

Mid-Infrared Spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$

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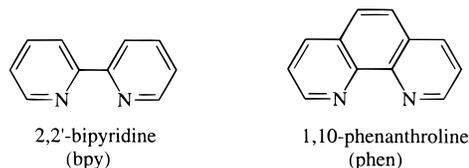
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Time-resolved infrared spectra in the fingerprint region (1300–1700 cm^{-1}) are reported for the metal-to-ligand charge-transfer (MLCT) excited state(s) of $[\text{Ru}(\text{phen})_3]^{2+*}$ and $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$ (phen is 1,10-phenanthroline; DAS is 1,2-bis(diphenylarsino)ethane) in acetonitrile- d_3 at 298 K. The spectra are assigned by comparison to electrochemically generated $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$. The data provide clear evidence for the localized description $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+*}$ on the ~ 100 ns time scale. They also give insight into electronic distribution in the excited state, aid in the interpretation of the time-resolved resonance Raman spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$, and suggest why measuring ground- and excited-state resonance Raman spectra of phen complexes is difficult.

Introduction

Two decades ago Dallinger and Woodruff reported the first time-resolved resonance Raman (TR^3) spectrum of $[\text{Ru}(\text{bpy})_3]^{2+*}$ (bpy is 2,2'-bipyridine),¹ suggesting that the lowest lying MLCT state or states² were best described as localized, $[\text{Ru}^{\text{III}}(\text{bpy}^{\bullet-})(\text{bpy})_2]^{2+*}$, on the nanosecond time scale. Since that time, a number of independent experiments have verified this conclusion and the interpretation has become widely accepted.³ Due to the structural and electronic similarities between bpy and phen (phen is 1,10-phenanthroline), it has been assumed that the lowest lying MLCT state(s) of $[\text{Ru}(\text{phen})_3]^{2+*}$ are also localized, $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+*}$. This assumption was challenged recently in a paper that interpreted resonance Raman and TR^3 spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ by assuming that its lowest lying MLCT excited state is delocalized, $[\text{Ru}(\text{phen}^{1/3\bullet-})_3]^{2+*}$.⁴

The results of a recent electroabsorption study demonstrate the presence of a significant molecular dipole in $[\text{Ru}(\text{phen})_3]^{2+*}$, consistent with the localized description, $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})-$



$(\text{phen})_2]^{2+*}$.⁵ Questions remain regarding the vibrational spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$, but it is difficult to obtain good resonance Raman and TR^3 spectra of phen complexes because resonance enhancements are weak.⁶

In this paper, we present the time-resolved infrared (TRIR) spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ in the fingerprint region (1300–1800 cm^{-1}). The infrared data complement the Raman data in providing previously unavailable information about asymmetric vibrational modes in the excited state. The spectra include information about both chromophoric and ancillary ligands since the infrared experiment is independent of the requirement of resonance enhancement. Comparison of the TRIR spectra of $[\text{Ru}(\text{phen})_3]^{2+*}$ and $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$ (DAS is 1,2-bis(diphenylarsino)ethane) and IR spectra of $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$ support the localized description $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+*}$ on the ~ 100 ns time scale and give insight into why resonance Raman and TR^3 spectra of phen complexes are difficult to measure.

Experimental Section

Materials. Acetonitrile- d_3 was obtained from Cambridge Isotope Labs and used without further purification. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained from Aldrich and recrystallized twice from ethanol. $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{phen})(\text{DAS})_2](\text{PF}_6)_2$ were prepared according to literature procedures.⁷

Infrared Measurements. Infrared measurements utilized a BioRad FTS 60A/896 step-scan interferometer with an external MCT detector

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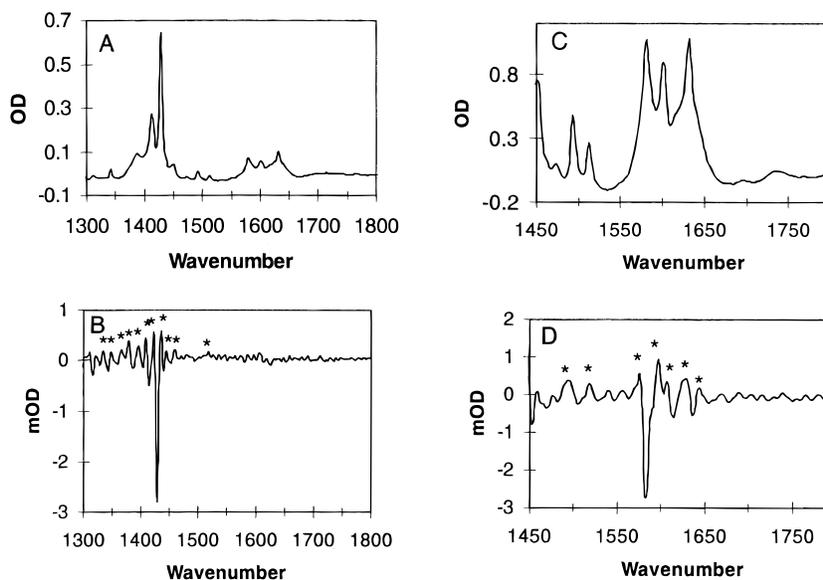


Figure 1. Ground-state (A) and TRIR (B) spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ between 1300 and 1800 cm^{-1} and ground-state (C) and TRIR (D) spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ between 1450 and 1800 cm^{-1} at an increased concentration (in acetonitrile- d_3 at 298 K). Bands assigned to the excited-state are labeled with an asterisk (*).

as previously described.^{3a} A recent upgrade of this instrument utilizes fast data processing techniques. In this arrangement, the IR signal from the detector was amplified and processed by a Bio-Rad Fast TRS board installed in a Pentium PC. This board also controlled the synchronization of the laser firing with the 10 Hz stepping of the moving mirror. The laser excitation pulse was a 7 ns, 200 μJ pulse at 355 nm from a 10 Hz, Q-switched Nd:YAG laser (Spectra-Physics GcR11).

Individual points on the interferogram were collected every 200 ns after the laser pulse for 5 μs . The data were organized into individual interferograms representing the interferogram at every 200 ns point, then Fourier transformed into spectra. Spectra were averaged between the laser pulse and 1 μs to give the final TRIR spectra. Ground-state spectra shown are an average of 64 scans, and excited-state spectra are an average of 640 scans.

Samples for TRIR Studies. All IR spectra were measured in acetonitrile- d_3 , in a 1 mm path length sealed CaF_2 cell. Sample concentrations were adjusted to give an absorbance of ~ 0.7 for the most intense phenanthroline bands in the region of interest. The sample cell and sample solutions were deoxygenated by sparging with argon for 15 min. Solutions were transferred to the cell under an inert atmosphere. Spectra were acquired in blocks of 64 to prevent sample decomposition.

$[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\ominus})(\text{phen})_2]^{+}$. These ions were generated by controlled potential electrolysis of $[\text{Ru}^{\text{II}}(\text{phen})_3](\text{PF}_6)_2$ in acetonitrile- d_3 with 0.1 M TBAH as electrolyte. The solutions used were 0.01 M in $[\text{Ru}^{\text{II}}(\text{phen})_3]^{2+}$, giving an absorbance of ~ 0.4 for the most intense phenanthroline bands. The reduced and oxidized forms were prepared by exhaustive electrolysis at -1.44 V vs SSCE (reduction) and 1.35 V vs SSCE (oxidation) with platinum working and counter electrodes and a $\text{Ag}/(0.01 \text{ M}) \text{AgNO}_3$ reference electrode in a standard three-compartment cell. Samples were prepared and transferred to a 0.25 mm path length CaF_2 IR cell under an inert atmosphere. Infrared spectra were measured on a Mattson Galaxy 5000 Series FTIR spectrometer and were the average of 64 scans.

Results

The ground-state and time-resolved infrared (TRIR) difference spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ between 1300 and 1800 cm^{-1} (in acetonitrile- d_3 , 298 K) are shown in Figure 1, panels A and B. The ground-state and TRIR spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ between 1450 and 1800 cm^{-1} (in acetonitrile- d_3 , 298 K) are shown in Figure 1, panels C and D, at an increased concentration so that the weaker, higher frequency bands could be observed. There are 12 bands between 1300 and 1800 cm^{-1} in the ground-state

Table 1. Infrared Band Energies (cm^{-1}) for $[\text{Ru}^{\text{II}}(\text{phen})_3]^{2+}$, $[\text{Ru}(\text{phen})_3]^{2+*}$, $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$, and $[\text{Ru}^{\text{II}}(\text{phen}^{\ominus})(\text{phen})_2]^{+}$ in Acetonitrile- d_3 at 298 K

$[\text{Ru}^{\text{II}}(\text{phen})_3]^{2+}$	$[\text{Ru}(\text{phen})_3]^{2+*}$	$[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+ a}$	$[\text{Ru}^{\text{II}}(\text{phen}^{\ominus})(\text{phen})_2]^{+ b}$
1342	1335		1330
1360 ^c	1349	1350	1349
	1366	1363	
1389	1379		1380
1402 ^c	1396	1392	1398
1413	1408	1411	1409
	1421	1427	
1429	1435		1430
	1444	1442	1440
1452	1458	1462	
1492	1490	1490	1489
1512	1517	1517	1510
	1576	1584	
1582	1596	1600	1590
1602	1607		1610
	1628	1633	
1636	1640		1649

^a Electrochemically generated. ^b Electrochemically generated. Bands corresponding to $[\text{Ru}^{\text{II}}(\text{phen})_3]^{2+}$ are also observed from the unreduced phen ligands. ^c Shoulder.

spectrum; 17 bands can be discerned in the TRIR spectra. Bands assigned to the excited-state in the TRIR spectra are labeled with an asterisk (*). The band energies are listed in Table 1. Band energies for $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\ominus})(\text{phen})_2]^{+}$ (generated electrochemically in acetonitrile- d_3) are also listed in Table 1. Ground-state and TRIR spectra of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+}$ between 1300 and 1600 cm^{-1} (in acetonitrile- d_3 , 298 K) are shown in Figure 2. There are seven bands in the ground-state spectrum and seven bands in the TRIR spectrum. Bands assigned to the excited-state in the TRIR spectrum are labeled with an asterisk (*). Band energies are listed in Table 2.

The TRIR difference spectra of both excited states appear cluttered at first glance. This is due to the presence of a large number of excited-state bands in both spectra which appear within a narrow spectral region. The signal-to-noise ratio for the weakest band in the TRIR spectrum of $[\text{Ru}(\text{phen})_3]^{2+}$ is 2.8:1; for $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+}$, the ratio is 2.7:1.

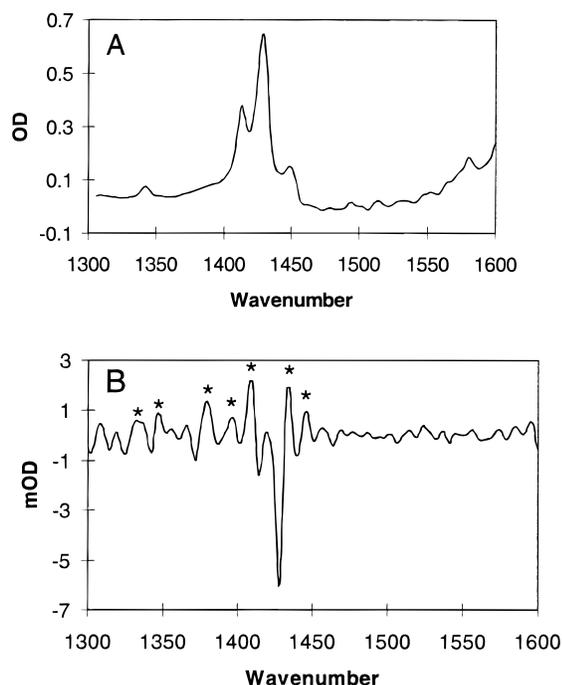


Figure 2. Ground-state (A) and TRIR (B) spectra of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+}$ between 1300 and 1600 cm^{-1} (in acetonitrile- d_3 at 298 K). Bands assigned to the excited-state are labeled with an asterisk (*).

Table 2. Infrared Band Energies (cm^{-1}) for $[\text{Os}^{\text{II}}(\text{phen})(\text{DAS})_2]^{2+}$ and $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$ in Acetonitrile- d_3 at 298 K

$[\text{Os}^{\text{II}}(\text{phen})(\text{DAS})_2]^{2+}$	$[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$
1341	1335
1360 ^a	1346
1387	1380
1401 ^a	1395
1414	1409
1427	1434
1448	1446

^a Shoulder.

Discussion

Interpretation of the TRIR spectrum of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$ is straightforward. In the ground-state spectrum there are seven bands; there are also seven bands in the excited-state spectrum. The lowest lying excited state(s) of $[\text{Os}^{\text{II}}(\text{phen})(\text{DAS})_2]^{2+}$ is an MLCT state localized on phen, $[\text{Os}^{\text{III}}(\text{phen}^{\bullet-})(\text{DAS})_2]^{2+*}$. The local symmetry at phen is C_{2v} in the ground state and remains C_{2v} in the excited state. In the absence of a normal coordinate analysis for a transition metal–phen complex, it is not possible to predict the directions of the band shifts upon excitation on a mode-by-mode basis. However, given the simplicity of the spectrum of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$, the following correlations appear reasonable:

Ground State (cm^{-1})	Excited State (cm^{-1})
1341	→ 1335
1360	→ 1346
1387	→ 1380
1401	→ 1395
1414	→ 1409
1427	→ 1434
1448	→ 1446

The bands shift predominantly to lower energy in the excited state as expected because of the increase in electron density at

Table 3. Mid-Infrared Band Energies (cm^{-1}) and Proposed Origins for $[\text{Ru}(\text{phen})_3]^{2+*}$ in Acetonitrile- d_3 at 298 K

$[\text{Ru}(\text{phen})_3]^{2+*}$	origin	$[\text{Ru}(\text{phen})_3]^{2+*}$	origin
1335	phen ^{•-} , Ru ^{III} (phen)	1458	Ru ^{III} (phen)
1349	phen ^{•-} , Ru ^{III} (phen)	1490	phen ^{•-} , Ru ^{III} (phen)
1366	Ru ^{III} (phen)	1517	phen ^{•-} , Ru ^{III} (phen)
1379	phen ^{•-}	1576	Ru ^{III} (phen)
1396	phen ^{•-} , Ru ^{III} (phen)	1596	phen ^{•-} , Ru ^{III} (phen)
1408	phen ^{•-} , Ru ^{III} (phen)	1607	phen ^{•-}
1421	Ru ^{III} (phen)	1628	Ru ^{III} (phen)
1435	phen ^{•-}	1640	phen ^{•-}
1444	phen ^{•-}		

phen. The shifts are smaller by 1–2 cm^{-1} than those observed for $[\text{Ru}(\text{bpy})_3]^{2+*}$.^{3a}

The TRIR spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ is more complex, with 12 bands appearing in the ground-state spectrum and 17 in the excited-state spectrum. The greater complexity is consistent with a lowered symmetry in the excited state and the localized description, $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+*}$. If the D_3 symmetry of the ground state were maintained, as it would be in the delocalized description $[\text{Ru}(\text{phen}^{1/3\bullet-})_3]^{2+*}$, 12 bands would be expected, the same number as in the ground-state spectrum.

The analysis of the TRIR spectrum is greatly aided by comparisons with the spectra of $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^{+}$. On the basis of these comparisons, there are 12 bands in the TRIR spectrum which correspond to bands in $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$ and 12 bands which correspond to bands in $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^{+}$. The energies of these bands are indicated in Table 3. The bands in the spectrum of $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^{+}$ assigned to (phen^{•-}) correspond well with those observed in the TRIR spectrum of $[\text{Os}^{\text{III}}(\text{phen}^{\bullet-})(\text{DAS})_2]^{2+*}$. There are slight differences in energy, but this is expected given the difference in electronic content between the fully oxidized and reduced forms and the excited state. Due to the large number of bands and the small magnitudes of the shifts, seven of the bands observed in the TRIR spectrum result from overlapping phen^{•-} and Ru^{III}(phen) bands. However, 10 of the bands can be unambiguously assigned as arising from either phen^{•-} or Ru^{III}(phen), consistent with a localized description for the excited state.

It is difficult to correlate ground and excited state bands and discuss band shifts meaningfully due to the large number of bands and the lack of information about normal coordinates. It is reasonable to assume that the shifts are small, as they are for $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$. The data point to a localized excited state, $[\text{Ru}^{\text{III}}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+*}$, so each ground-state band is predicted to split into two bands in the excited state: one corresponding to phen^{•-}, for the chromophoric ligand, and the other to Ru^{III}(phen), for the ancillary ligands. This prediction is confirmed by the data. There are 12 bands observed in the ground state. The 17 excited-state bands can be interpreted as arising from two sets of 12 bands, one set corresponding to phen^{•-}, and one to Ru^{III}(phen), but with a significant number of bands overlapping. On the basis of these assumptions and the known spectrum of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$, the correlations presented in Table 4 seem reasonable, but they are tentative.

Two immediate observations can be made by comparing the TRIR difference spectra of $[\text{Ru}(\text{phen})_3]^{2+*}$ and $[\text{Ru}(\text{bpy})_3]^{2+*}$.^{3a} First, for $[\text{Ru}(\text{phen})_3]^{2+*}$ the excited-state shifts are predominantly to lower energy for phen^{•-} and to higher energy for Ru^{III}(phen), although some of the shifts are reversed. This is similar to the pattern for $[\text{Ru}(\text{bpy})_3]^{2+*}$. Second, the excited-state shifts are slightly smaller for $[\text{Ru}(\text{phen})_3]^{2+*}$ than for $[\text{Ru}(\text{bpy})_3]^{2+*}$ (by 1–2 cm^{-1} on average). This is consistent with the more

Table 4

Ground State (cm ⁻¹)	Excited State (cm ⁻¹)
1342	1335 (phen ⁻)
	1349 (Ru ^{III} phen)
1360	1349(phen ⁻)
	1366 (Ru ^{III} phen)
1389	1379 (phen ⁻)
	1396 (Ru ^{III} phen)
1402	1396 (phen ⁻)
	1408 (Ru ^{III} phen)
1413	1408 (phen ⁻)
	1421 (Ru ^{III} phen)
1429	1435 (phen ⁻)
	1444 (Ru ^{III} phen)
1452	1444 (phen ⁻)
	1458 (Ru ^{III} phen)
1492	1490 (Ru ^{III} phen)
	1517 (phen ⁻)
1512	1490 (phen ⁻)
	1517 (Ru ^{III} phen)
1582	1576 (Ru ^{III} phen)
	1596 (phen ⁻)
1602	1596 (Ru ^{III} phen)
	1607 (phen ⁻)
1636	1628 (Ru ^{III} phen)
	1640 (phen ⁻)

rigid structure of phen compared to bpy, smaller average changes in equilibrium displacements for the phen normal modes, ΔQ_e , and decreased distortion at phen in the MLCT excited state of $[\text{Ru}(\text{phen})_3]^{2+*}$.⁸ The same conclusion was reached earlier based on a Franck–Condon analysis of the two emission spectral profiles.⁶

Decreased excited-state distortion contributes to a decreased resonance effect in the resonance Raman and TR³ spectra of phen complexes as compared to bpy, since resonance Raman intensities scale as the square of ΔQ_e .⁹ Interference effects may also play a role.¹⁰ The lowest LCAO π^* orbitals of bpy and phen are similar in orbital composition, but the first two π^* orbitals of phen are much closer in energy than for bpy (~ 2000 cm⁻¹ for phen vs ~ 8000 cm⁻¹ for bpy).^{8d} The resulting overlapping MLCT transitions to the two closely spaced π^* orbitals cause the broadening observed in the MLCT absorption spectrum of $[\text{Ru}(\text{phen})_3]^{2+}$ compared to $[\text{Ru}(\text{bpy})_3]^{2+}$. Due to the overlap, both states contribute to resonance Raman scattering for $[\text{Ru}(\text{phen})_3]^{2+}$. The displacements that occur from excitation into the two different MLCT absorptions will be approximately orthogonal since the two lowest π^* orbitals are orthogonal.^{8d} This could result in destructive interference between the two resonances, decreasing resonance Raman intensities. More complex molecular orbital calculations are in progress to determine the importance of this phenomenon.

There is an additional factor contributing to limited resonance Raman scattering in the TR³ experiment. When 355 nm excitation is used as a source of both excitation and scattering, the scattering wavelength is far removed from the nearest phen⁻ $\pi \rightarrow \pi^*$ electronic transition in the excited state, which occurs at 392 nm (for bpy, the nearest bpy⁻ $\pi \rightarrow \pi^*$ transition is at 370 nm). This experimental arrangement further decreases resonance enhancement, making it even more difficult to obtain high-quality TR³ spectra of phen complexes.

Conclusions

The TRIR spectra of $[\text{Ru}(\text{phen})_3]^{2+*}$ and $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$ provide previously unavailable information about the asymmetric vibrational modes of the MLCT excited state. The spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$, when interpreted with the aid of the spectra of $[\text{Os}(\text{phen})(\text{DAS})_2]^{2+*}$, $[\text{Ru}^{\text{III}}(\text{phen})_3]^{3+}$, and $[\text{Ru}^{\text{II}}(\text{phen}^-)(\text{phen})_2]^+$, confirms that the excited state is best represented by the localized description, $[\text{Ru}^{\text{III}}(\text{phen}^-)(\text{phen})_2]^{2+*}$. The combination of reduced distortion and interference effects explains why resonance Raman and TR³ spectra of phen complexes are difficult to obtain compared to those of analogous bpy complexes.

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