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Application of Transient Resonance Raman Spectroscopy to the Structure of a Photoinduced Electron-Transfer Intermediate

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Transient resonance Raman spectra have been acquired for the chromophore-quencher complexes *fac*-$[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}$ and *cis*-$[(bpy)_2Os^{II}(CO)(MQ^+)]^{3+}$ (MQ^+ is monoquat, *N*-methyl-4,4′-bipyridinium cation; bpy is 2,2′-bipyridine) following metal-to-ligand charge-transfer excitation. The transient spectra verify that $bpy^{\bullet-} \rightarrow MQ^+$ intramolecular electron transfer occurs ($\tau < 7$ ns) with the excited electron residing ultimately on the monoquat ligand. By comparison to vibrational data for biphenyl, 4,4′-bipyridine, *N,N′*-dihydro-4,4′-bipyridinium dication, and methyl viologen (paraquat) and their corresponding, one-electron reduced forms, it can be inferred that, in the MQ^+-based MLCT excited state, the electron is delocalized over the entire ligand and the two pyridyl rings assume a coplanar geometry.

Introduction

Vibrational spectroscopy is a powerful tool for examining molecular structure and chemical bonding. Since the initial experiments of Dallinger and Woodruff,[1] transient resonance Raman spectroscopy has proven to be a valuable technique for extending vibrational measurements to the electronic excited states of coordination compounds.[2–4] It has been especially useful in identifying the electron acceptor ligand in the metal-to-ligand charge-transfer (MLCT) excited states of mixed-ligand, polypyridyl complexes of Ru^{II}.[4] The technique has also been used to probe intermediates formed following MLCT excitation and intramolecular electron or energy transfer.[5]

Differences between ground- and excited-state vibrational frequencies provide a basis for inferring structural and conformational changes induced by differences in electron content. In this paper, we describe the application of resonance Raman spectroscopy to the study of structural changes in chromophore-quencher complexes where the *N*-methyl-4,4′-bipyridinium cation (monoquat or MQ^+) is the acceptor ligand. For example, following $Re^{I}(d\pi) \rightarrow bpy(\pi^*)$ excitation of *fac*-$[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}$ (bpy is 2,2′-bipyridine) intramolecular electron transfer ($bpy^{\bullet-} \rightarrow MQ^+$) occurs to give the lower energy, $Re^{II}(MQ^{\bullet})$-based MLCT excited state, Scheme 1.[6]

The structure of the salt *fac*-$[(bpy)Re^{I}(CO)_3(MQ^+)](PF_6)_2$ has been determined by X-ray crystallography. The dihedral angle (θ) between the two pyridyl rings of the MQ^+ ligand was found to be 47° and, on the basis of spectroscopic measurements, was suggested to remain at ~47° in solution.[7] Numerous structural and vibrational studies have been undertaken on molecules with structures analogous to MQ^+. Data are available for biphenyl,[8–11] 4,4′-bipyridine (4,4′-bpy),[12,13] the *N,N′*-dihydro-4,4′-bipyridinium dication (PV^{2+}), and methyl viologen (paraquat or PQ^{2+}).[14,15] In the case of biphenyl, for example, the two phenyl rings are noncoplanar due to steric repulsion between the 2,2′- and 6,6′-hydrogen atoms.[8,9] The repulsion is countered by π–π interactions between the two rings which favor a planar conformation by increasing electronic delocalization. The balance between the two leads to a nonzero dihedral angle the magnitude

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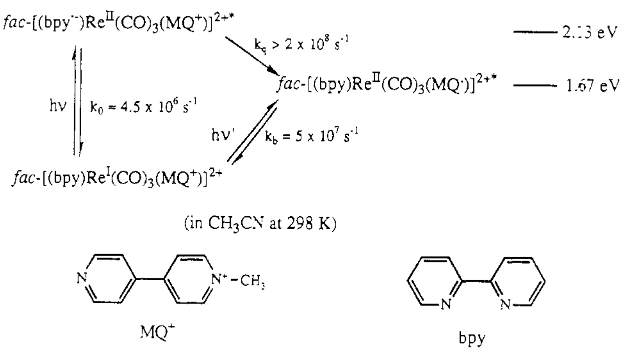
Scheme 1



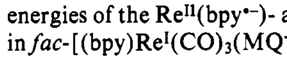
of which is dependent on the medium.[9] In its lowest π–π^* excited state, and in the one-electron-reduced radical anion, π^*–π^* interactions are enhanced, the inter-ring C–C bond gains considerable double bond character, and a planar conformation is adopted.[10,11]

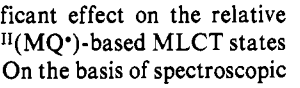
The dihedral angle has a significant effect on the relative energies of the $\mathrm{Re^{II}(bpy^{\bullet-})}$- and $\mathrm{Re^{II}(MQ^{\bullet})}$-based MLCT states in *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}}$. On the basis of spectroscopic measurements, it has been estimated that the difference in energy between the $\mathrm{Re^{II}(MQ^{\bullet})}$-based state at $\theta \sim 47°$ and $\theta \sim 0°$ (which was assumed to be the stable conformer) is $\sim$0.3 eV.[16] The goal of this work was to utilize the transient Raman technique to explore the equilibrium structure at the $\mathrm{MQ^+}$ acceptor ligand in this and the Os-based exited state, *cis*-$\mathrm{[(bpy)_2Os^{III}(CO)(MQ^{\bullet})]^{3+*}}$.

Experimental Section

Materials. Spectrograde $\mathrm{CH_2Cl_2}$ and $\mathrm{CH_3CN}$ (Burdick & Jackson) were used as received. The salts *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)](PF_6)_2}$, *fac*-$\mathrm{[Re^{I}(CO)_3(MQ^+)_2Cl](PF_6)_2}$, *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(4\text{-}Etpy)](PF_6)}$, and *cis*-$\mathrm{[(bpy)_2Os^{II}(CO)(MQ^+)](PF_6)_3}$ were prepared as previously described.[16] *N*-methyl-4,4′-bipyridinium cation ($\mathrm{MQ^+}$), *N*,*N*′-dimethyl-4,4′-bipyridinium dication ($\mathrm{PQ^{2+}}$), and *N*,*N*′-3,3′-tetramethyl-4,4′-bipyridinium dication ($\mathrm{Me_2PQ^{2+}}$) were prepared as $\mathrm{PF_6^-}$ salts by literature methods.[16] Tetra-*n*-butylammonium hexafluorophosphate, $\mathrm{[N(\textit{n}\text{-}C_4H_9)_4](PF_6)}$ or TBAH, was purchased from Aldrich, recrystallized in 2:1 (v:v) ethanol–$\mathrm{H_2O}$ twice, and thoroughly dried in a vacuum oven (72 h).

Electrochemical Generation of Radicals. *N*,*N*′-Dimethyl-4,4′-bipyridinium cation ($\mathrm{PQ^{\bullet+}}$), *N*-methyl-4,4′-bipyridinium radical ($\mathrm{MQ^{\bullet}}$), *N*,*N*′-dimethyl-3,3′-dimethyl-4,4′-bipyridinium cation ($\mathrm{Me_2PQ^{\bullet+}}$), and *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^{\bullet})]^+}$ were generated by controlled-potential electrolysis in a drybox under $\mathrm{N_2}$. The electrochemical experiments utilized a PAR Model 273 potentiostat/galvanostat in a three-compartment cell consisting of Pt bead or Pt gauze working electrodes, a Pt coil auxiliary electrode, and a Ag/$\mathrm{AgNO_3}$ reference electrode. In a typical electrolysis, approximately 5 mL of 0.1 M TBAH in $\mathrm{CH_3CN}$ was placed in the three-compartment cell with a Pt bead working electrode. A solvent background was cycled to ensure solvent, electrolyte, and electrode integrity. The sample (1–2 mg) was added to the working compartment, and a cyclic voltammogram was obtained by scanning between 0.0 and −2.0 V at 100 mV/s. The Pt bead working electrode was replaced by a Pt gauze, and controlled-potential electrolysis was performed on a stirred solution at an applied potential ~100 mV past the peak potential for the first reductive couple while monitoring the change in current. The electrolysis was continued until the change in current was negligible. Two aliquots were transferred from the working compartment to NMR tubes which were sealed onto a tip off manifold. The manifold was removed from the drybox, and the samples freeze–pump–thaw degassed and sealed off in NMR tubes under vacuum for the Raman studies.


$\mathrm{Me_2PQ^{2+}}$


$\mathrm{PQ^{2+}}$

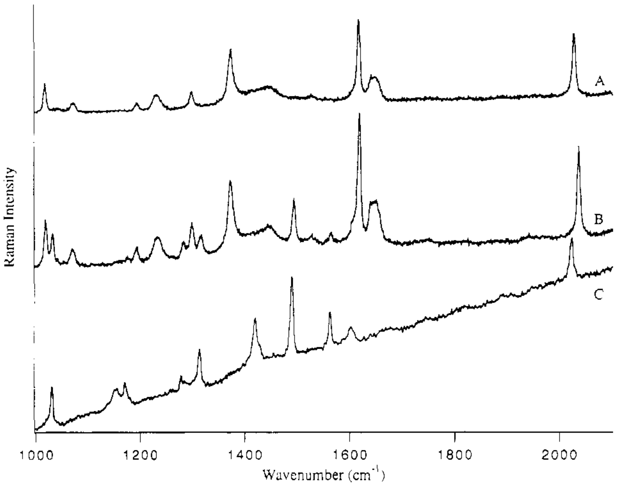


Figure 1. Resonance Raman spectra of (A) *fac*-$\mathrm{[Re^{I}(CO)_3(MQ^+)_2Cl]^{2+}}$, (B) *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}}$, and (C) *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(4\text{-}Etpy)]^+}$ measured with 406.7-nm excitation in $\mathrm{CH_3CN}$ at 298 K. Very similar spectra are observed with 363.8-nm excitation. The spectra are the result of 16 co-added scans. The nonlinear background in (C) is due to emission from the MLCT excited state.

Raman Spectroscopy. Continuous wave and transient Raman studies were performed at the UNC Laser Facility on instrumentation previously described.[5] Samples for transient Raman studies were 1–3 mM in $\mathrm{CH_3CN}$ and freeze–pump–thaw degassed at least three cycles. The 363.8-nm Raman spectra were obtained at CLS-4 at Los Alamos National Laboratory with a Model 2045 Spectra-Physics $\mathrm{Ar^+}$ laser, a SPEX 1877D triple spectrograph, and a liquid nitrogen cooled Photometrics PN12CCD.

Results

In Figure 1 are shown resonance Raman spectra (1000–2200 cm⁻¹) of *fac*-$\mathrm{[Re^{I}(CO)_3(MQ^+)_2Cl]^{2+}}$ (A), *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}}$ (B), and *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(4\text{-}Etpy)]^+}$ (C) in $\mathrm{CH_3CN}$ at 298 K. The spectra were measured with 406.7-nm excitation in near resonance with $\mathrm{Re^{I}} \rightarrow$ bpy and/or $\mathrm{Re^{I}} \rightarrow \mathrm{MQ^+}$ metal-to-ligand charge-transfer (MLCT) bands.[6,7,16] Spectra obtained with 363.8-nm excitation were virtually identical. In the spectrum of *fac*-$\mathrm{[Re^{I}(CO)_3(MQ^+)_2Cl]^{2+}}$ bands appear for the $\mathrm{MQ^+}$ ligand which are resonantly enhanced with $\mathrm{Re^{I}} \rightarrow \mathrm{MQ^+}$ excitation, and for *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(4\text{-}Etpy)]^+}$, bpy bands are resonantly enhanced with $\mathrm{Re^{I}} \rightarrow$ bpy excitation. In the spectrum of *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}}$ there are contributions from both bpy and $\mathrm{MQ^+}$. In addition, all spectra show one resonantly enhanced ν(CO) band which has been assigned to the stretch of the CO group cis to bpy in $\mathrm{[(bpy)Re(CO)_3Cl]}$.[17] In the spectrum of powdered samples of *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)](PF_6)_2}$ and *fac*-$\mathrm{[Re^{I}(CO)_3(MQ^+)_2Cl](PF_6)_2}$ diluted with KCl or $\mathrm{K_2SO_4}$ Raman bands appear at 1019, 1232, 1302, 1619, and 1650 cm⁻¹, nearly the same energy as in $\mathrm{CH_3CN}$ (1019, 1231, 1298, 1617, and 1644 cm⁻¹).

The transient resonance Raman spectra (600–1700 cm⁻¹) of *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(4\text{-}Etpy)]^+}$ and *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}}$ are shown in Figure 2. The spectra were measured under the same conditions ($\mathrm{CH_3CN}$, 298 K) with 354.7-nm laser pulses both to pump the $\mathrm{Re^{I}} \rightarrow$ bpy absorption and to act as a source for the Raman scattering. The 354.7-nm laser excitation is in resonance with excited-state absorptions ($\pi \rightarrow \pi^*$) of both the $\mathrm{bpy^{\bullet-}}$ and $\mathrm{MQ^{\bullet}}$ ligands. The band energies for $\mathrm{MQ^{\bullet}}$ were established independently by measurements on solutions containing the electrochemically generated, one-electron-reduced complex *fac*-$\mathrm{[(bpy)Re^{I}(CO)_3(MQ^{\bullet})]^+}$ in $\mathrm{CH_3CN}$ (0.1 M in

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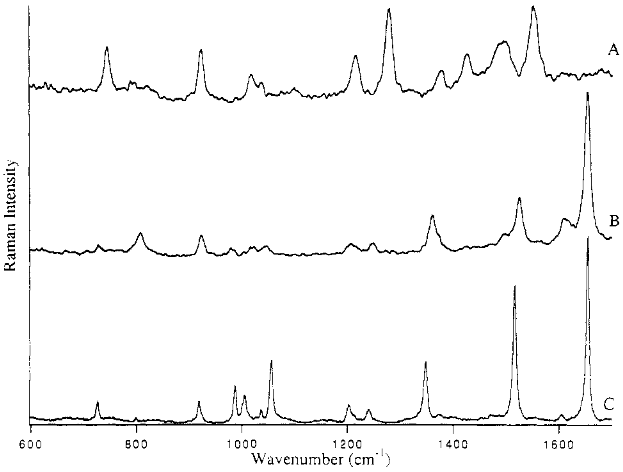

Figure 2. Transient resonance Raman spectra of 1–3 mM samples of (A) *fac*-[(bpy)Re^I(CO)$_3$(4-Etpy)]$^+$ and (B) *fac*-[(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$ in CH$_3$CN. Samples for the Raman experiment were freeze–pump–thaw degassed several times before being sealed in an NMR tube. The spectra were measured with 354.7-nm laser pulses both to excite the sample in the Re^I → bpy MLCT band and to act as a source for the Raman scattering from the bpy$^{\bullet-}$ or MQ$^\bullet$ transient. Spectrum C is the resonance Raman spectrum of electrochemically generated *fac*-[(bpy)-Re^I(CO)$_3$(MQ$^\bullet$)]$^+$ in CH$_3$CN measured with 568.2-nm excitation.

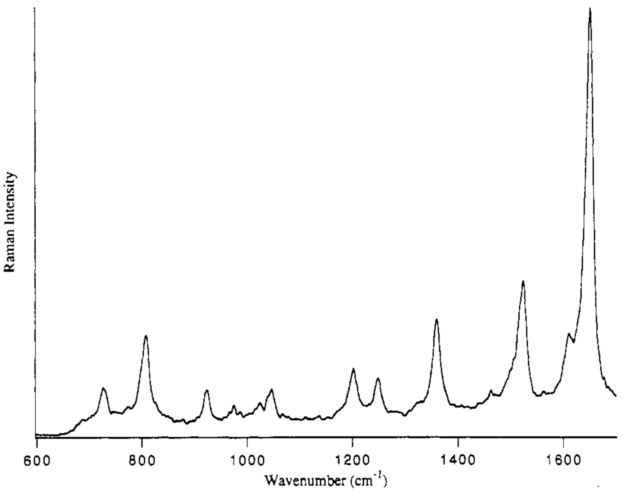

Figure 3. Transient resonance Raman spectrum of *cis*-[(bpy)$_2$-Os^{II}(CO)(MQ$^+$)]$^{3+}$ in CH$_3$CN. The experimental conditions were the same as in Figure 2.

TBAH) at 298 K with 568.2- or 363.8-nm CW excitation into the $\pi \rightarrow \pi^*$ bands near 600 or 370 nm, Figure 2C. The transient Raman spectrum of *cis*-[(bpy)$_2$Os^{II}(CO)(MQ$^+$)]$^{3+}$ measured under the same conditions as for the Re complexes is shown in Figure 3.

Table 1. Comparison of Raman Band Energies (cm^{-1}) for the Monoquat-Based Vibrations in [(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$, [(bpy)Re^{II}(CO)$_3$(MQ$^\bullet$)]$^{2+*}$, and [(bpy)Re^I(CO)$_3$(MQ$^\bullet$)]$^+$ in CH$_3$CN at Room Temperature

[(bpy)Re^I(CO)$_2$(MQ$^+$)]$^{2+}$ (CW 363.8, 406.7 nm)	[(bpy)Re^{II}(CO)$_3$(MQ$^\bullet$)]$^{2+*}$ (pulsed 354.7 nm)	[(bpy)Re^I(CO)$_3$(MQ$^\bullet$)]$^+$ (CW 568.2 nm)
734	726	727
	808	800
1019	975	987
	1025	1005
1072	1043	1036
1193	1202	1204
1231	1250	1241
1298	1359	1348
	1465	1472
	1502	1500
1528	1523	1517
1617	1609	1606
1644	1649	1655

In Table 1 are presented ground state and transient resonance Raman band energies for monoquat vibrations in *fac*-[(bpy)-Re^I(CO)$_3$(MQ$^+$)]$^{2+}$, *fac*-[(bpy)Re^I(CO)$_3$(MQ$^\bullet$)]$^+$, and *fac*-[(bpy)Re^{II}(CO)$_3$(MQ$^\bullet$)]$^{2+*}$. The ground-state bands for MQ$^+$ were discerned by comparing spectrum B to spectrum A in Figure 1, and the bands for MQ$^\bullet$ by comparing spectra B and C in Figure 2. Bands for MQ$^+$ from the ground state and transient Raman experiments are compared to Raman data for biphenyl, 4,4′-bipyridine (4,4′-bpy), *N*,*N*-dihydro-4,4′-bipyridinium dication (PV^{2+}), and methyl viologen (paraquat or PQ^{2+}) and their corresponding one-electron-reduced forms in Table 2. The correlations across the table are comparisons of analogous bands and are not intended to represent the same vibrations. The vibrational modes which are the largest contributors to the potential energy distributions from the normal coordinate analyses for biphenyl[10c] and paraquat[14b] are cited as assignments in order to provide insight into what may be analogous modes at monoquat. Raman features for monoquat, which include contributions from the attached methyl group, are readily identified in these comparisons, as is the C–C inter-ring vibration. The Raman modes which consist predominantly of ring vibrations appear at energies comparable to those of 4,4′-bpy and paraquat.

Data for paraquat (PQ^{2+} and PQ$^{\bullet+}$) and the *N*,*N*′-dimethyl-3,3′-dimethyl-4,4′-bipyridinium radical cation (Me$_2$PQ$^{\bullet+}$) are compared in Table 3. These spectra were measured with 363.8-nm excitation in CH$_3$CN at room temperature. The ion PQ$^{\bullet+}$ is believed to adopt a planar structure,[15] while Me$_2$PQ$^{\bullet+}$ is restrained to a twisted structure due to steric repulsion by the methyl groups in the rings.[7]

Discussion

The study of light-induced electron and energy transfer in chromophore-quencher complexes has typically taken advantage of transient absorption and emission measurements.[6,18,19] Following Re^I → bpy excitation of *fac*-[(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$ transient absorption features appear at 370 and 610 nm.[6] For *fac*-[(bpy)Re^I(CO)$_3$(4-Etpy)]$^+$ under the same experimental conditions, an intense transient feature appears near 370 nm.[6] The absorption features in the chromophore-quencher complex have been interpreted as indicating the presence of –MQ$^\bullet$ formed via direct Re^I → MQ$^+$ excitation and by intramolecular electron transfer following Re^I → bpy excitation, Scheme 1. The goal here was to utilize resonance Raman spectroscopy to probe the intramolecular electron transfer in further detail and to establish changes in geometry at the monoquat ligand.

The occurrence of intramolecular electron transfer following Re → bpy excitation of *fac*-[(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$ is clear when the transient spectra of *fac*-[(bpy)Re^I(CO)$_3$(4-Etpy)]$^+$ and *fac*-[(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$ in Figure 2 are compared. The resonantly enhanced Raman bands for *fac*-[(bpy)Re^I(CO)$_3$(4-Etpy)]$^+$ appear at 745, 1215, 1279, 1425, 1490, 1500, and 1551 cm^{-1}. These are energies typical of bpy$^{\bullet-}$ as found in the excited-state spectra of *fac*-[(bpy)Re^I(CO)$_3$Cl] and [Ru^{II}(bpy)$_3$]$^{2+}$ and

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Table 2. Raman Band Energies (cm^{-1}) for Monoquat Vibrations in $[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ in CH_3CN at 298 K Including Comparisons with Biphenyl (bp),[10d,e] 4,4′-Bipyridine (4,4′-bpy),[12a] *N,N′*-Dihydro-4,4′-bipyridinium Dication (PV^{2+}),[12b] and Paraquat (PQ^{2+})[14] and Their Corresponding One-Electron-Reduced Forms

$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ (CW 363.8, 406.7 nm)	$[(bpy)Re^{II}(CO)_3(MQ^•)]^{2+*}$ (pulsed 354.7 nm)	bp	$bp^{•-}$	4,4′-bpy	4,4′-$bpy^{•-}$	PV^{2+}	$PV^{•+}$	PQ^{2+}	$PQ^{•+}$	assgnt[a]
734	728	743	721	753	742	757	740			$\nu(CC) + \gamma(CCC)$
	808							841	818	$\nu(CC) + \nu(N^+{-}CH_3)$
1019	975	1005	974	1000	990	1016	1002			$\nu(CC) + \gamma(CCC)$
	1025	1033	1017					1061	1028	$\gamma(CCN) + \nu(CN)$
1072	1043				1043	1075	1045		1046	
1193	1202	1190	1201					1193	1212	$\nu(CC) + \gamma(CCH)$
1231	1250		1250	1220	1230	1216	1234	1234	1250	$\gamma(CCH) + \nu(N^+{-}CH_3)$
1298	1359	1287	1326	1298	1350	1288	1358	1301	1356	$\gamma(CCH) + \nu(CC)_{ir}$
	1465							1371	1430	$\gamma(CH_3)$
	1502	1510	1493	1510	1509					$\nu(CC) + \gamma(CCH)$
1528	1523					1528	1525	1538	1534	$\nu(CN) + \gamma(CCH)$
1617	1609	1605	1587							$\nu(CC) + \gamma(CCH)$
1644	1649			1605	1612	1644	1660	1654	1662	$\nu(CC)_{ir} + \nu(CC)$

[a] Only the dominant vibrational modes contributing to the potential energy distributions for PQ^{2+} [14b] and bp [10c] are listed; ν = stretch, γ = bend, ir = inter-ring.

Table 3. Raman Band Energies (cm^{-1}) for Paraquat (PQ^{2+}), Its One-Electron-Reduced Cation ($PQ^{•+}$), and the *N,N′*-Dimethyl-3,3′-dimethyl-4,4′-bipyridinium Radical Cation (3,3′-$Me_2PQ^{•+}$) with 363.8-nm Excitation in CH_3CN at 298 K

PQ^{2+}	$PQ^{•+}$	3,3′-$Me_2PQ^{•+}$
660	683	671
		683
		728
841	817	
		956
1061	1027	1011
		1038
1193	1209	1190
1234	1248	1233
1301	1354	1327
1371	1430	1429
		1444
1538	1533	1497
		1513
1654	1661	1651

the CW spectrum of the bpy radical anion.[1,17a,20] For *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ only bands originating from $-MQ^•$ are observed in the transient spectrum, Table 1. Similarly, in the transient spectrum of *cis*-$[(bpy)_2Os^{II}(CO)(MQ^+)]^{3+}$ there is no evidence for bands from $bpy^{•-}$. The effect of intramolecular electron-transfer quenching in *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ is also apparent in comparing the emission background in its CW resonance Raman spectrum with that of *fac*-$[(bpy)Re^I(CO)_3(4\text{-}Etpy)]^+$, Figure 1.

The results of vibrational analyses are available for biphenyl and PQ^{2+} and their one-electron-reduced forms.[10c,14b] On the basis of these analyses, bands in the region 700–1700 cm^{-1}, analogous to bands observed for MQ^+, arise from modes associated with complex motions involving bond stretches (C–C, C–N), ring deformations, and C–C–H wagging. Contributions are also expected from the methyl group bound to nitrogen and from a mode which is predominantly inter-ring C–C stretching in character. A reasonable correlation can be made between Raman bands arising from ring vibrations that appear in the CW Raman spectrum of the Re complexes containing MQ^+ and those that appear for biphenyl,[10d,e] 4,4′-bpy,[12a] PV^{2+},[12b] and PQ^{2+} (Table 2).[14]

With these correlations in place it is possible to use the transient Raman results to probe structural changes at monoquat that accompany intramolecular electron transfer. Changes in the ring–ring separation distance and the extent of coplanarity of the two rings are reflected in differences in band energies for the inter-ring C–C stretch between the ground and transient spectra. Additional changes in structure can be inferred by comparing ground and transient spectral differences with those that occur between PQ^{2+} and $PQ^{•+}$, for example, where the structural differences are established.

The Raman band with a large contribution from the inter-ring C–C stretch appears at 1287 cm^{-1} in biphenyl, 1298 cm^{-1} in 4,4′-bpy, and 1301 cm^{-1} in PQ^{2+} (Table 2). The band at 1298 cm^{-1} for *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ can be assigned to this mode in MQ^+. In the one-electron-reduced forms in Table 2, this band shifts to higher energy consistent with an increase in bond order. These shifts are $\Delta\nu$ = +39 cm^{-1} for biphenyl, +52 cm^{-1} for 4,4′-bpy, +70 cm^{-1} for PV^{2+}, and +55 cm^{-1} for PQ^{2+}. In the transient spectrum of *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ this band appears at 1359 cm^{-1}, a shift of +61 cm^{-1} compared to the ground state. The shift is comparable to the shift between *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ and its reduced form, *fac*-$[(bpy)Re^I(CO)_3(MQ^•)]^+$, $\Delta\nu$ = +50 cm^{-1}. The shifts are different in magnitude because of the oxidation state at the metal (Re^{II}, Re^I) in the excited–ground state comparison. In any case, the shifts show that there is a significant amount of charge transfer to MQ^+ in the monoquat-based, MLCT excited state. They also point to a shortening in the inter-ring separation distance, a planar, quinoidal structure with $\theta \sim 0°$, and enhanced aromatic character extending across the two rings by comparison with reduction of PQ^{2+} to $PQ^{•+}$.

The conclusions regarding planarity and $\theta \sim 0°$ are reinforced by comparisons to 3,3′-Me_2PQ^{2+}. In 3,3′-$Me_2PQ^{•+}$ the methyl groups in the rings prevent the pyridines from adopting a coplanar conformation. As seen in the data in Table 3, the Raman spectrum of 3,3′-$Me_2PQ^{•+}$ is substantially different from that of $PQ^{•+}$. The shift in the inter-ring C–C stretch is only 1327 cm^{-1}, consistent with less double bond character between the rings and a lower degree of coplanarity.

When the ground and transient resonance Raman data are combined, a relatively clear picture emerges of the structural changes at the monoquat ligand induced by electron transfer. For *fac*-$[(bpy)Re^I(CO)_3(MQ^+)]^{2+}$ in the solid state $\theta \sim 47°$ by crystallography.[7] The frequencies of the inter-ring stretches in the solid state (1302 cm^{-1}) and in CH_3CN (1298 cm^{-1}) are comparable suggesting that $\theta \sim 47°$ in solution as well. $Re^I \rightarrow$ bpy excitation followed by $bpy^{•-} \rightarrow MQ^+$ electron transfer (Scheme 1) causes the dihedral angle to decrease to $\theta \sim 0°$, Figure 4. The conversion between forms implies both a structural change and an associated change in electronic delocalization and resonance energy. It has been estimated that the energy difference betweeen $\theta \sim 47°$ and $\theta \sim 0°$ for *fac*-$[(bpy)Re^{II}(CO)_3(MQ^•)]^{2+*}$ is ~0.3 eV because of the enhanced resonance energy at $\theta \sim 0°$.[16] One manifestation of the strong coupling between the

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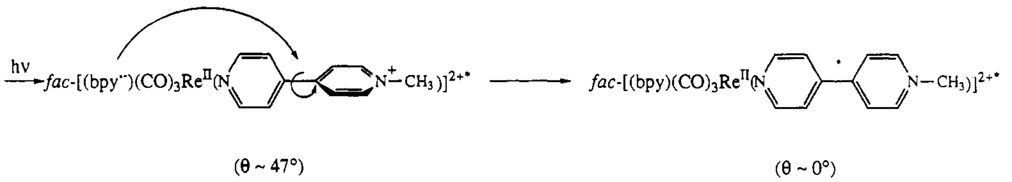

Figure 4. Illustration of the coupling between the inter-ring dihedral angle θ and electron transfer in *fac*-$[(bpy^{\bullet-})Re^{II}(CO)_3(MQ^+)]^{2+*}$.

rotational motion of the rings and electronic delocalization is that the usual Born–Oppenheimer separation of nuclear and electronic coordinates (which is assumed in time-dependent perturbational approaches to electron-transfer theory) is inappropriate for this mode.[21]

There are other structural changes as well. Between PQ^{2+} and $PQ^{\bullet+}$, $\Delta\nu = +59$ cm^{-1} for $\gamma(CH_3)$ consistent with enhanced electron density at $-CH_3$ in $PQ^{\bullet+}$.[14] This is in agreement with electron paramagnetic resonance results which demonstrate the unpaired electron to be delocalized over the entire cation including the methyl groups.[22] In the transient Raman spectrum of *fac*-$[(bpy)Re^{I}(CO)_3(MQ^+)]^{2+}$ bands appear at 808, 1250, and 1465 cm^{-1} which are analogous to bands in $PQ^{\bullet+}$ having known methyl character (818, 1250, and 1430 cm^{-1}). From the similarities in band energies, the excited electron in *fac*-$[(bpy)Re^{II}(CO)_3(MQ^{\bullet})]^{2+*}$ appears to be delocalized over the methyl group as well.

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