# Resonance Raman Spectroscopic Studies of *trans*-Dioxorhenium(V) Tetrapyridyl Species

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## Introduction

Resonance Raman spectroscopy is a powerful tool for the identification of major features in electronic absorption spectra and for the assessment of selected ground-state/excited-state vibrational structural differences. We describe here a brief study of the excitation-wavelength-dependent Raman spectroscopy of *trans*-$(O)_2Re(py-x)_4^+$ (py-x is pyridine or a pyridine derivative), a species which has attracted appreciable attention because of its persistent luminescence and photoredox properties[1,2] and because of its abundant ground-state electrochemistry.[1c,3,4] The primary foci of the present spectroscopic study are a weak metal-based d–d transition in the blue portion of the dioxorhenium absorption spectrum and a much stronger transition in the near-UV region (see Figure 1). The nature of the latter is somewhat controversial, having been assigned as both an oxo-to-metal[2] and a metal-to-pyridine[1b,4] transition. The current study clearly establishes the metal-to-ligand charge-transfer (MLCT) nature of the transition while providing an interesting structural contrast to MLCT processes occurring in closely related cis complexes.[4] Finally it should be noted that the current report corrects an earlier preliminary observation on the (apparent) Raman spectrum of the title complex.[1c] We find that the spectrum reported previously is not that of $(O)_2Re(py)_4^+$ but is instead the vibrational scattering spectrum of the solvent ($CH_3CN$).

## Experimental Section

**Materials.** Reagent grade acetonitrile (Mallinckrodt) and methylene chloride (Fisher) were used as received. $CD_3CN$ (99.5 atom % D; Aldrich) was also used as received. Hexafluorophosphate salts of the following complexes: *t*-$(O)_2Re(py)_4^+$, *t*-$(O)_2Re(py-d_5)_4^+$, *t*-$(O)_2Re(py)_2(dmap)_2^+$, and *t*-$(O)_2Re(dmap)_4^+$ (dmap is 4-(dimethylamino)pyridine), were prepared by standard literature methods.[5,6]

**Measurements.** Raman scattering was typically obtained (180 or 135° backscattering geometry) from a dilute sample contained in a spinning NMR tube. $CH_3CN$, $CD_3CN$, and $CH_2Cl_2$ were each employed as solvent. Measurements at Northwestern were performed with 514.5- and 488.0-nm excitation wavelengths by using an air-cooled $Ar^+$ laser (Ion Laser Technologies). Additional experiments were performed with 647.1-nm excitation by using a Spectra Physics Series 2000 $Kr^+$ source,
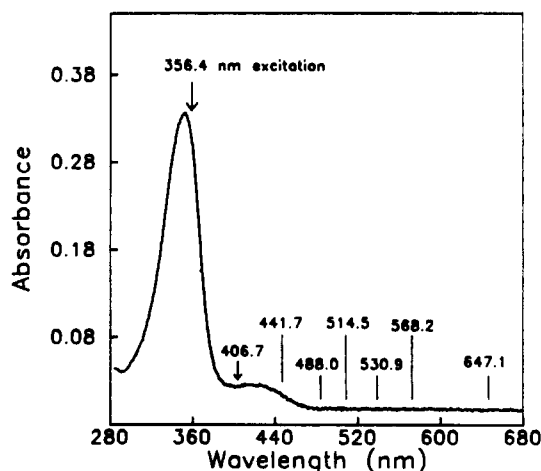
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**Figure 1.** Electronic absorption spectrum of *t*-$(O)_2Re(py)_4^+$ (14 mM; $b = 0.1$ cm) in acetonitrile as solvent. (Markers indicate excitation energies used in Raman studies; see Figure 3.)
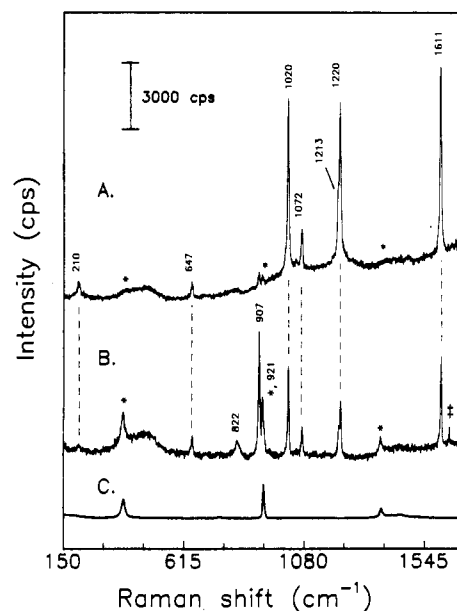


**Figure 2.** Resonance Raman spectra for 14 mM *t*-$(O)_2Re(py)_4^+$ in $CH_3CN$ as solvent. Spectrum A was obtained with 356.4-nm excitation and spectrum B with excitation at 406.7-nm. Spectrum C is a normal Raman spectrum (514.5-nm excitation) of $CH_3CN$ alone. Asterisks in spectra A and B denote solvent modes. The double dagger (1643 cm⁻¹) marks a peak due to stray room light (Hg fluorescent lamp emission).

as previously described.[7] At Marquette, samples were excited with both a $Kr^+$ laser (Coherent Innova 100-K3; $\lambda$ = 356.4, 406.7, 530.9, 568.2 nm) and an He–Cd laser (Liconix Model 4240NB; $\lambda$ = 441.6 nm). Data collection and analysis were performed as previously described.[7]

## Results and Discussion

Resonance-enhanced Raman scattering was observed from all four complexes. Polarization measurements revealed that all modes (with the possible exception of a mode at 650 cm⁻¹ in $(O)_2Re(py)_4^+$) are polarized and therefore totally symmetric. As noted above, the *trans*-dioxo complexes display two absorption features: one centered at ca. 440 nm and one at ca. 350 nm. Figure 2 shows representative spectra for *t*-$(O)_2Re(py)_4^+$ (in $CH_3CN$) based on resonant excitation in these two regions. Also shown is a normal Raman spectrum of the solvent. The most striking feature of the spectral comparison is the tremendous

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**Table I.** Observed Raman Frequencies (cm$^{-1}$) and Preliminary Mode Assignments for $t$-(O)$_2$Re(py-x)$_4^+$ Species

| $t$-(O)$_2$-Re(py)$_4^+$ | $t$-(O)$_2$-Re(py-$d_5$)$_4^+$ | $t$-(O)$_2$-Re(py)$_2$-(dmap)$_2^+$ | $t$-(O)$_2$-Re-(dmap)$_4^+$ | assgnt$^{a,b}$ |
|---|---|---|---|---|
| 210 | 205 | 210 | | $\nu$(Re–N(py)) |
| 647 | 625 | 651 | | ring breathing (py) |
| 822 | $c$ | 817 | 813 | $\nu$(O=Re=O), asym |
| 907 | 908 | 906 | 902 | $\nu$(O=Re=O), sym |
| 921 | 804 | 916 | 910 | ? |
| 950 | 958 | 950 | 954 | ? |
| 1020 | 985 | 1021 | 1030 | ring breathing (py) |
| 1050$^d$ | | | | $e$ |
| 1072 | 842 | 1075 | 1075 | ip C–H def (py) |
| 1213 | 899 | 1217 | 1227 | ip C–H def (py) |
| 1220 | 985 | 1235 | 1238 | ip C–H def (py) |
| 1430 | 1346 | | | ip C–H def (py) |
| 1611 | 1573 | 1611 | | ip ring breathing (py) |
| 1655$^d$ | | | | ? |
| 1668$^d$ | | | | 647 + 1020 |

$^a$ $\nu$ = stretch; asym = asymmetric; sym = symmetric; ip = in plane; def = deformation. $^b$ References: Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; John Wiley and Sons: New York, 1974; p 522 and refs 1b and 4. $^c$ Possibly obscured by modes at 804 and 842 cm$^{-1}$. $^d$ Observed only with 356-nm excitation; note that only $t$-(O)$_2$Re(py)$_4$ was evaluated at this wavelength. $^e$ Possibly solvent based.

difference in scattering intensities in the two spectral regions. (Note the intensities relative to nonresonant solvent peaks in each case.) The intensity effects are clearly a consequence of electronic selection rules. The longer wavelength transition is Laporte forbidden, comparatively weak ($\epsilon \approx 2000$ M$^{-1}$ cm$^{-1}$)[1b] and therefore likely to exhibit small scattering cross sections. The shorter wavelength transition, on the other hand, is a charge-transfer transition and is both spin and electric dipole allowed.[1b]

Returning to the ligand-field transition, the most interesting features perhaps are those at 822, 907, 950, and 1020 cm$^{-1}$, i.e. the metal–oxo stretching region. (Table I summarizes data for all four complexes.) Experiments in CH$_2$Cl$_2$ reveal an additional peak at 921 cm$^{-1}$, which is otherwise masked by solvent (CH$_3$-CN). The peak at 1020 cm$^{-1}$ is evidently pyridine based, as it shifts to 985 cm$^{-1}$ upon replacement of pyridine by pyridine-$d_5$. The peak at 921 cm$^{-1}$ might also be pyridine based, as it appears to shift to 804 cm$^{-1}$ (however, note the unusual excitation profile below). The peak at 822 cm$^{-1}$, on the other hand, does not seem to shift upon deuteration[8] but does apparently lose most or all of its intensity. The remaining two peaks are unaffected by ligand deuteration.

Of the peaks still unassigned, two are easily identified. The peak at 822 cm$^{-1}$ is clearly an asymmetric oxygen–metal stretch. It appears in the infrared spectrum as well and exhibits (in the IR) the expected shift to lower energy upon isotopic oxygen substitution.[1b] Its appearance here, however, is something of a puzzle: in $D_{4h}$ symmetry (or in any centrosymmetric configuration) the stretch should be Raman forbidden. Crude excitation profile studies (Figure 3) suggest that the observed scattering intensity does *not* come from vibronic coupling to higher-lying states of differing symmetry. An alternative is that pyridine rotation (about the Re–N axes) leads to less than perfect $D_{4h}$ ground-state symmetry and perhaps, therefore, to slight changes in polarizability upon vibrational activation.[9]

The second feature which is readily established is the symmetric O=Re=O stretch at 907 cm$^{-1}$.[10] This mode has been assigned previously on the basis of low-temperature ligand-field emission
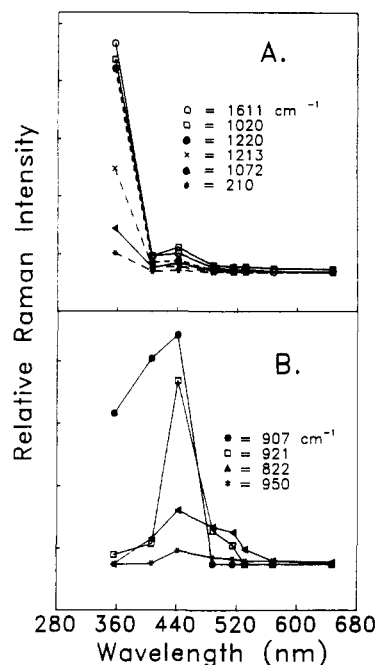


**Figure 3.** Raman excitation profiles for $t$-(O)$_2$Re(py)$_4^+$ (14 mM) in acetonitrile. Intensities are normalized to solvent peaks (nonresonant) but are uncorrected for residual differences in sample self-absorption and instrument throughput. Profile A: $\nu$(Re–N) and various pyridine-based modes (see Table I). Profile B: four modes found in the metal–oxo stretching region (see text). (Note that intensity scales differ for panels A and B.)

studies.[1b] It is worth noting that the symmetric stretch is among the more prominent modes in the visible-region scattering spectrum. This implies a significant displacement in O=Re=O coordinates upon d–d excitation,[11] consistent again with conclusions from the Winkler and Gray emission study.[1b]

Assignment of the remaining modes (921 and 950 cm$^{-1}$) is problematic. These weak modes exhibit excitation profiles which are similar to those for the symmetric and asymmetric rhenium–oxo stretches (i.e. d–d enhancement only; see Figure 3). Also, like the established oxo stretches, they are shifted to slightly lower energy following dmap replacement of pyridine (either two or four ligands; see Table I). It is tempting, therefore, to ascribe them to metal–oxo interactions as well. Simple group theoretical considerations suggest, however, that only two metal–oxo stretches (total) are possible; furthermore, the allowed bending mode(s) should appear only at much lower energy.[12,13]

In the charge-transfer region, vibrational scattering is tremendously enhanced, as noted above. Curiously, however, the enhancement phenomenon extends only to the pyridyl and rhenium–pyridyl modes (i.e. *not* to the oxo–rhenium core). On

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(8) Given the loss of Raman intensity, our conclusion here is based also on IR measurements where the peak does not shift or lose intensity upon deuteration.

(9) Crystallographic structural data, which point to a loss of symmetry as result of packing interactions,[17c] might also allow for a loss of symmetry in solution via either ion pairing or H-bonding to trace water.

(10) In the one previous report[1c] on (apparent) Raman scattering from $t$-(O)$_2$-Re(py)$_4^+$, excitation was nonresonant ($\lambda_{ex}$ = 532 nm), and the Q$''$(C–C) mode of CH$_3$CN (923 cm$^{-1}$ here; 916 cm$^{-1}$ in ref 1c) was mistakenly assigned as the symmetric rhenium–oxygen stretch (cf. 907 cm$^{-1}$, Table I). (Indeed the previously reported spectrum[1c] matches almost exactly the pure solvent spectrum ($\lambda_{ex}$ = 514 nm), shown in Figure 1.)

(11) The spectral results also imply displacement of Re–N and localized pyridyl modes. (Support for the former is clearly evident in high-resolution luminescence spectra.[1b]) Note however that, for these modes, intensity enhancement via an Albrecht "$B$-term" effect (Herzberg–Teller coupling to the neighboring MLCT excited state) may be possible. If so, then the observed intensities for those modes would not reflect (or, at least, not entirely reflect) simple Franck–Condon displacement effects.

(12) Experiments with $t$-($^{18}$O)$_2$Re(py)$_4^+$ presumably would clarify some of these issues. Unfortunately, a needed starting material, $^{18}$O-labeled water, is commercially unavailable at present.

(13) We further observe (a) that scattering at 921 and 950 cm$^{-1}$ occurs from samples prepared by two different routes and (b) that no photodecomposition is evident. These observations argue against scattering from an initial impurity or subsequent degradation product. Nevertheless, these possibilities cannot be rigorously ruled out.

this basis, the near-UV absorption may now be unambiguously assigned as rhenium-to-pyridine (rather than oxo-to-rhenium) charge transfer.[14]

The observations reported here provide an interesting contrast to those for related cis complexes.[4,15] In cis-$(O)_2Re(bpy)(py$-x$)_2^+$ species (bpy is 2,2'-bipyridine), both rhenium-to-bpy and rhenium-to-pyridine charge-transfer transitions are observable, and both exhibit significant metal–oxo resonance enhancements.[4] The differences (in comparison to the trans species) reflect, of course, the differences in how the one filled d$\pi$ orbital of rhenium(V) interacts with the pair of oxo ligands. In the trans geometry, the interaction is expected to be minimal, as the lowest energy orbital (i.e. the filled orbital) is d$_{xy}$ (where the metal–oxo core defines the $z$ axis).[1c] Removal of a d$\pi$ electron (by charge transfer) should have minimal effect, therefore, upon bonding along the $z$ axis—a picture which is clearly supported by the near-UV Raman studies (Figure 2A). It is also supported in an interesting way by crystallographic studies: X-ray structures for dioxorhenium(V)(d$^2$) versus dioxorhenium(VI)(d$^1$) show essentially identical rhenium–oxygen bond lengths.[16,17]

In the cis-dioxo case, the two available d$\pi$ electrons also reside in a single ground-state metal orbital, presumably a linear

combination of the nearly equivalent d$_{xz}$ and d$_{yz}$ orbitals.[4,18] Regardless of which of the three d$\pi$(Re) orbitals is lowest, however, a loss of bonding interaction with one or more p(oxo) donor orbitals is unavoidable. Removal of a d$\pi$ electron by charge transfer should lead to an increase in rhenium–oxygen bond order, an increase in stretching frequency, and a compression in bond length. These effects, in turn, should provide a basis for resonance enhancement, as indeed observed experimentally.

Finally, it should be noted that the cis-dioxorhenium bond compression effect should exist even when the d$\pi$(Re) electron is removed thermally (for example, by electrochemical oxidation). This, in turn, implies that a significantly higher vibrational activation barrier to Re(V/VI) interconversion should exist for the cis versus the trans species. If the effect is great enough, then it should be detectable kinetically. We hope to explore this interesting possibility.

(14) A reviewer has pointed out that the Raman data alone would also be consistent with an LMCT (py → Re) transition and has argued for the assignment on the basis of the comparatively high potential for Re-(VI/V) (which might shift the MLCT transition beyond the near-UV). The alternative LMCT transition, however, should also require high or very high energies, because of the extremely low potential for Re(V/IV). (Note that Re(V/IV) evidently lies much lower than the directly observable Re(V/III) potential, which itself occurs at ca. –0.8 V vs SCE at pH = 7.)[4] Clear support for the original MLCT assignment comes from studies of the solvent dependence of the transition: $E^{MLCT}$ systematically blue shifts as the Lewis acidity of the solvent increases. Importantly, the spectral shifts are paralleled by positive shifts in the Re(VI/V) potential (implying, therefore, a systematic increase in the Re$^V$py/Re$^{VI}$py$^{\cdot-}$ energy gap, as observed experimentally).[4]
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