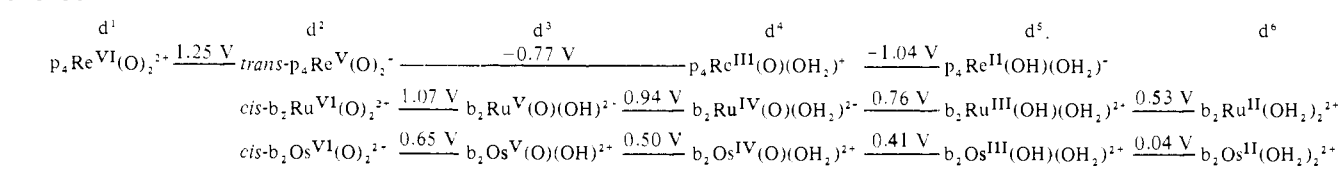
Scheme I[a]



[a] $\mu = 0.1$ M at pH 4.0, volts vs. SSCE; p is pyridine and b is bipyridine.

With the data on the Re system available, it is possible to compare redox characteristics for coordinately closely related complexes of Ru, Os, and Re as shown in Scheme I, where the classification is based on the d-electron configuration at the metal. The compilation of data is revealing in illustrating the sometimes remarkable differences in redox potentials that can exist for closely related metal complexes.[5] These differences play an important role in the underlying descriptive chemistry as evidenced by the appearance of the d^1 Re(VI) case and the nonappearance of the d^6 Re(I) case within the potential limits imposed by oxidation or reduction of the solvent.[6] The "disappearance" of oxidation states like Re(IV) has been observed in related monomeric[1] and dimeric[7] systems of Ru and Os. An important role in such cases is played by differences in pH dependences for adjacent couples, e.g.,

$$(\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})^{2+} \underset{-e^-,\,-H^+}{\overset{e^-,\,H^+}{\rightleftharpoons}} (\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}(\text{OH})^{2+}$$

$$(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}(\text{OH})^{2+} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{OH})^{+}$$

trpy is 2,2′:6,2″-terpyridine

which can lead to an instability toward disproportionation,

$$\text{OH}^- + 2(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}(\text{OH})^{2+} \rightarrow (\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})^{2+} + (\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{OH})^{+} + \text{H}_2\text{O}$$

for the intermediate oxidation state as the pH is increased.

In terms of implied reactivity the strongly reducing potentials for the Re(V/III) and Re(III/II) couples are notable. In fact, reduction at potentials more negative than the potential of the Re(III/II) couple gives Re(II), which is an electrocatalyst for the reduction of H_2O to H_2 over the pH range 0.5–13. For example, electrolysis at a mercury pool electrode of $(py)_4Re^V(O)_2^+$ (5.2×10^{-4} M, 0.1 M triflic acid) at $E_{app} = -0.87$ V and pH 1.0 in a gas-tight electrochemical cell gave a sustained (26 cycles based on reduction of Re(III) to Re(II)) catalytic current and in approximately 40 min. H_2 was produced at >90% efficiency as shown by GC analysis. Electrochemical generation of Re(II) (λ_{max} = 458 nm, ϵ_{max} 8600 M^{-1} cm^{-1}) in a spectroelectrochemical cell at pH 1.0 was followed by the appearance of Re(III) (λ_{max} = 387 nm, ϵ_{max} = 6300 M^{-1} cm^{-1}) with an isosbestic point maintained at 398 nm during the course of the reaction. From the electrochemical, spectral, and GC results, the stoichiometry of the *net* reaction in acidic solution is

$$2(py)_4Re^{II}(OH_2)_2^{2+} \rightarrow 2(py)_4Re^{III}(OH)(OH_2)^{2+} + H_2$$

The H_2 evolution reaction followed first-order kinetics in Re(II) with $k = 2.4\ (\pm 1.5) \times 10^{-3}\ s^{-1}$ at pH 1.0.

At pH 6.8, where the rate of H_2 evolution is actually enhanced compared to pH 1.0, added NO_2^- (0.1 M) suppresses catalytic H_2 production at −1.39 V because of competitive catalytic reduction of NO_2^-. The electrocatalytic reduction of NO_2^- is currently under investigation. We have identified NH_3 as a major reduction product by GC under conditions where the direct electroreduction of NO_2^- to NH_3 is negligible. The reactivity that we find for the Re system appears to parallel that found earlier for (catecholato)$_2$Mo^{VI}(O)$_2^{2-}$ by Schultz and Finklea,[8] for $Ni(CN)_3^-$ by Vincente-Perez et al.,[9] for polypyridine–nitrosyl complexes of Ru(II) and Os(II),[10] and for a tetrasulfonated, water-soluble iron porphyrin.[11]

Acknowledgments are made to the National Science Foundation under Grant CHE-8304230 and National Institutes of Health under Grant 5-RO1-GM32296-02 for support of this research.

(6) At high pH, evidence from cyclic voltammetry exists for a further reduction (pH 13, $E_{p,c} = -1.72$ V), which shows current enhancement due to H_2O reduction.

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Time-Resolved Resonance Raman Studies of the $\delta\delta^*$ Excited State of $Re_2Cl_8^{2-}$

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The characterization of excited electronic states continues to be an important problem in inorganic photochemistry. Recent work has demonstrated that the technique of time-resolved resonance Raman (TR^3) spectroscopy has been extremely useful in elucidating excited-state molecular structure.[1-10] The TR^3 method provides specific structural information, from the vibrational frequencies, on excited-state transients at submillimolar concentrations in room temperature fluid solution. A class of molecules whose excited-state structure has been the subject of intense experimental and theoretical effort are the multiply metal–metal bonded dimers.[11-15] In this paper, we wish to report the results of a TR^3 study of the prototypical molecule of this group, the quadruply bonded octachlorodirhenate dianion ($Re_2Cl_8^{2-}$).

The photochemically important excited state of $Re_2Cl_8^{2-}$ has

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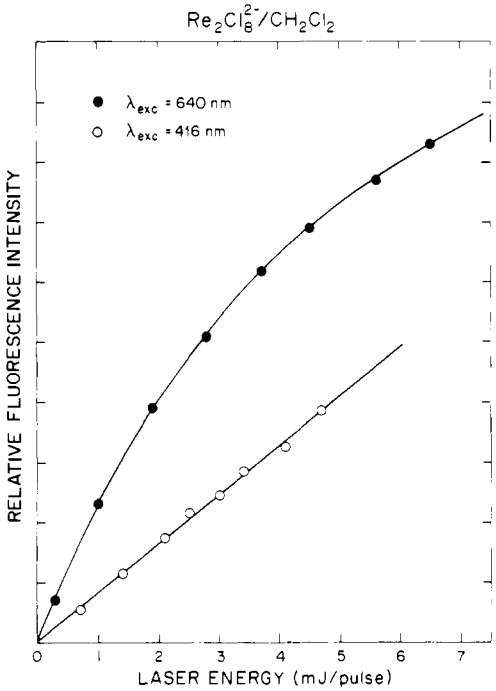

Figure 1. Fluorescence intensity at 790-nm vs. laser pulse energy for CH_2Cl_2 solution of $Re_2Cl_8^{2-}$ from excitation wavelengths of 640 (●) and 416 nm (○). These data were taken with the Raman spectrometer system used for the TR^3 experiments. Relative intensities were read directly from the boxcar integrator, which smoothed the readings with a 3-s time constant. The vertical intensity axis is *not* the same for the two excitation wavelengths ($I_{640} >> I_{416}$); no attempt to relate the emission intensities between the two curves should be made.

been assigned as the $^1\delta\delta^*(^1A_{2u})$ state,[16] which is accessed by the allowed $\delta \rightarrow \delta^*$ electronic transition at 685 nm.[17] Room temperature emission spectroscopy yielded a $\delta\delta^*$ excited-state lifetime of 75 ns (CH_2Cl_2 solution),[16] and transient absorption measurements showed that the $\delta\delta^*$ excited state absorbs at 390 nm.[18] The ground-state stretching frequency of 275 cm^{-1} has been determined by Raman[20] and resonance Raman[21] experiments, while low-temperature single-crystal absorption results were interpreted as indicating an excited-state Re–Re stretching frequency of 248 cm^{-1}.[19] The goal of this work is to directly measure the Re–Re stretching frequency in the $\delta\delta^*$ excited state of $Re_2Cl_8^{2-}$ using TR^3 spectroscopy and to use the TR^3 results to deduce the excited-state geometry.

The TR^3 spectrum of the $\delta\delta^*$ state of $Re_2Cl_8^{2-}$ was obtained by using a pump/probe technique, in which a transient population of excited-state species is created by using the pump laser wavelength and the resonance Raman spectrum of this transient is obtained with probe laser wavelength excitation. Both pump and probe wavelengths were generated simultaneously by using a single Nd:YAG (Quanta-Ray DCR-1) laser system. The pump wavelength was the 640-nm output of a pulsed dye laser (Quanta-Ray PDL-1 with DCM dye), near the ground state $\delta \rightarrow \delta^*$ absorption of $Re_2Cl_8^{2-}$. The probe wavelength was the first hydrogen Stokes-shifted line from the 355-nm Nd:YAG third harmonic at 416 nm, in resonance with the transient absorption at 390 nm. Raman-scattered light was detected and processed by using common Raman instrumentation.[22] The tetrabutylammonium salt of $Re_2Cl_8^{2-}$ was dissolved (~6 mM) in Burdick and Jackson CH_2Cl_2 and was deoxygenated by bubbling with nitrogen.

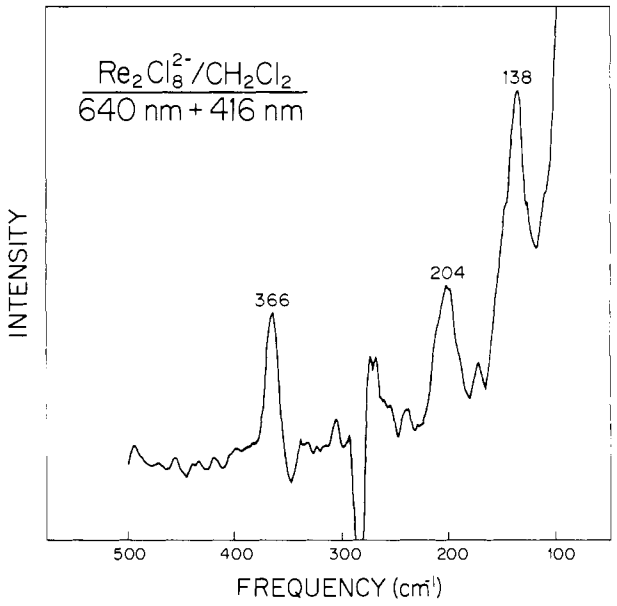

Figure 2. Time-resolved resonance Raman spectrum of $Re_2Cl_8^{2-}$ in CH_2Cl_2. This is the difference spectrum derived from subtracting the Raman spectrum obtained by using 416-nm excitation from the Raman spectrum obtained by using a 640-nm pump/416-nm probe configuration. Conditions: 7 mJ/pulse at 640 nm; 4.5 mJ/pulse at 416 nm; 4.7-cm^{-1} spectral slit width; 3-s boxcar time constant. The feature near 280 cm^{-1} is an artifact of subtracting the intense CH_2Cl_2 Raman band.

The $Re_2Cl_8^{2-}$ solution was studied by several different pulsed-laser experiments. With only 640-nm light incident on the sample, two important observations were made. First, the resonance Raman spectrum of $Re_2Cl_8^{2-}$ measured with pulsed 640-nm excitation is virtually identical with the ground-state resonance Raman spectrum of $Re_2Cl_8^{2-}$ measured with 647.1-nm excitation from a continuous-wave ion laser; the strong 272-cm^{-1} Re–Re stretch along with its overtones, the weaker 359-cm^{-1} Re–Cl stretch, and the 272 + 359 cm^{-1} combination mode are observed. Second, the emission intensity at 790 nm as a function of the laser pulse energy is distinctly non-linear (see Figure 1). This is consistent with saturation behavior (a plot of the reciprocal of the intensity vs. the reciprocal of the pulse energy is linear) and shows that 640-nm pulsed excitation of 7 mJ/pulse will create a significant transient $\delta\delta^*$ excited-state population.

With only the 416-nm pulsed excitation incident on the $Re_2Cl_8^{2-}$ solution, only nonresonant Raman scattering from the CH_2Cl_2 solvent is detected. The red emission seen using 416-nm excitation is much less intense than with 640-nm excitation. The plot of emission intensity vs. pulse energy is linear (Figure 1). This result is simply interpreted as meaning that under our experimental conditions (wavelength, light source, focusing conditions) the 416-nm wavelength is relatively inefficient at populating the $\delta\delta^*$ excited state.

The two-color pump/probe experiment gives the TR^3 spectrum of the $\delta\delta^*$ excited state of $Re_2Cl_8^{2-}$ (see Figure 2). The figure actually shows the TR^3 difference spectrum of the 640-nm pump/416-nm probe spectrum minus the 416-nm spectrum only; therefore, the Raman spectral features present must be due to the $\delta\delta^*$ excited state populated by the 640-nm beam.[23] We note three features in this spectrum, at 138, 204, and 366 cm^{-1}. All three bands are polarized.

We assign the 366-cm^{-1} excited-state band as being Re–Cl stretch and correlate this feature with the 359-cm^{-1} ground-state

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(23) In the pump/probe experiment, the 416-nm probe beam was delayed by ~12 ns from the 640-nm pump beam. The delay was not varied in any of our experiments. The absorption spectra of the sample before and after the TR^3 experiment showed little sample decomposition.

Re–Cl stretch. A small shift is expected as the Re–Cl bonding is relatively unaffected by the Re–Re axis localized $\delta \rightarrow \delta^*$ transition. We assign the 138-cm^{-1} excited-state Raman band as the Cl–Re–Re bending vibration. This mode has not been observed in the ground-state $Re_2Cl_8^{2-}$ Raman spectrum; the A_{2u} Cl–Re–Re bend has been observed in the IR at 165 cm^{-1}.[20,21] The observation that the 366- and 138-cm^{-1} bands are the two most intense features in the excited-state spectrum is consistent with the assignment of the 390-nm transient absorption band as e_u(Cl) $\rightarrow \delta$ charge transfer.

We are left to assign the 204-cm^{-1} excited-state Raman band as the excited-state Re–Re stretch. Although we expect a decrease in Re–Re frequency in going from the ground state (bond order = 4) to the $\delta\delta^*$ excited state (bond order = 3), the 204-cm^{-1} frequency represents an unexpectedly large shift from the 272-cm^{-1} ground-state Re–Re stretch and also from the 248-cm^{-1} excited-state Re–Re stretch deduced from low-temperature absorption measurements.[19] There are several possible explanations for these results: (i) The *interpretation* of the 248-cm^{-1} progression in the low-temperature absorption experiment as the excited-state Re–Re stretch is incorrect and the true frequency is 204 cm^{-1}. (ii) The 248-cm^{-1} Re–Re stretch is for an excited state *eclipsed* geometry, due to the constraining effects of the low-temperature crystalline environment, while the 204-cm^{-1} assignment reflects the solution-phase, room temperature relaxed (possibly staggered) $^1\delta\delta^*$ geometry.[24] (iii) In our TR^3 experiment, we are observing a state other than the singlet $\delta\delta^*$, such as the triplet $\delta\delta^*$ state; this would require a reassignment of the emissive excited state since our TR^3 spectra *are* of the emissive excited state. Further TR^3 work is now being done to try to sort out the geometric and electronic properties of quadruply bonded metal dimers, which will lead to a more complete understanding of the excited-state structure of $Re_2Cl_8^{2-}$.

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(24) Simple group theory predicts three polarized Raman vibrations for both the eclipsed (D_{4h}) and staggered (D_{4d}) $Re_2Cl_8^{2-}$ geometries. Thus, we cannot easily deduce the excited-state geometry from group theory alone.

Photochemistry of the Carbonyl Ylide Produced by Reaction of Fluorenylidene with Acetone. A Comparison of Carbonyl and Nitrile Ylides[1]

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Fluorenylidene (**2**) forms unstable ylides with solvents such as acetone and acetonitrile.[2,3] In this work we investigate the photochemistry of the carbonyl ylide **3** formed by reaction of **2** with acetone in order to compare its photochemical and thermal decay processes. Ylide **3** was produced by nitrogen laser excitation (λ = 337.1 nm, ~8 ns, <10 mJ/pulse) of deaerated 1×10^{-3} M solutions of diazofluorene (**1**) in acetone at room temperature (Scheme I). The transient absorption spectrum of **3** exhibits[2,3] a broad band centered at 640 nm appearing within 10 ns (in pure acetone) after excitation[2] and decaying with a lifetime of ca. 3.4 μs.

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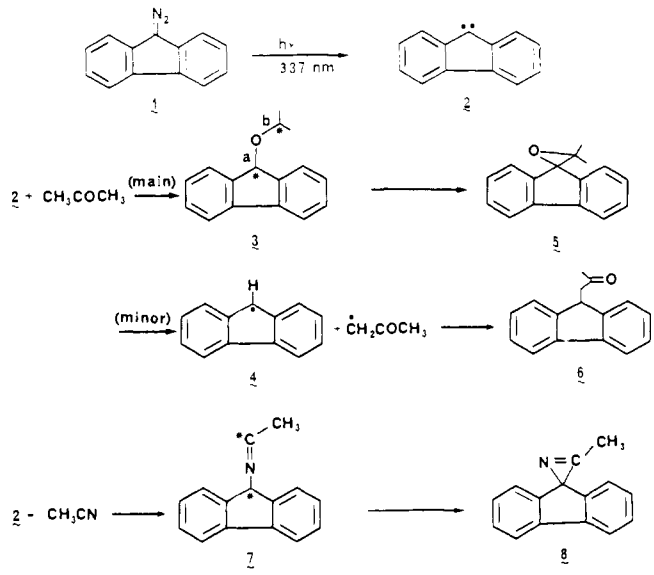
Scheme I



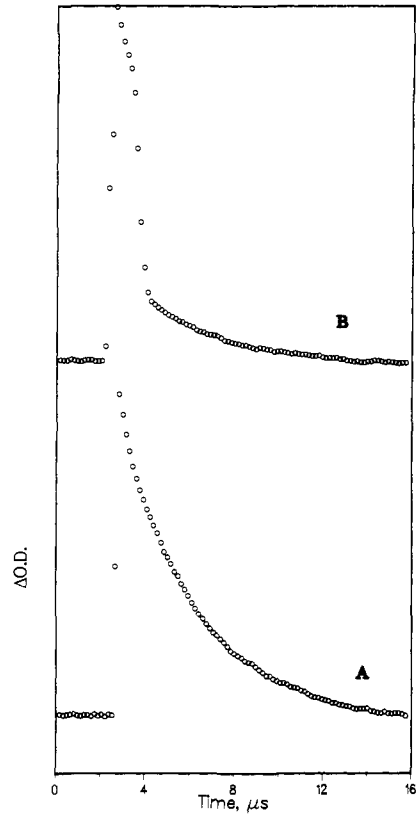


Figure 1. Comparison of the traces monitored at 640 nm from one- and two-laser experiments in the photodecomposition of 1×10^{-3} M diazofluorene (**1**) in acetone at 300 K. (A) Resultant trace after 337-nm laser excitation; (B) result of 337-nm laser excitation followed (after 1.5 μs) by 591-mm laser photolysis.

Excitation of **3** with the delayed pulse from a Candela UV-500 M flash-lamp pumped dye laser (λ = 591 nm, ~250 ns, 200–800 mJ/pulse) resulted in concurrent bleaching of the 640-nm absorption band;[4] the transient absorptions due to **3** are sufficiently small (typically ≤0.06) that only a small fraction of this energy is actually absorbed. Figure 1A shows the decay of the 640-nm ylide absorption produced by 337-nm laser excitation alone, while Figure 1B illustrates the effect of the second 591-nm excitation,

(4) A description of our setup for two-laser experiments has been published: Weir, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

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