

ketones cyclize quite inefficiently.<sup>14</sup> We presume that the quantum yields below unity reflect some biradical disproportionation<sup>15</sup> and not direct triplet radiationless decay, which for phenyl ketones is too slow to compete with these measured lifetimes.<sup>16</sup>

We are extending this study to ketones other than phenones. We have confirmed the report<sup>17</sup> that type I cleavage is too rapid in *o*-tolylacetone for cyclization to compete. Such unfortunately would be expected for alkyl benzyl ketones.<sup>18</sup> We are currently investigating furyl ketones, with the expectation that the furan ring of the resulting 2-indanols will allow further functional group manipulations.

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### Resonance Raman Spectra of the Ground and Excited States of Specifically Deuterated Tris(2,2'-bipyridine)ruthenium(II)

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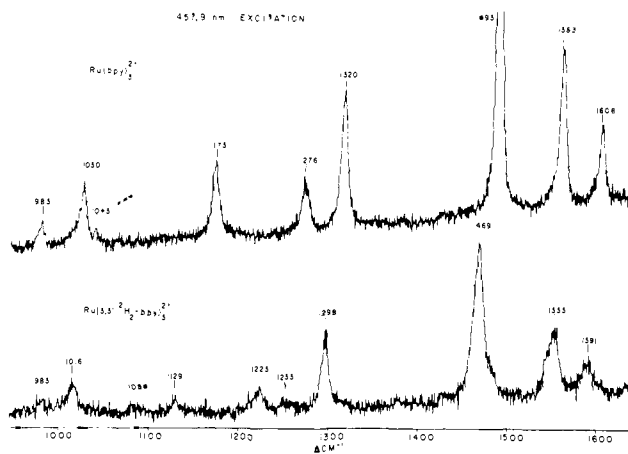
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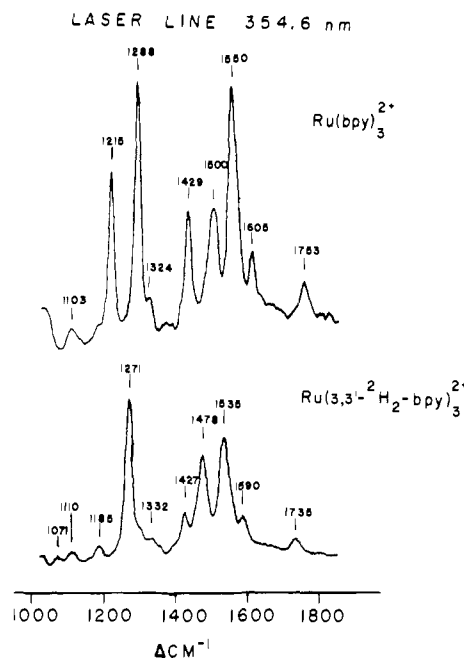
We report the resonance Raman (rR) spectra of a specifically deuterated analogue of the title complex in both its ground and lowest electronic excited states. The sensitivity of vibrational frequencies to deuterium substitution permits a more reliable correlation of ground- and excited-state frequencies and provides insight into the nature of the vibrational modes in each state. These results are of interest in light of the recent reports by Woodruff and Dallinger and co-workers<sup>2</sup> and Forster and Hester,<sup>3</sup> in which such a correlation was invoked as evidence for the localized excited-state model.

The preparation of the deuterated complex, Ru(bpy-3,3'-d<sub>2</sub>)<sub>3</sub><sup>2+</sup>, was recently reported<sup>4</sup> although detailed reaction conditions were not given. We have found that other positions are susceptible to deuterium exchange and that conditions must be carefully controlled to ensure specific deuteration at the 3,3'-ring positions. The complex was purified by chromatography on Sephadex LH-20 with ethanol eluant and was shown by <sup>1</sup>H NMR to be 95% deuterated at the 3,3'-positions with negligible exchange occurring at other sites. The electronic absorption spectrum is identical with that of the natural abundance compound.

Ground state rR spectra were obtained at 4579 Å by using a continuous wave argon ion laser and a Spex 1403 monochromator equipped with photon-counting detection. Excited-state spectra were obtained by employing the 354.7-nm third harmonic line of a Nd:YAG laser as both the pulse and probe beams (7 ns/pulse, 18-Hz pulse rate, 3 mJ/pulse). A triplemate (Spex Industries) monochromator was used to disperse the scattered radiation onto a PAR OMA-II multichannel detector. Toluene was used for wavelength calibration. For both the ground- and excited-state



**Figure 1.** Ground-state resonance Raman spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> (top) and Ru(bpy-3,3'-d<sub>2</sub>)<sub>3</sub><sup>2+</sup> (bottom) in H<sub>2</sub>O. In both cases, the excitation source was the 457.9-nm line of a continuous wave Ar<sup>+</sup> laser. The peaks at 983 cm<sup>-1</sup> are due to the 0.5 M SO<sub>4</sub><sup>2-</sup> added internal reference.



**Figure 2.** Excited-state resonance Raman spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> (top) and Ru(bpy-3,3'-d<sub>2</sub>)<sub>3</sub><sup>2+</sup> (bottom) in H<sub>2</sub>O. The 354.7-nm third harmonic of a Nd:YAG laser served as both the pulse and probe beams (7 ns/pulse, 18-Hz pulse rate, 3 mJ-pulse).

spectra, ~1 mM solutions were circulated through capillary tubes and 90° scattering geometry was employed.

The ground- and excited-state rR spectra of the deuterated and parent compounds are given in Figures 1 and 2, respectively. The observed frequencies and proposed correlation of bands are given in Table I.

Eleven totally symmetric modes are expected to appear in the ground-state rR spectrum between 1600 and 1000 cm<sup>-1</sup> with the remaining five modes (excluding four C-H stretches) occurring below 800 cm<sup>-1</sup>.<sup>5,6</sup> Indeed, consideration of the data presented here, along with those previously reported by using excitation at 400 and 350 nm,<sup>2,3</sup> reveals that at least 11 bands are observed between 1620 and 1000 cm<sup>-1</sup>.

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Table I. Ground- and Excited-State Resonance Raman Frequencies

ground state			excited state		
Ru(bpy) <sub>3</sub> <sup>2+</sup>	Ru-(bpy-d <sub>2</sub> ) <sub>3</sub> <sup>2+</sup>	$\Delta d$	Ru(bpy) <sub>3</sub> <sup>2+</sup>	Ru-(bpy-d <sub>2</sub> ) <sub>3</sub> <sup>2+</sup>	$\Delta d$
1608	1591	17	1608	1590	18
			1550	1535	15
1563	1553	10			
1493	1469	24	1500	1478	22
			1429	1427	2
1320	1298	22	1324	<i>b</i>	~20
			1288	1271	17
1276	1253				
			1215	1186	
1266	1223		1103	1110	
1175	1129		1025	1071	
1043	1084			1022	
1030	1016		1015	1004	11
			744	737	7
669	660	9			

<sup>a</sup>  $\Delta d$  is a given for correlated modes only. <sup>b</sup> Appears as an unresolved shoulder.

The excited-state spectra were obtained with an excitation line nearly coincident with the  $\pi-\pi^*$  excited-state absorption band at  $\sim 350$  nm, which presumably corresponds to a transition of a coordinated ligand anion radical. As Woodruff and Dallinger and co-workers<sup>2</sup> have pointed out, the localized model is also consistent with observation of bands assignable to the neutral ligand through resonance with the  $\pi-\pi^*$  transition at  $\sim 280$  nm. The data presented in Table I, including the observed deuterium shifts, are entirely consistent with expected behavior.

The most noteworthy feature of the excited-state spectrum is the appearance of a band at  $1429\text{ cm}^{-1}$ , which exhibits an insignificant deuterium shift. No ground-state bands observed in this region under visible (MLCT) excitation exhibit similar behavior. It is likely that the  $1429\text{-cm}^{-1}$  band corresponds to the very weak ground-state band at  $1450\text{ cm}^{-1}$ , which is only observed with excitation at  $\sim 350$  nm (continuous wave).<sup>2,3,9</sup> Evidently this band is not enhanced under MLCT excitation. We have attempted to observe a corresponding band in the spectrum of the deuterated analogue using  $363.8\text{-nm}$  (continuous wave) Ar<sup>+</sup> laser excitation but were unable to confirm its appearance, possibly because of overlap with the  $1469\text{-cm}^{-1}$  band. The  $1608\text{-cm}^{-1}$  ground-state band corresponds to the  $1608\text{-cm}^{-1}$  (neutral ligand) and  $1550\text{-cm}^{-1}$  (radical anion) bands in the excited state; all bands exhibited comparable deuterium shifts. Similarly, the  $1320\text{-cm}^{-1}$  ground-state band occurs at  $1324\text{ cm}^{-1}$  (neutral ligand) and  $1288\text{ cm}^{-1}$  (radical anion) in the excited state again exhibiting deuterium shifts of similar magnitude. The  $1493\text{-}$  and  $1563\text{-cm}^{-1}$  ground-state bands<sup>2,3,9</sup> as well as the first overtone of the  $744\text{-cm}^{-1}$  band probably all contribute to the excited-state feature at  $\sim 1500\text{ cm}^{-1}$ , although we were not able to resolve the components in this region. No band was observed that could be correlated with a radical anion band corresponding to the  $1493\text{-cm}^{-1}$  ground-state band. Apparently this band exhibits an insignificant shift in the radical anion or is not enhanced in the excited state ( $\pi-\pi^*$  excitation). Several bands below  $1300\text{ cm}^{-1}$  in the ground- and excited-state spectra shift substantially upon deuteration but are too weak to correlate reliably at this time. However, future work involving deuteration at other sites combined with excitation profiles of the excited state will help to establish correlations of these and higher frequency bands. The excited-state band observed at  $1735\text{ cm}^{-1}$  ( $1004 + 737\text{ cm}^{-1}$ ) in the spectrum of the deuterated analogue is consistent with the assignment of the  $1753\text{-cm}^{-1}$  ( $1015 + 744\text{ cm}^{-1}$ ) combination band in the parent compound.<sup>3</sup>

In summary, consideration of deuterium shifts for ground- and excited-state bands provides a more reliable estimate of excited-state frequency shifts. The observations presented here indicate

that ground- and excited-state bands may not be correlated on a strict one-to-one basis and that some ground-state bands that correspond to "radical anion" ( $\pi-\pi^*$  enhanced) bands in the excited state are not enhanced under visible (MLCT) excitation. Nevertheless, substantial shifts are associated with formation of the excited state. These are, in fact, comparable to shifts observed for the well-studied biphenyl<sup>7</sup> and bipyridyl<sup>8</sup> anion radicals and lend further support to the previous interpretations<sup>2,3,9</sup> of rR data as evidence for the localized excited state model.

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### Structure and Bonding of the First $\eta^2$ -Coordinated P<sub>4</sub> Ligand: Molecular Structure of *trans*-[Rh(P<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cl]·2CH<sub>2</sub>Cl<sub>2</sub> at 185 K

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Although the complex Rh(P<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cl (**1**)<sup>1,2</sup> and related derivatives of Rh<sup>1,2</sup> and Ir<sup>2</sup> were synthesized several years ago, the precise nature of the novel M-P<sub>4</sub> interaction was not established. In the more recently characterized complexes M[N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>]P<sub>4</sub> (**2**, M = Ni; **3**, M = Pd)<sup>3-5</sup> the P<sub>4</sub> tetrahedron is  $\eta^1$ -coordinated to the metal. For complex **1**, however, the alternative  $\eta^2$ - or  $\eta^3$ -coordination modes are also feasible. Indeed, a very recent NMR study<sup>6</sup> of **1** suggested  $\eta^2$ -coordination for the P<sub>4</sub> unit.

It was clearly of considerable importance to characterize **1** by X-ray diffraction, to corroborate the conclusions of the NMR experiment and also to furnish accurate structural parameters for the coordinated P<sub>4</sub> moiety (errors in P-P lengths in the structural study of **2** being rather large). Progress had been initially frustrated by decomposition of solutions and crystals of **1** at temperatures  $>260$  K. Recrystallization from dichloromethane at 195 K has now, however, afforded suitable crystals as a solvate (Rh:CH<sub>2</sub>Cl<sub>2</sub> = 1:2), which on rapid transference to a diffractometer equipped with a low-temperature attachment enabled an accurate structural study to be undertaken.<sup>7</sup>

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