levels;[6] here λ_{max} (MCLT) = 407 nm (see inset in Figure 2). The Raman spectra observed under both low-power 441.6-nm and high-power 354.7-nm (Figure 2) excitation exhibit scattering only from the complexed ground-state py ligand[21] and show only slight variation in relative peak intensities at the two excitation wavelengths. Although excitation in either case leads initially to MLCT, rapid deactivation by internal energy relaxation presumably leaves the complex in a lower lying LF excited level. It is possible that scattering from a short-lived $Ru^{III}(NH_3)_5(py^{-}\cdot)^{2+}$ species might not be enhanced at 355 nm. Although the pyridine radical anion has an absorption peak near 340 nm in MTHF solution,[22] the proximity of the metal cation may blue-shift the transition sufficiently to move it off resonance. Thus failure to observe $py^{-}\cdot$ scattering in these experiments does not prove that the photoactive LF state lies below the MLCT state in **1**, although it is consistent with Ford's picture.[6]

Excited-state Raman scattering from transition-metal complexes had been reported heretofore only for molecules containing the bpy ligand.[1-5] The observation of MLCT scattering from $Ru(NH_3)_5(acpy)^{2+}$ suggests that the resonance Raman technique may be utilized to charaterize low-lying excited electronic states of complexes containing multiple pyridyl ligands. We report the result of one such investigation in the following paper.[23]

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Resonance Raman Spectra of Ground and Lowest Excited Electronic States of Some Ruthenium(II) Mixed-Ligand Complexes

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Several examples of resonance Raman (RR) scattering from excited electronic states of d^6 transition-metal complexes which contain the 2,2'-bipyridine (bpy) ligand have been published.[1-6] In the preceding paper we report the first observation of such scattering from a different ligand, 4-acetylpyridine (acpy) in $Ru(NH_3)_5(acpy)^{2+}$.[7] Here we describe RR spectra of complexes that contain both bpy and monodentate pyridyl ligands. The results suggest that the localized excitation model proposed by Woodruff and co-workers for $Ru(bpy)_3^{2+}$ (**1**)[1,2] and supported in subsequent work[3-6] applies as well to these more general coordination complexes. They also indicate some limitations of ns timescale measurements.

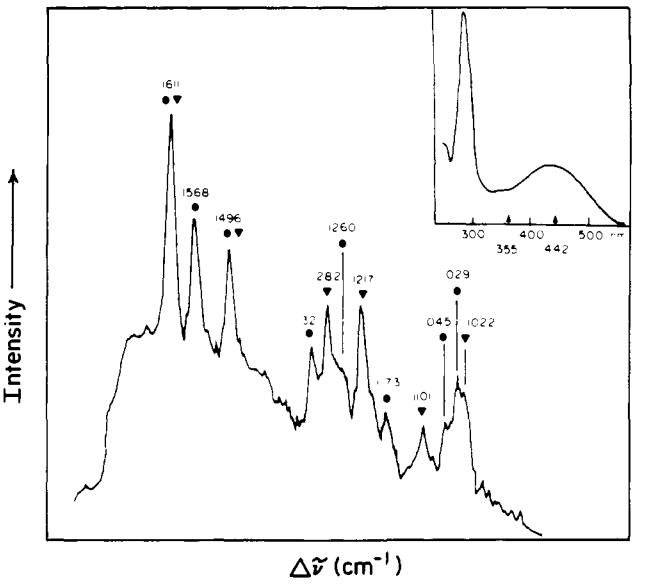

Figure 1. Resonance Raman spectrum of deoxygenated 10^{-4} M aqueous solution of $Ru^{II}(bpy)_2(acpy)_2(BF_4)_2$ under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Key to band assignments: (●) bpy, (▼) acpy. (Inset: Absorption spectrum in the 250–600-nm region.)

RR spectra at selected excitation wavelengths have been obtained for $\sim 10^{-4}$ M aqueous solutions of *cis*-$Ru^{II}(bpy)_2(L)_2(BF_4)_2$ salts, where L = acpy (**2**) or pyridine (py) (**3**). The complexes were synthesized and identified according to the literature,[8,9] and RR spectra were acquired as described in the accompanying paper.[7]

The UV–vis spectrum of **2** (Figure 1, inset) differs little from that of **1**, the metal-to-ligand charge-transfer (MLCT) absorption in the blue being somewhat broadened here due to overlapping transitions to the bpy and acpy ligands. RR spectra of each group in its lowest MLCT excited state have been observed previously under pulsed 355-nm excitation.[1,2,4-7] Yet in the mixed-ligand complex **2** *no* excited electronic state Raman scattering is obtained under these conditions; the RR spectrum shown in Figure 1 is essentially a superposition of the ground-state scattering from bpy and acpy under UV excitation. An excitation profile obtained at several points in the composite MLCT absorption shows smooth variations in the relative intensities of the ground state bpy and acpy Raman peaks, reflecting the changing mixture of π^* levels of the two ligands across the absorption envelope.[10] The absence of detectable excited-state scattering from **2** may indicate that the lifetimes of the excited states formed by 355-nm excitation are too short for the nanosecond timescale of these Raman measurmenets. Even the lowest excited state may be shorter lived than that of **1**, since we have been able to detect only very weak luminescence from **2**, and that only at 77 K.[11]

The lowest MLCT state of $Ru(bpy)_2(py)_2^{2+}$ (**3**), however, has a lifetime approaching that of the tris bpy complex, **1**.[12] The absorption spectrum of **3** (inset, Figure 2) is distinguished from those of **1** and **2** primarily by the presence of a peak at 338 nm (ϵ 20.4 × 10^3), which we attribute to metal-to-pyridine CT. RR spectra of **3** in the 1000–1650-cm^{-1} region are shown in Figure 2. Under 442-nm CW excitation (top frame) seven peaks are observed; all have been previously identified as ring stretching modes of the bpy ligand in its ground state.[1,5,13] No py scattering

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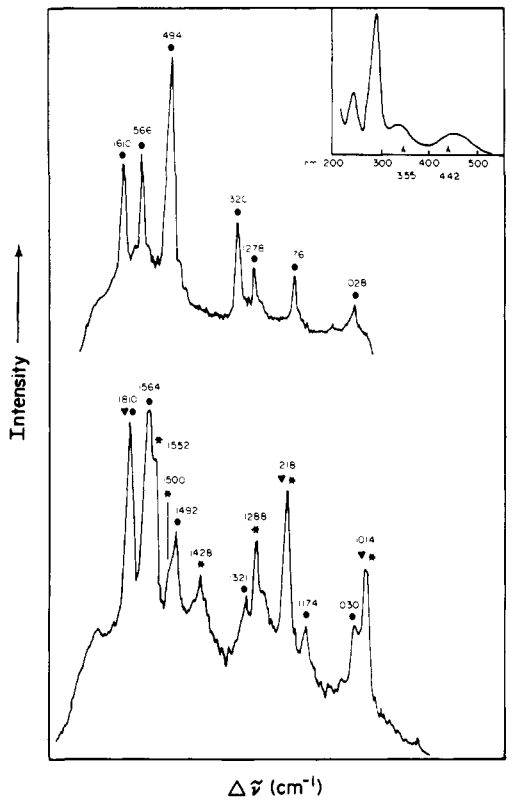

Figure 2. Resonance Raman spectra of deoxygenated 10^{-4} M aqueous solutions of $Ru^{II}(bpy)_2(py)_2(BF_4)_2$. Top frame: under CW excitation at 441.6 nm. Bottom frame: under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Key to band assignments: (●) bpy, (*) $bpy^{-\cdot}$, (▼) py. (Inset: Absorption spectrum in the 250–600-nm region.)

is observed at this excitation wavelength, which is resonant with metal-to-bpy CT absorption. The bottom frame of Figure 2 displays the RR spectrum of **3** upon excitation with ~5-mJ pulses at 355 nm. In comparison to the top frame, the more intense, higher energy illumination produces many additional peaks and gives rise to strong variations in relative peak intensities. Although **3** is being excited in resonance with Ru-to-py CT absorption, rapid internal energy relaxation apparently leaves a significant proportion of the complex in its lowest MLCT excited state, such that RR scattering characteristic of bpy* is observed. However, the spectrum differs from that of **1** excited under similar conditions[1,2,4,5] in that ground-state bpy scattering predominates for **3**. (For example, the excited-state peak at 1552 cm^{-1} is much stronger than the ground-state mode at 1564 cm^{-1} in the RR spectrum of **1** excited by 355-nm laser pulses.) Moreover, the intensity pattern is altered by the underlying presence of ground-state py scattering.[7] The origins of the peaks are denoted directly in the figure.

The wavennumber shifts and relative intensities of the Raman peaks observed for **3** under 355-nm excitation suggest that the localized exctation model applies as well to this mixed ligand system; i.e., the species responsible for the excited state scattering can be represented as $Ru^{III}(bpy^{-\cdot})(bpy)(py)_2^{2+}$ (**3***). Because the excitation is resonant primarily to metal-to-py CT absorption and alternative decay channels exist (e.g., photochemistry, internal conversion), the relative population of **3*** suffers in comparison to the corresponding state in the tris bpy complex. The Raman probe photons in a given laser pulse encounter a larger concentration of ground-state molecules in **3** than in **1**, giving rise to a relatively large contribution to the Raman scattering from $Ru^{II}(bpy)_2(py)_2^{2+}$. Within the limitations set by the time scale of these experiments and the requirement that the pump radiation used to excite the sample molecules be in resonance with an absorption of the electronically excited species so prepared, our results indicate that the localized excitation model previously advanced for $Ru(bpy)_3^{2+}$ and its analogues applies also to transition-metal complexes having multiple ligands with different low-lying π^* levels.

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Registry No. $Ru^{II}(bpy)_2(acpy)_2(BF_4)_2$, 94570-84-0; $Ru^{II}(bpy)_2(py)_2(BF_4)_2$, 94596-79-9.

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Studies of Enzyme Stereochemistry. Elucidation of the Stereochemistry of the Reaction Catalyzed by *S*-Adenosylhomocysteine Hydrolase

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S-Adenosylhomocysteine (SAH, **1**) (Scheme I) is a product of biological transmethylation reactions that utilize *S*-adenosylmethionine as methyl donor. SAH acts as a potent inhibitor of most methyltransferases thus far examined and this finding has led to proposals that SAH plays a regulatory role in vivo.[1] The only known mechanism for the catabolism of SAH in eucaryotic cells is via its reversible hydrolysis to adenosine (**2**) and homocysteine (**3**) catalyzed by the enzyme *S*-adenosylhomocysteine hydrolase (Scheme I). This enzyme was first isolated from rat liver[2] and subsequently found to occur in a variety of eucaryotes[3] and procaryotes.[4] The inhibitory effects of SAH and the fact that adenosine is cytotoxic to individuals lacking adenosine deaminase have made SAH hydrolase an attractive target for pharmacological studies.[5] The enzyme from beef liver has been crystallized,[3d] and elegant mechanistic studies have been carried out.[3e] These studies established that the enzyme contains bound NAD and that the cleavage of SAH to homocysteine and adenosine is accomplished by oxidation of the 3′-hydroxyl group of SAH followed by β-elimination of homocysteine to yield 3′-keto-4′,5′-dehydro-5′-deoxyadenosine. The latter substance then undergoes a Michael-type addition of water to produce 3′-ketoadenosine, which is finally reduced to adenosine.[3e] The importance of *S*-adenosylhomocysteine hydrolase in mammalian systems and its novel mechanistic features prompted us to carry out a stereochemical analysis whose results are summarized here.

The analysis was carried out in two stages. The first stage began with the synthesis of (5′*S*)- and (5′*R*)-(5′-$^2H_1$)-*S*-adenosyl-

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