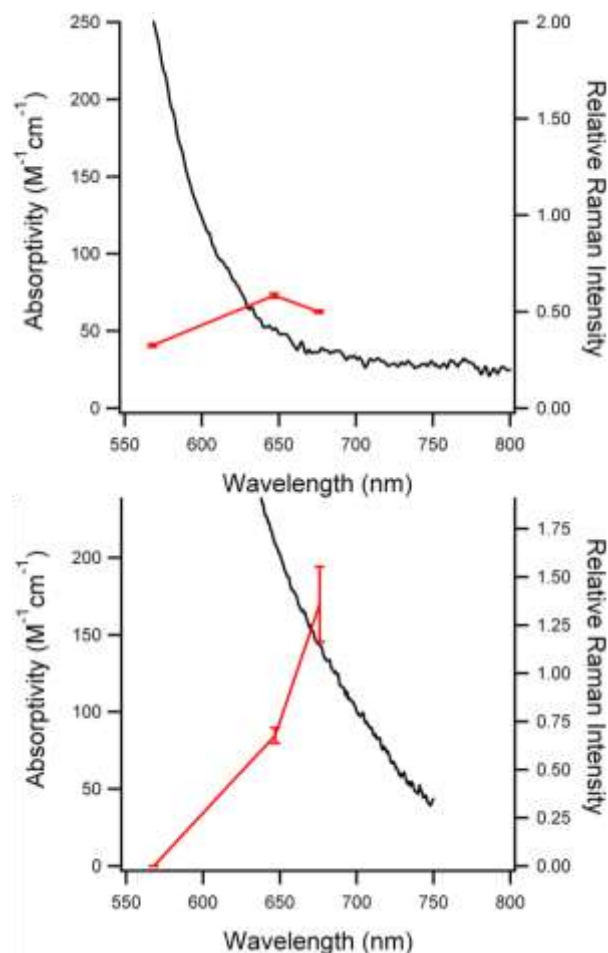


Figure 12. Raman intensity for 347 cm^{-1} mode of **6** (top) and 330 cm^{-1} mode of **5** (bottom) as a function of excitation wavelength superimposed with absorption spectra. Raman intensities for both compounds are scaled relative to 750 cm^{-1} vibration of PF_6^- (internal standard). Intensities are calculated by fitting vibrations with Gaussian functions. Error bars are derived from the error in fitting.

In order to validate this method, we first undertook resonance Raman spectroscopy studies on the pair of previously reported complexes, $[(\text{dppf})\text{Pd}(\text{PPh}_3)][\text{BF}_4]_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene), **5**, which exhibits metal-to-metal charge transfer, and $[(\text{dppf})\text{Pd}(4\text{-picoline})_2][\text{BF}_4]_2$, **6**, which does not.³⁹ As expected, **5** showed enhancement of a

vibration at 330 cm^{-1} with displacement along the iron-palladium axis as the excitation wavelength passed the metal-to-metal charge transfer (Figure 5-12). In contrast, **6** showed no significant vibrational enhancement upon red excitation (Figure 5-12). Other vibrations of **6** displayed a similar trend of lowered relative intensity at 568 nm. That loss was attributed to Raman de-enhancement and was only observed at 568 nm for **6** due to the red shift of the Fe d-d transitions.

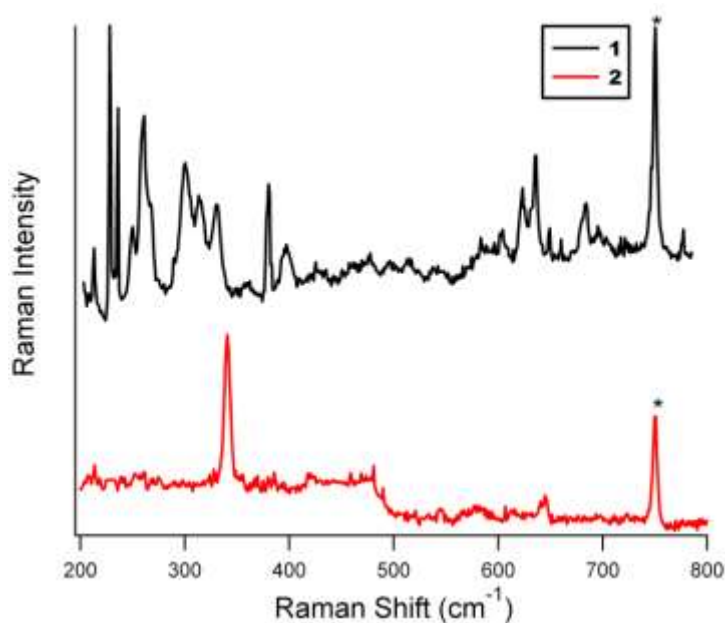


Figure 5-13. Raman spectra of **1** and **2** upon 676.4 nm excitation. Asterisks indicate the vibration (715 cm^{-1}) of the internal standard, KNO_3 .

The Raman spectra of **1** and **2** were obtained at excitation wavelengths of 407, 476, 530, 568, 647, and 676 nm (Figure 5-13), using a Kr^+ ion laser. As expected, the Raman spectra for **1** showed no trend of enhancement in any of the vibrational modes as the excitation wavelength increased (Figure 5-14). In the case of **2**, however, significant enhancement of the 342 cm^{-1} mode was observed as the excitation wavelength of the laser was increased (Figure 5-14). Examination

of the resonance Raman spectra of **1** and **2** upon higher excitation energies reveals de-enhancement trends typical of cyclopentadienyl sandwich compounds.^{72, 73}

The vibrational modes that appear in the resonance Raman spectra were assigned using DFT calculations at the PW91/TZP level. The vibration at 342 cm⁻¹ was assigned to a normal mode consisting primarily of an iron-ruthenium stretch in conjunction with nitrogen-ruthenium stretches. The calculated frequency for this vibration is 256 cm⁻¹. Additionally, a significant change from nonbonding to anti-bonding character along the iron-ruthenium axis between the HOMO and LUMO (Figure 5-10) supports this assignment. The enhancement of this normal mode in **2** is expected based on its NIR spectrum and is indicative of charge transfer between iron and ruthenium. Specifically, the NIR metal-to-metal charge transfer weakens the iron-ruthenium bond, thereby elongating it and producing a stretch along the metal-metal axis. In addition to the increase of the Ru-Fe distance, this mode shows contraction of the Ru-N bonds. The calculated maximum contraction of the Ru-N bonds is 0.20 Å. The lengthening of the Ru-Fe distance is more significant, at 0.60 Å. Thus, the strengthening of the Ru-N bonds is not sufficient to explain the lengthening of the Ru-Fe distance; an interaction between the two metal centers is also responsible.

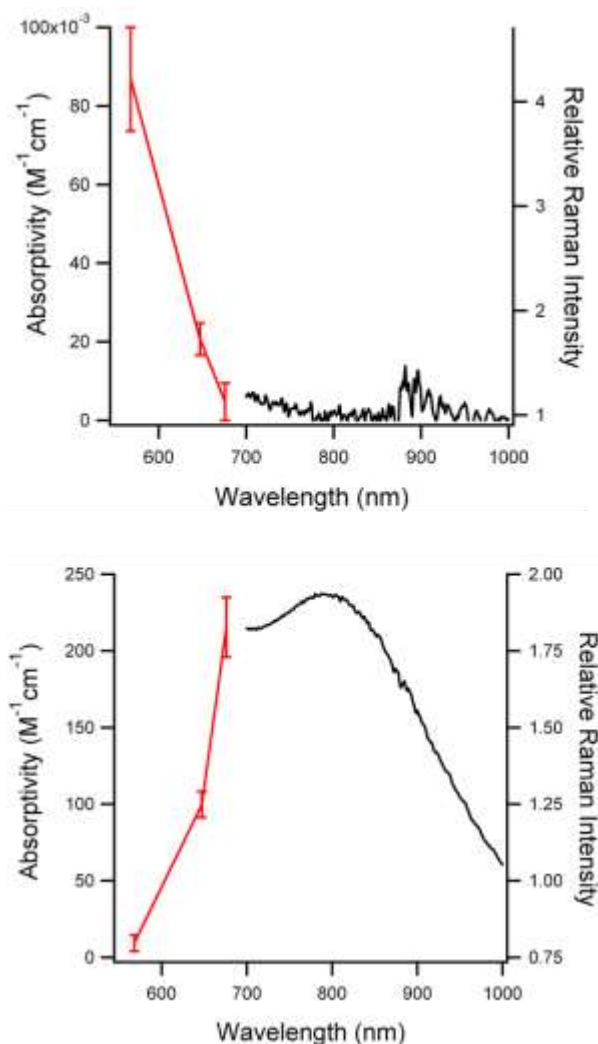


Figure 5-14. Raman intensity for 300 cm^{-1} mode of 1 (top) and 342 cm^{-1} mode of 2 (bottom) as a function of excitation wavelength superimposed with the corresponding NIR spectrum. Raman intensities for both compounds are scaled relative to 750 cm^{-1} vibration of PF_6^- (internal standard). Intensities are calculated by fitting vibrations with Gaussian functions. Error bars are derived from the error in fitting.

5.3 Conclusions

In summary, a weak, donor-acceptor interaction between iron and ruthenium in complexes 2 and 3 was described. This interaction was characterized by 1H NMR, UV-Vis, NIR, Mössbauer,

and Raman spectroscopy, X-ray crystallography, and DFT calculations. The Raman spectra of **2** and **5** exhibit similar features indicating that resonance Raman spectroscopy, in conjunction with UV-Vis/NIR spectroscopy, is a useful tool for determining whether or not a weak interaction between two metal centers exists in such complexes. Furthermore, DFT calculations indicate that the metal-metal interaction is primarily an Fe-Ru donor-acceptor interaction with iron acting as the Lewis base. The present work shows that an in-depth, combined spectroscopic and computational study is powerful in investigating weak metal-metal interactions with complexes **2**, **3**, and **5** representing well characterized examples.

5.4 References

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Chapter 6

Photophysical Pore Control in an Azobenzene-Containing Metal Organic Framework

Adapted from recently published Brown, J. W.; Henderson, B. L.; Kiesz, M. D.; Whalley, A. C.;
Morris, W.; Deng, H.; Furukawa, H.; Zink, J. I.; Stoddart, J. F.; Yaghi, O. M., Photophysical
Pore Control in an Azobenzene-Containing Metal Organic Framework. *Chemical Science* 2013,
4, 2858-2864

6.1 Introduction

Metal-organic frameworks (MOFs), are extended crystalline structures containing metal oxide units bridged by organic linkers. They are highly porous and typically exhibit large surface areas. A wide variety of organic linkers have been incorporated into MOFs, highlighting the isorecticular principle whereby the organic linkers can be changed, yet analogous structural types can be synthesized.¹⁻⁴ Variation of the functional groups present in MOFs have led to applications in chemical sensing,^{5,6} gas separation,⁷ gas storage,^{8,9} catalysis,¹⁰ and drug delivery.¹¹ Despite the large library of MOFs reported in the literature, to date the storage and release of guest molecules has relied¹² solely on the uncontrolled diffusion of cargo into and out of the extended structures of the MOFs. Although many MOFs have been synthesized, none have demonstrated on-command release of stored guest molecules using a controllable external stimulus.

One such functionality, which demonstrated promise for the controlled release of cargo from the pores of a MOF, is the azobenzene unit. Azobenzene provides a source of reversible and photo-controllable *cis/trans* isomerizations¹³⁻¹⁵. This conformational switching results in significant changes in the length of the molecule (9 Å in the trans form to 5.5 Å in the cis form)¹⁶ and, as a result, this photoswitchable system has been incorporated into a variety of rigid materials including films and nano-structures.¹⁷⁻³⁰ Furthermore, the integration of azobenzene units has been employed recently in the one-dimensional (1-D) pores of mesoporous silica nanoparticles where it was demonstrated^{31,32} that the on-command release of cargo molecules from the pores is possible. Photoactive linkers have been incorporated into MOFs and shown interesting adsorption and storage properties that have been directly linked to the photoactivity of those frameworks³³⁻³⁷.

Recently two MOFs were synthesized^{38,39} containing azobenzene units, however, the nature of the pores in these MOFs produced steric restrictions that limited photoswitching applications. We chose to incorporate the photoswitch into a MOF-74 based structure, to combat these steric limitations. Due to a unique binding motif inherent to MOF-74, the inorganic clusters and organic struts form linear stacks producing large, non-interpenetrated 1-D hexagonal pores. This unique architecture will force the azobenzene units directly into the channels where the isomerization of each unit will have a direct impact on the aperture size of a single 1-D channel. Therefore, the photodynamic switching of azobenzene combined with the 1-D structure of this MOF has the potential to allow for controlled cargo delivery from a MOF.

Here, we report the synthesis and photoisomerization studies of a non-interpenetrated azobenzene-derivatized MOF, azo-IRMOF-74-III, which contains 1-D pores. In this particular MOF, the size and shape of the apertures are controlled by the conformational changes in the azobenzenes, which can be reversibly switched from *trans* to *cis* or *cis* to *trans* using UV or visible irradiation, respectively. When all of the azobenzene units are in the *trans* conformation the pore apertures are 8.3 Å in diameter, but upon switching to the *cis* conformation the size of the aperture is increased significantly (10.3 Å).



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6.2 Experimental Detail

6.2.1 Synthesis of azo-IRMOF-74-III

The synthesis of the azobenzene-functionalized linkers involves (Scheme 6-1) a palladium-catalyzed *Suzuki-Miyaura* cross-coupling reaction between 2,5-dibromonitrobenzene and the phenylboronic ester **1** in a degassed 1,4-dioxane/H₂O mixture employing PdCl₂(dppf) as the catalyst and CsF as the base to yield the nitro derivative **2**. Treatment of **2** with Raney Ni and H₂ gas in EtOAc at 50 °C, serves to facilitate both the removal of the benzyl protecting groups and reduce the nitro group to produce the aniline derivative **3** in nearly quantitative yield. Subjecting **3** to excess of nitrosobenzene in acetic acid at 80 °C yielded the azobenzene **4**, which could be converted to the dicarboxylic acid **5**, by saponification of the methyl esters.

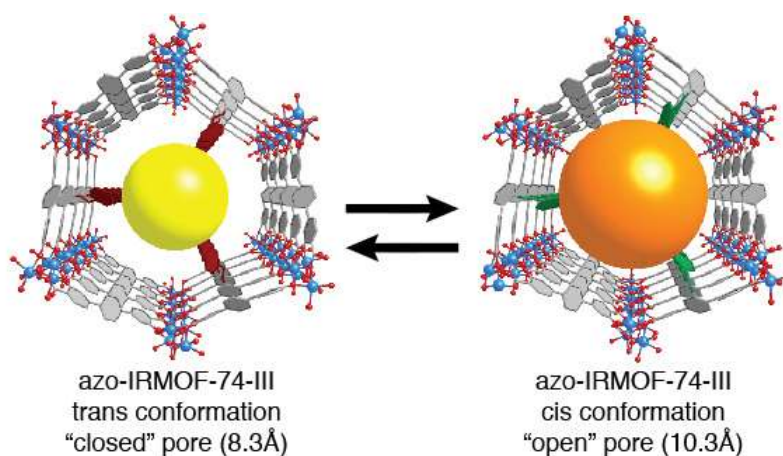


Figure 6-1. Viewing idealized azo-IRMOF-74-III down the c-axis displays one-dimensional pores and azobenzene functional groups projecting into the pores. The yellow and orange balls represent pore aperture in idealized azo-IRMOF-74-III, when the azobenzene functional groups are in *trans* and *cis* conformation, respectively.

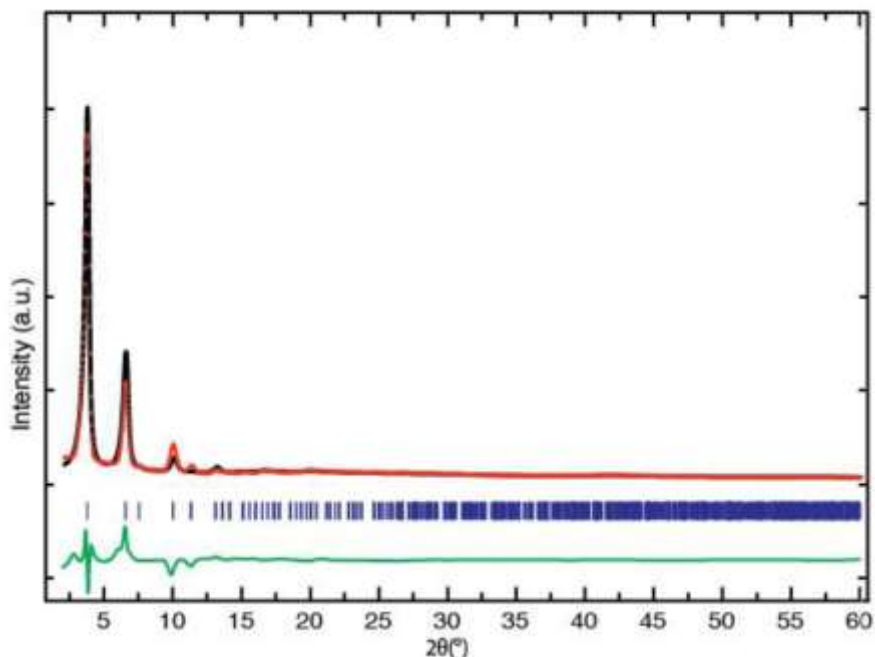


Figure 2. Indexed experimental (red) and refined (black) PXRD patterns of azo-IRMOF-74-III after Rietveld refinement. The difference plot is indicated in green. Blue ticks indicate the positions of Bragg reflections.

Azo-IRMOF-74-III was synthesized by combining $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (80 mg, 0.315 mmol) and the azobenzene-functionalized linker (42.5 mg, 0.09 mmol) in a solution of N,N-dimethylformamide (DMF) (7.5 mL), EtOH (0.5 mL) and H_2O (0.5 mL) for 24 h at 120 °C. After 24 h, the red crystals were collected by filtration.

6.2.2 Characterization of azo-IRMOF-74-III

Powder X-ray diffraction was used for structural determination as the microcrystalline material produced from the MOF synthesis did not diffract sufficiently for single crystal elucidation. Since a higher level of characterization is achieved by producing a solvent and guest

free framework, the crystals were sequentially washed with DMF (3×10 mL) and methanol (3×10 mL) and then evacuated on a supercritical CO₂ dryer over the course of 12 hours. Following this activation process, thermal gravimetric analysis (TGA) was used to confirm that all of the solvent had been removed from the pores of the framework; i.e., there was no significant weight loss up to 275 °C.

Azo-IRMOF-74-III is an isorecticular expansion of MOF-74, in which helical Mg–O–C rods are constructed from hexacoordinate Mg(II) centers. The rods are connected via azobenzene functionalized terphenylene unit **5** to produce one-dimensional pores, which have a diameter of 19.5 Å. This structure was simulated using the Forcite module of Materials Studio and was confirmed with the Rietveld method. Because the one-

dimensional pores in azo-IRMOF-74-III are lined with azobenzene groups that project toward the middle of the pore, the size and shape of the pore aperture directly depend on the *cis* or *trans* configuration. With all azobenzene functionalities in the *trans* configuration the idealized pore aperture is 8.3 Å, but if all functionalities are *cis*, the aperture is larger 10.3 Å (Figure 6-1). The PXRD pattern for azo-IRMOF-74-III was indexed on a trigonal unit cell and refined using the Rietveld method in the Reflex module of Materials Studio, yielding cell parameters $a = 46.771(26)$ Å, $b = 46.771(26)$ Å and $c = 6.869(83)$ Å (residuals: $R_p = 12.08\%$, $R_{wp} = 17.68\%$) (Figure 6-2).

Azo-IRMOF-74-III was further characterized by cross-polarization magic-angle spinning (CP/MAS) ¹³C NMR spectra. From experiments on the activated material, the expected resonances at 174 ppm for the carbonyl carbon atoms and 166 and 114 ppm for the aromatic carbon atoms of incorporated **5** were found. No free **5** was observed in the MOF spectra, confirmed by a lack of peaks at 176, 160, and 108 ppm.

To confirm the porosity of azo-IRMOF-74-III, N₂ isotherms at 77 K were measured on activated samples. From the Brunauer-Emmett-Teller (BET) analysis a surface area of 2410 m²/g was calculated (Figure 6-3). To date, this is the highest recorded surface area of a MOF containing photoswitchable units.

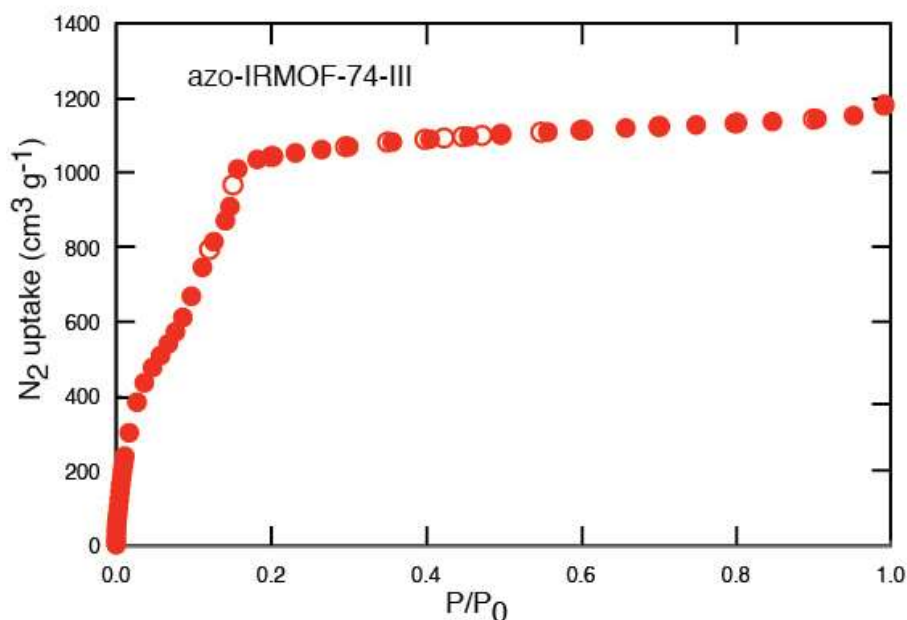


Figure 6-3. Nitrogen isotherm of azo-IRMOF-74-III carried out on activated sample at 77 K. Adsorption and desorption branches are represented by solid and open circles respectively. A surface area of 2410 m²/g was calculated from Brunauer-Emmett-Teller (BET) analysis.

6.3 Results and Discussion

6.3.1 Photophysics of the Azobenzene Linker

The azobenzene functionalized linker used to synthesize azo-IRMOF-74-III exhibits the expected isomerization when exposed to UV and visible light. While previous studies of azobenzene and its derivatives have examined the photophysical properties in solution and various

molecular environments, incorporation to a new platform warrants investigation of its photochromic properties. The UV-vis absorption experiments discussed in this section will thus demonstrate the performance of the azobenzene moiety within the rigid confines of a MOF.

The UV-vis absorption spectrum of non-irradiated **5** exhibits two prominent peaks, close in energy, in the near UV (Figure 6-4a). Irradiation of **5** with UV light (which typically induces a *trans*-to-*cis* isomerization for azobenzene) results in dramatic changes in the absorption spectrum; i.e. the emergence of a new absorption band in the visible region. Although the photoisomerization process is evident, transitions due to the terphenyl moiety overshadow those of the azobenzene functional group in both the pre- and post-irradiation absorption spectra. In addition, the fact that the absorption spectra of the photostationary states are not necessarily purely those of the *trans* or *cis* isomers, respectively, further complicates analysis. Correlation of absorption spectra with ¹H-NMR data elucidated spectral assignments and will be discussed in more detail below.

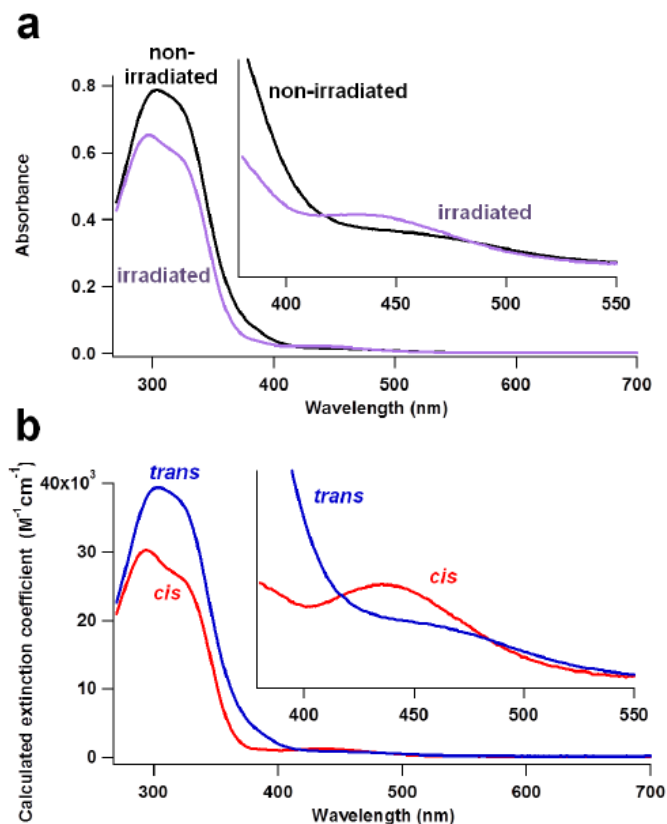


Figure 6-4. Pre- (black trace) and post- (cyan trace) irradiation UV-vis absorption spectra of 5 (a) and *cis* (red trace) and *trans* (blue trace) spectra calculated from Equation 7.1 using relative *cis* and *trans* peak integrations from 1H NMR spectra (b). Spectra for (a) (20 M in DMSO) were irradiated with 15 mW of light from a 377 nm diode laser for 30 minutes.

Relative concentration ratios of the isomers were determined with 1H NMR (Supplementary Information) and combined with UV-vis spectroscopy to calculate pure *cis* and *trans* spectra. Examination of the NMR data for a pre-irradiated solution of azobenzene in DMSO (5 mM for NMR experiments, but diluted to 20 μM for absorption spectra) stored in the dark at room temperature revealed the absence of the *cis* isomer. In contrast, the NMR spectrum of the photostationary state achieved after 30 minutes of irradiation with near-UV light (377 nm, 15 mW) contained peaks from both the *cis* and *trans* isomers. Integration of the *cis* and *trans* peaks in the

irradiated solution yielded a *trans/cis* ratio of 0.43 (70% of *trans*-azobenzenes had converted to the *cis* configuration). Pre- and post-irradiation absorption data were correlated with the relative isomer concentrations to calculate a pure *cis* absorption spectrum according to the following equation:

$$\varepsilon_c = \frac{\frac{1}{cl} \left[A_2 \left(\frac{1}{r_2} + 1 \right) - A_1 \left(\frac{1}{r_1} + 1 \right) \right]}{\frac{1}{r_2} - \frac{1}{r_1}} \quad (1)$$

where ε_c is the calculated *cis* extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$), c is the concentration of **5** (M), l is the path-length of the cuvette (cm), A_1 and A_2 are the pre- and post-irradiation absorbances, respectively, and r_1 and r_2 are the pre- and post- irradiation *trans/cis* isomer ratios, respectively. The resulting pure *cis* and *trans* spectra (Figure 6-4b) reveal a clearer representation of the transitions of **5**. While each of the calculated *cis* and *trans* spectra contain appreciable absorption in the UV region due to the inherent absorption from the ter-phenylene structure, the *trans* isomer absorbs more than the *cis* isomer in the UV and the *cis* isomer absorbs more than the *trans* in the visible region as expected.

The UV and visible absorption peaks of the azo-benzene moiety are assigned to π - π^* and n - π^* electronic transitions, respectively. Both *cis* and *trans* calculated spectra contain a peak near 300 nm with a shoulder at 315 nm, which are attributed to the common ter-phenylene moiety. The higher energy transition near 300 nm is assigned to a π - π^* transition that does not shift when the linker is coordinated to the metal atoms in the MOF. However, the shoulder at 315 nm, which is assigned to a π - π^* transition involving the C=O functionalities on the outer rings, shifts to 337 nm upon coordination within the MOF structure (Figure 6-5). In the calculated spectrum of the *trans*

isomer, a shoulder near 365 nm is attributed to an azobenzene π - π^* transition. A weaker n- π^* azobenzene transition is found at 438 nm in the calculated *cis* spectrum.

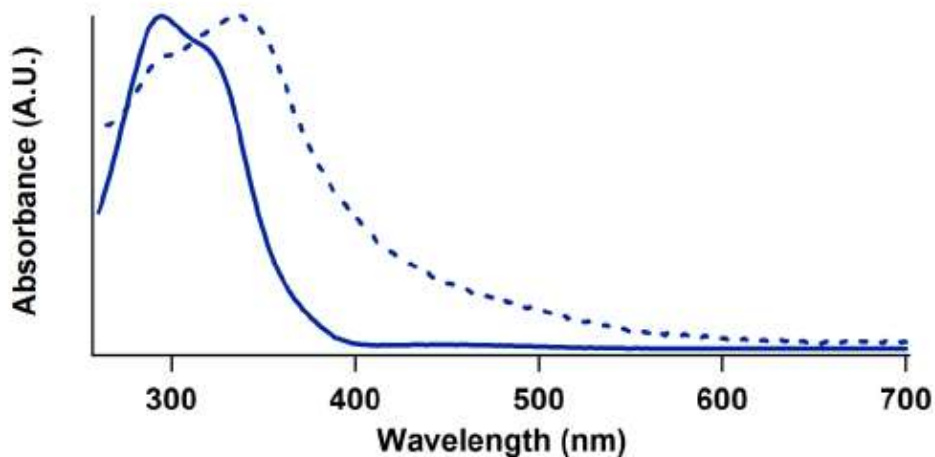


Figure 6-5. Comparison of absorption spectra of **5** (solid trace) with the absorption spectrum of azo-IRMOF-74-III (dotted trace). The transition seen at ~315 nm shifts to 337 nm upon coordination of the linker with the magnesium atoms is attributed to a π - π^* transition involving the C=O functionalities on the outer rings.

To characterize the photoproperties of linker **5** used in this MOF, absorption spectra were obtained as a function of irradiation time with UV and blue light. A 50 μ M solution of **5** was exposed to 15 mW of 377 nm excitation with continuous stirring; its absorption spectra upon irradiation are plotted in Figure 6. Irradiation of **5** in the near UV (377 nm, Figure 6-6a) leads to excitation of the azobenzene π - π^* transition seen in the calculated *trans* spectrum.

Since the *cis* isomer has no appreciable absorbance in the near-UV, the probability of *trans* to *cis* isomerization is higher than *cis* to *trans* isomerization and thus the population of the *cis* species increases. Additionally, competing absorption from the terphenylene portion of the linker is relatively low at 377 nm, so the incident photons are able to reach the azobenzene more efficiently. To convert the molecule back to the *trans* species, the azobenzene linkers were

irradiated in the visible region (457 nm, Figure 6-6b) where the absorbance of the *cis* isomer is higher than the absorbance of the *trans* isomer. The absorption spectra show an increase in the $n\text{-}\pi^*$ band at 438 nm and a decrease in the 300 nm peaks upon near-UV irradiation and the opposite trend with visible irradiation, indicating reversible isomer population changes without decomposition of the linker.

The *cis* and *trans* isomers of the linker have an isosbestic point at 402 nm that does not shift when coordinated to magnesium. Excitation wavelengths in this region can be utilized for stimulating repetitive large amplitude motions. These large amplitude motions have been used to activate the release of cargo from porous substances,^{40,41} and *cis-trans* isomerization expels cargo in a similar way to the MOFs in this study.

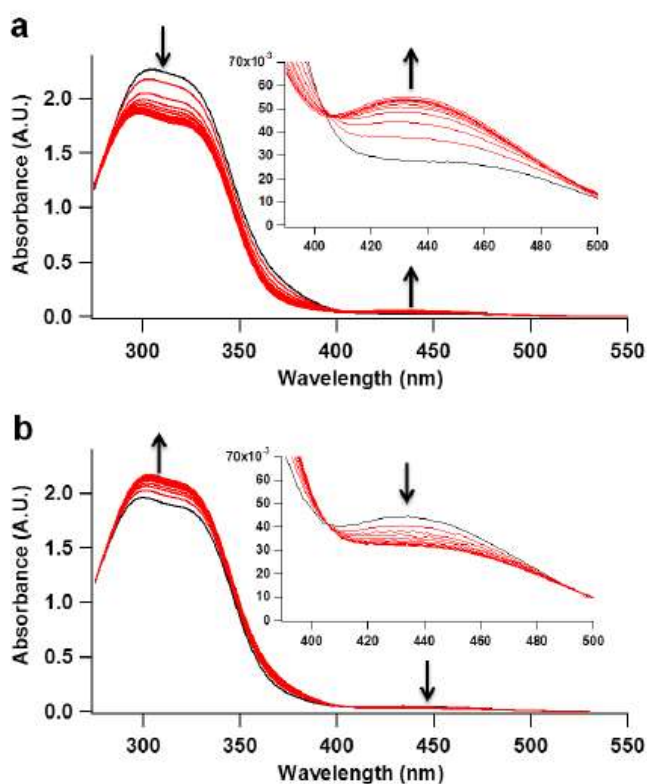


Figure 6-6. Change in absorbance of the azobenzene linker with (a) 377 nm irradiation followed by (b) 457 nm irradiation. Each trace represents 15 seconds of irradiation. The first trace is plotted in black for clarity.

6.3.2 Trapping and Release of Cargo on Command

To test the ability of azo-IRMOF-74-III to store and release cargo, a luminescent dye (propidium iodide, Sigma) was loaded into the hexagonal channels so that the release due to photoisomerization could be observed spectroscopically. This dye was specifically chosen because its size, $8 \times 11 \times 16 \text{ \AA}$ without counterion, matches well with the pore aperture of azo-IRMOF-74-III, between 8.3 and $10.3 \text{ \AA}$ depending on conformation of azobenzene linker. When comparing pore diameter to the dye, it can be seen that the dye cannot easily diffuse into the MOF unless the azobenzene functionalities are in the *cis* conformation. To load the azo-MOFs, 100 mg of particles were stirred in a 1 mM ethanolic solution of propidium iodide for 3 days under exposure to room lights. The loading process is driven by a concentration gradient and the photoisomerization afforded by room lights. UV-vis spectra of a propidium iodide solution acquired before and after loading demonstrate a loading capacity of $0.4 \text{ wt\%}$. While minimizing light exposure the particles were washed thoroughly with ethanol to remove surface adsorbed dye. Subsequently the sample was placed in the corner of a $2 \text{ cm} \times 1 \text{ cm}$ fluorimetric cuvette. A stir bar was placed in the opposite corner to facilitate mixing of the solution, and the cuvette was filled with spectroscopic-grade ethanol. The solution in the cuvette was stirred carefully to avoid disturbing the azo-IRMOF-74-III particles yet facilitate the diffusion of the dye. A probe beam (30 mW , 568 nm) was used to excite the propidium dye in the ethanol solution above the particles, and its fluorescence intensity was integrated and plotted as a function of time (Figure 6-7a).

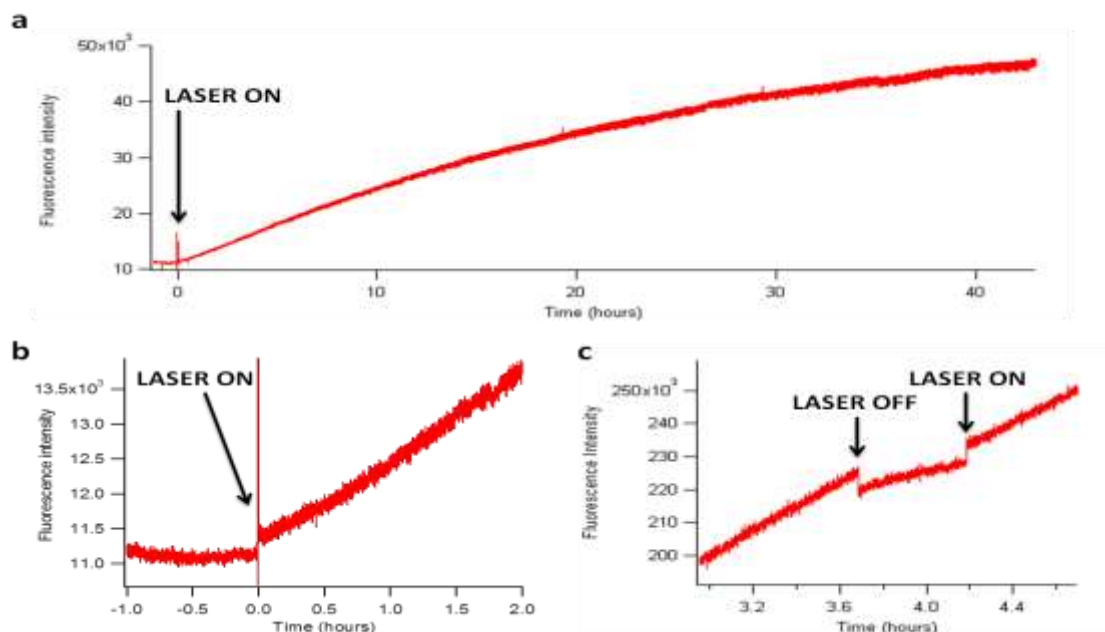


Figure 6-7. (a) Typical release of propidium dye from azo-IRMOF-74-III as a function of time, (b) detailed view of the baseline and start of laser irradiation (marked by the sharp line), and (c) an on/off trial, where the excitation beam was temporarily removed mid-release. The dye continues to diffuse away from the MOF, but the rate of release is drastically reduced.

As seen in Figure 6-7b, there is no increase in propidium iodide intensity prior to laser activation of the *cis/trans* isomerization motions in the azo-IRMOF-74-III particles. This indicates that the azobenzene-functionalized MOF acts as an excellent container, and that no dye escapes from the MOF channels until an external light source of the proper wavelength is added.

After a baseline was established with the probe beam, a 50 mW pump beam at 408 nm (wavelength near the isosbestic point) activated the *cis-trans* wagging motions and expelled the dye from the MOF channels. A clear release was observed which began to level off after 40 hours (Figure 6-7a). This release, which took much longer than in azobenzene-derivatized MCM-41 nanoparticles, can possibly be attributed to the fact that the MOF structure's pores are longer and

narrower⁴². Additionally, the physical interactions between the guest molecules and the host metal-organic framework may be vastly different than those seen in MCM-41. To demonstrate the necessity of the pump beam near the isosbestic point of the azobenzene moiety, a 647 nm laser was employed as a pump beam in a subsequent experiment. No release was observed until the 647 nm laser was replaced with one near the isosbestic point. The release seen in Figure 6-7a can also be controlled by increasing or decreasing the incident power or removing the beam entirely; blockage of the 408 nm pump beam caused the release to slow down (see Figure 6-7c), but upon reintroduction of the beam the original release rate resumed. The sharp increases and decreases seen in the fluorescence spectra of Figure 6-7 when the laser is turned on and off, respectively, are due to effects from laser scattering. When the laser impinges upon the MOF particles, the uneven surfaces of these particles scatter the incoming laser light and increase the overall intensity counts in the spectra. When the laser is turned off, the source of scattering is removed, and an equivalent drop is seen in the spectra. The slope of the release does not immediately go to zero, most likely due to the following factors: (1) pores have larger apertures in the *cis* orientation (see Figure 6-1), allowing for some residual diffusion of cargo molecules, (2) a delay caused by diffusion of cargo from the MOF particles to the laser detection area is expected, and (3) thermal back-conversion processes continue to generate a small amount of motion in the dark. Most of these effects are short-lived, however, and discontinuation of laser irradiation will eventually reduce the rate of dye release to a negligible level. Since continuous laser irradiation is needed for efficient expulsion of the dye into solution, the pattern and duration of release can be adjusted as necessary. Azo-IRMOF-74-III, therefore, is useful in applications where longer release or stop-start release is desired.⁴³⁻⁴⁵

6.4 Conclusions

An azobenzene-derivatized MOF has been synthesized and studied spectroscopically. Azobenzene *trans* and *cis* isomerizations of the linker molecule have been observed via NMR and absorption spectroscopy to ascertain the relative concentrations and the absorption spectra of the *cis* and *trans* species as well as the most appropriate wavelength choices for irradiation.

Irradiation at 408 nm, near the linker's isosbestic point, causes both *cis-trans* and *trans-cis* excitations. The large amplitude motions due to these wagging motions led to an increase in dye mobility, expelling cargo from the structure on demand. The storage and release capabilities of the system could be studied with the aid of fluorescent propidium iodide, and the dye release rate was diminished when irradiation was removed. No release was observed prior to irradiation, indicating that the dye molecules are well contained.

The photo-driven azo-MOF structure, the focal point of this paper, is an improvement over recently made photoswitchable frameworks in that this structure contains only one-dimensional pores. The one-dimensional pores permit more efficient storage and release of the dye, and the microporous particles allow filtration in a new size domain. Here, we have shown that the azo-MOF structure is capable of storing dye molecules and releasing them on command via a photoisomerization process. This new MOF creates unprecedented possibilities for the use of light in the realm of robust dynamics.

6.5 References

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