2618 *Inorg. Chem.* **1993,** *32,* 2618-2619

Application of Time-Resolved Resonance Raman Spectroscopy to Intramolecular Electron Transfer

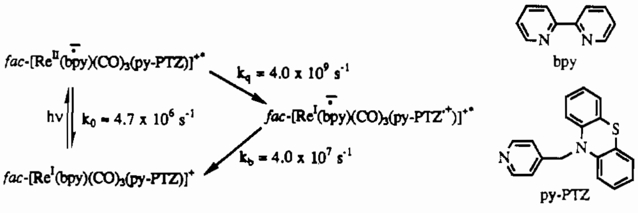
Jon R. Schoonover, Geoffrey F. Strouse, Pingyun Chen, W. Douglas Bates, and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Received January 14, 1993

Time-resolved resonance Raman spectroscopy has been used to establish the site of localization of the excited electron following metal-to-ligand charge-transfer (MLCT) excitation in mixed-chelated ruthenium polypyridyl complexes.[1] We recently extended this technique to identify intermediates following MLCT excitation and intramolecular energy transfer in Re–Ru cyano-bridged polypyridyl oligomers.[2] Others have demonstrated the utility of transient Raman measurements in identifying electron-transfer products that appear upon photolysis of a mixture of donors and acceptors.[3] McMahon *et al* have also followed intramolecular electron transfer in a covalently linked porphyrin–viologen complex by transient Raman spectroscopy.[4] We present here the first example of the application of this technique to intramolecular electron transfer in a series of chromophore–quencher complexes based on MLCT excited states.[5]

Scheme I^{a}



^{a} In CH$_3$CN at 295 K.

One example is *fac*-[Re^{I}(bpy)(CO)$_3$(py-PTZ)]$^+$ (bpy is 2,2′-bipyridine; py-PTZ is 10-(4-picolyl)phenothiazine), where the quenching of MLCT emission and the appearance of transient absorption bands for bpy$^{\bullet-}$ (at 370 nm) and -PTZ$^{\bullet+}$ (at 510 nm) following Re^{I}(dπ) → bpy(π^*) excitation have been cited as evidence for intramolecular electron transfer (see Scheme I).[5b] The transient Raman spectrum acquired with 355-nm excitation and 355-nm probe pulses in CH$_3$CN unequivocally show (Figure 1B) the expected features for bpy$^{\bullet-}$; the spectrum of the MLCT excited state of *fac*-[Re^{I}(bpy)(CO)$_3$(4-Etpy)]$^+$ (4-Etpy is 4-ethylpyridine; Re^{II}(bpy$^{\bullet-}$)) is shown in Figure 1A for comparison. The Raman features of -PTZ$^{\bullet+}$ are shown in Figure 1C and were measured by probing with 532-nm laser pulses after 355-nm excitation. The spectrum of -PTZ$^{\bullet+}$ was verified by the CW Raman spectrum (λ_{ex} = 530.9 nm) of electrochemically generated *fac*-[Re^{I}(bpy)(CO)$_3$(py-PTZ$^{\bullet+}$)]$^{2+}$ in CH$_3$CN (0.1 M [(n-C$_4$H$_9$)$_4$](PF$_6$)) and by comparison to the spectrum of the 10-methylphenothiazine cation.[6] Similarly, the transient absorption difference spectrum of the modified amino acid assembly (cf. ref 7), [Anq-Lys(Ru^{II}(bpy)$_2$m-)-PTZ]$^{2+}$ (Anq is anthraquinone; Lys is a lysine derivative; m is a modified bpy), following MLCT excitation into the Ru polypyridyl unit suggests the presence of -PTZ$^{\bullet+}$ (500 nm) and -Anq$^{\bullet-}$ (570 nm) and the appearance of a redox-separated state which returns to the ground state[7] (Scheme II). Consistent with this result, the transient Raman spectrum, probing at 532 nm where both -PTZ$^{\bullet+}$ and -Anq$^{\bullet-}$ absorb, includes Raman peaks typical of -PTZ$^{\bullet+}$ (1294, 1599 cm^{-1}) and Anq$^{\bullet-}$ (1175, 1333, 1506 cm^{-1}).

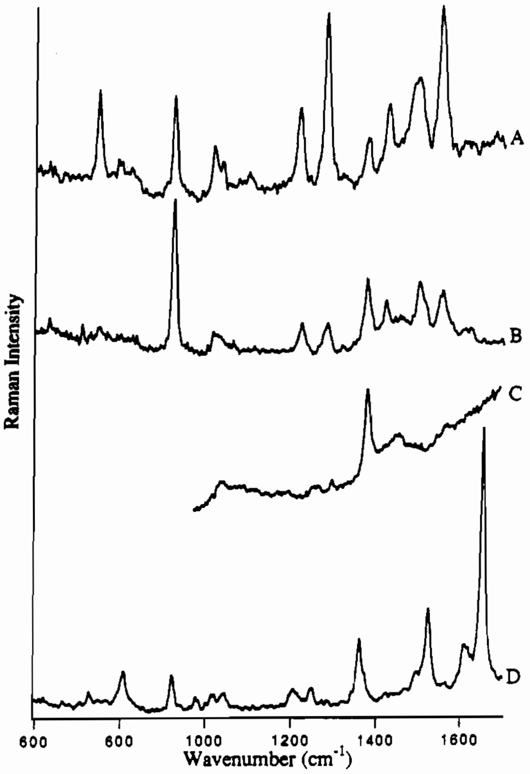


Figure 1. Time-resolved resonance Raman spectra of 1–3 samples of (A) *fac*-[Re^{I}(bpy)(CO)$_3$(4-Etpy)]$^+$, (B) *fac*-[[Re^{I}(bpy)(CO)$_3$(py-PTZ)]$^+$, (C) *fac*-[Re^{I}(bpy)(CO)$_3$(py-PTZ)]$^+$ measured at a different probe wavelength (532 nm), and (D) *fac*-[Re^{I}(bpy)(CO)$_3$(MQ$^+$)]$^{2+}$ in CH$_3$CN. Samples for the Raman experiment were freeze–pump–thaw degassed several times before being sealed in an NMR tube. Spectra A, B, and D were measured with 355-nm laser pulses to both excite the sample in the Re^{I} → bpy MLCT band and provide a source of the Raman scattering for the bpy$^{\bullet-}$ (A and B) and MQ$^{\bullet}$ transients (D). Spectrum C was measured with a pump/probe technique with 355-nm pulses used to excite the sample and 532-nm pulses to probe the -PTZ$^{\bullet+}$ transient. The spectra are uncorrected, and spectrum C shows interference due to emission. The experimental arrangement was as described in ref 2.

The transient Raman experiment becomes especially useful as a "fingerprinting" probe in those cases where transient absorption spectra are ambiguous with regard to intermediate states because of overlapping chromophores. An example is [(MQ$^+$)(CO)$_3$Re^{I}(μ-bbpe)Re^{I}(CO)$_3$(py-PTZ)]$^{3+}$ (MQ$^+$ is *N*-methyl-4,4′-bi-

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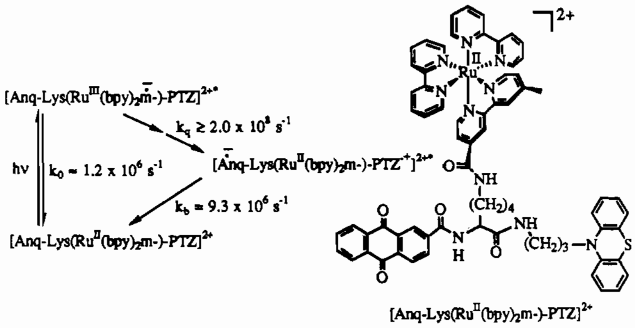
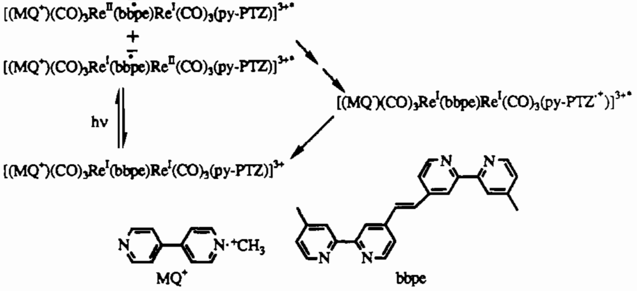
Scheme II[a]



$[\text{Anq-Lys(Ru}^{\text{II}}(\text{bpy})_2\text{m-)-PTZ}]^{2+}$

[a] In CH_3CN at 298 K.

Scheme III[a]



[a] In CH_3CN at 295 K.

pyridinium cation; bbpe is *trans*-1,2-bis(4-(4′-methyl)-2,2′-bipyridyl)ethene) in CH_3CN where following $Re^I(d\pi) \rightarrow bbpe(\pi^*)$ excitation at 420 nm a broad absorption appears extending from ca. 380 to 700 nm[9] (Scheme III). In the transient Raman spectrum following $Re^I \rightarrow$ bbpe excitation (at 355 nm), bands appear for $-MQ^{\bullet}$ and $-PTZ^{\bullet+}$ (Table I). The appearance of these features is consistent with MLCT excitation followed by multiple intramolecular electron transfers to give the final redox-separated state. The features for $bbpe^{\bullet-}$ and $-PTZ^{\bullet+}$ are evident in the transient spectrum of $[(PTZ\text{-}py)(CO)_3Re^I(\mu\text{-}bbpe)Re^I(CO)_3(py\text{-}PTZ)]^{2+}$ following MLCT excitation and $PTZ \rightarrow Re^{II}$ intramolecular electron transfer (Scheme IV).

There is an additional advantage of the Raman technique in the inference (or calculation) of structure from the vibrational spectra of photochemically produced intermediates. For *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ intramolecular electron transfer occurs rapidly following $Re^I \rightarrow$ bpy excitation[10] (Scheme V). This process is verified by the transient Raman spectrum in Figure 1D, where peaks due to $-MQ^{\bullet}$ appear (806, 978, 1206, 1247, 1362, 1525, 1612, 1654 cm^{-1}) but those due to $bpy^{\bullet-}$ (745, 1215, 1279, 1425, 1490, 1500, 1551 cm^{-1}) do not. Crystallographic data for *fac*-$[Re^I(bpy)(CO)_3(MQ^+)](PF_6)_2$ show that a dihedral angle of 47° exists between the two pyridyl rings of the MQ ligand in the solid state.[11] Comparison of $-MQ^+$ bands in the ground-state resonance Raman spectra of *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ and *fac*-$[Re^I(MQ^+)_2(CO)_3Cl]^{2+}$ with those for $-MQ^{\bullet}$ in the excited state, *fac*-$[Re^{II}(bpy)(CO)_3(MQ^{\bullet})]^{2+*}$, shows that there is a shift of 61 cm^{-1} for the band at 1298 to 1359 cm^{-1}. This band arises from a ring-stretching vibration which has significant inter-ring C–C character, and this frequency increase is indicative of an increase in π-bond order. Shifts of similar magnitude have been observed for this vibration between biphenyl,[12] methyl viologen,[13] and 4,4′-bipyridines[14,15] and their one-electron reduced forms and is consistent with a planar geometry in the reduced forms. By inference, a planar geometry is also adopted at $MQ^{\bullet}$ in *fac*-$[Re^{II}(bpy)(CO)_3(MQ^{\bullet})]^{2+*}$, demonstrating a significant change in structure at the acceptor ligand between the excited and ground states.

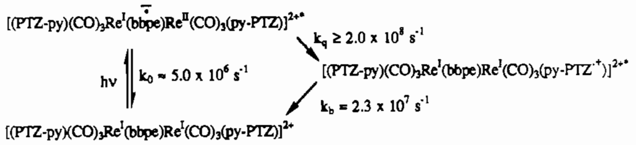
The use of time-resolved resonance Raman spectroscopy in the study of intramolecular electron transfer represents a powerful application of the technique. The Raman data can supplement transient absorption results, provide vibrational spectra when transient absorption spectra are inconclusive, and allow for the structures of short-lived intermediates to be inferred.

Table I. Frequencies (cm^{-1}) for Transient Raman Bands Observed by Following $Re^I \rightarrow$ bbpe Excitation of $[(PTZ\text{-}py)(CO)_3Re^I(\mu\text{-}bbpe)Re^I(CO)_3(py\text{-}PTZ)]^{2+}$ (PTZ/PTZ) and $[(PTZ\text{-}py)(CO)_3Re^I(\mu\text{-}bbpe)Re^I(CO)_3(MQ^+)]^{3+}$ (PTZ/MQ^+) in CH_3CN with Proposed Origins[a]

MTZ/PTZ (355/532)	PTZ/MQ^+ (355/532)	PTZ/MQ^+ (355)	origins
		807	$MQ^{\bullet}$
		992	$MQ^{\bullet}$
1022	1022		$PTZ^{\bullet+}$
1028	1029	1032	$MQ^{\bullet}$/bbpe
1050	1050		$PTZ^{\bullet+}$
1169	1167		$PTZ^{\bullet+}$
1189	1188		bbpe
1220	1217	1220	$PTZ^{\bullet+}$/bbpe
	1241	1243	$MQ^{\bullet}$
1249			$PTZ^{\bullet+}$
1266	1264 br[b]		$PTZ^{\bullet+}/MQ^{\bullet}$/bbpe
		1284	bbpe
1289	1291		$PTZ^{\bullet+}$
1327			bbpe
	1355	1359	$MQ^{\bullet}$
1427			bbpe
1456			$bbpe^{\bullet-}$
1490		1493	$PTZ^{\bullet+}$/bbpe
	1522		bbpe
		1537	$MQ^{\bullet}$
1550			$bbpe^{\bullet-}$
1566	1566		$PTZ^{\bullet+}/bbpe^{\bullet-}$
1588	1590		$PTZ^{\bullet+}$
1620	1615	1618	bbpe
1641		1642	bbpe
	1651	1650 sh[b]	$MQ^{\bullet}$

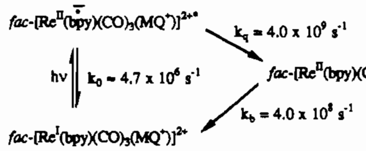
[a] The spectra were measured with 355-nm laser pulses to pump and 532-nm pulses to probe (355/532) or 355-nm pulses to both pump and probe (355). Experimental conditions were as in ref 2. [b] br indicates a broad peak and sh identifies a peak present as a shoulder on a more intense feature.

Scheme IV[a]



[a] In CH_3CN at 295 K.

Scheme V[a]



[a] In CH_3CN at 295 K.

Acknowledgment. This work was supported by the National Science Foundation Grant CHE-9022493. The complex $[Anq\text{-}Lys(Ru^{II}(bpy)_2m\text{-})\text{-}PTZ]^{2+}$ was generously supplied by S. L. Mecklenburg and B. M. Peek.

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