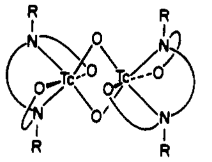
σ and δ metal bonding are comparable to that in the $Tc_2Cl_8^{2-}$ compound. However, the Tc polymer has a much smaller π-overlap population, because, as we analyzed above, some π orbitals are used for interaction with the oxygens.

The compound $Tc_2(\mu\text{-}O)_2(H_2EDTA)_2^{2e}$ (**10**) was suggested to have a long triple metal-metal bond, with a configuration of $\sigma^2\pi^2\delta^{*2}$. But its Tc-Tc overlap population is only 0.292, calculated by the extended Hückel method. Another interesting relevant compound is tris(μ-carbonyl)bis(1,2-diphenyl-3,4-di-*tert*-butylcyclobutadiene)diiron (**11**). Our group has done calculations on **11** in the past and suggested that it may have a multiple Fe-Fe bond.[6] The 18-electron rule would assign it a triple bond, and the Fe-Fe distance indeed is short, 2.18 Å. However, the Fe-Fe overlap population is only 0.165. Also, $Fe_2(CO)_9$ (**12**) has a single bond, even though the Fe-Fe overlap population in an extended Hückel calculation is -0.001.[11] So overlap populations by themselves do not always correlate with common preconceptions on the number of bonds.



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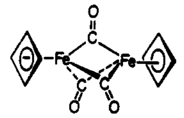

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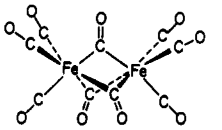

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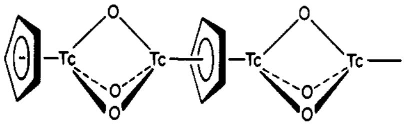
In general there are problems with describing the extent of metal-metal bonding in bridged or supported systems. We actually believe that the bond in Tc_2O_3Cp *is* very short not because it is extraordinarily strong but because it operates "on top" of a constrained short contact of the metals imposed by the bridges. Consider the simple triply bridged system, dimer or polymer, **13**.



13

At β = 70° and Tc-O = 1.88 Å, the Tc-Tc distance would be 2.16 Å, *in the absence of any Tc-Tc bonding*. A Tc-Tc bond of multiplicity around 2.5 (that is what we conclude from the model dimer) shortens Tc-Tc to 1.87 Å. We do not think this is unreasonable, given that a quadruple bond is 0.9 Å shorter for Tc than a single bond, with no bridging.

Acknowledgment. A.W.E.C. wishes to thank Pere Alemany and Yat-Ting Wong for helpful discussions. We are grateful to Jane Jorgensen and Elisabeth Fields for their drawings. This work was supported by the Cooperative Research Grant in Basic Science, CCB86/4004/88, from the U.S.-Spanish Joint Committee for Scientific and Technological Cooperation.

Appendix

All calculations are carried out by the tight-binding extended Hückel method.[7] Table III lists the atomic parameters used. A set of 20 *k* points were used.

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Time-Resolved Resonance Raman Study of the $\delta\delta^*$ Excited State of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$

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Time-resolved resonance Raman (TR^3) spectra have been obtained for $Re_2X_8^{2-}$ (X = Cl, Br) in the $^1A_{2u}$ ($\delta\delta^*$) electronically excited state, at ambient temperature in solution. The TR^3 spectra exhibit Raman peaks that are assigned to the three symmetric vibrations of the excited state: the Re-Re stretch, Re-X stretch, and the Re-Re-X deformation. In addition, a depolarized peak attributed to an asymmetric X-Re-X bend is observed. Comparison of the TR^3 results to single-crystal vibronic spectra reported by others clearly shows the effects of crystal constraints and observation time scale upon the structure of the $\delta\delta^*$ excited state. The excited-state metal-metal bond distance is inferred to be 0.03-0.04 Å shorter in solution than in the crystal. The TR^3 data, obtained in solution on the nanosecond time scale, indicate that the excited state relaxes to a staggered molecular structure (D_4 or D_{4d} symmetry). The vibronic data, obtained on single crystals under cryogenic conditions, are consistent with an eclipsed (D_{4h}) structure, similar to that of the ground state. A comparative TR^3 study of quadruply bonded complexes, including both octahalodirhenate ions and $Mo_2(PMe_3)_4Cl_4$ (which is precluded by steric factors from significant torsional distortion about the metal-metal bond), was essential in elucidating the excited-state structures.

Introduction

Time-resolved resonance Raman (TR^3) spectroscopy allows direct observation of the molecular vibrations of short-lived chemical species. An important application of TR^3 spectroscopy is in the determination of vibrational spectra of molecules in electronically excited states under ambient conditions (room temperature, fluid solution).[2,3] Previous experimental approaches to determining structural features of the electronically excited states of relatively complex molecules have been confined primarily to Franck-Condon analysis of the resolved vibronic spectra. This approach generally requires the absorption spectrum to be recorded

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[1] Permanent address: Chemistry Department, Wabash College, Crawfordsville, IN.

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under cryogenic and/or single-crystal conditions. These rigid environments frequently prevent structural or electronic relaxations, which are important in relatively unconstrained fluid solution. Accordingly, the elucidation of excited-state structure in solution is essential for adequate understanding of photochemical processes (in which excited states are the primary, unique reactants) under conditions where diffusional chemical reactivity can occur. In addition, comparison of vibronic and TR^3 results on the same systems may be expected to provide important information on the nature of the relaxations that follow electronic excitation. We have previously applied TR^3 spectroscopy to study the $^3(\sigma^* \rightarrow \sigma)$ ($^3A_{2u}$) excited state of weakly metal-metal-bonded d^8 dimer systems;[4,5] in this paper we extend these studies to the $^1(\delta \rightarrow \delta^*)$ ($^1A_{2u}$) excited state of strongly metal-metal-bonded d^4 dimers, specifically $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$.

The metal-metal quadruple bond was first characterized in $Re_2Cl_8^{2-}$.[6] M_2X_8 complexes continue to be the archetypical class of multiply metal-metal-bonded dimers, having been extensively studied both experimentally and theoretically.[7] Crystallographic analysis of the $Re_2X_8^{2-}$ (X = Cl, Br) molecules reveals a D_{4h} molecular symmetry for the ground state.[6] Two approximately square-planar ReX_4 units are held together cofacially by a quadruple bond, resulting in a short metal-metal bond distance with eclipsed halide ions.

The lowest lying allowed excited state in the $Re_2X_8^{2-}$ complexes is the $^1(\delta \rightarrow \delta^*)$ ($^1A_{2u}$) excited state, which involves the promotion of an electron from a bonding δ orbital to an antibonding δ^* orbital and a concomitant change in metal-metal bond order from 4 to 3. This $\delta \rightarrow \delta^*$ transition is centered at 685 and 715 nm in the absorption spectra of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, respectively. Vibronic progressions are observed in the single-crystal electronic absorption and emission spectra.[8-10] These progressions have been assigned to the Re-Re stretching motion and the symmetric Re-Re-X angle bend, the coordinates of which are presumed to be displaced in the excited state. Progressions in the Re-Re stretch, with an average spacing of 249 ± 1 and 252 ± 4 cm^{-1}, have been assigned in the absorption spectra of $(TBA)_2Re_2Cl_8$ and $(TBA)_2Re_2Br_8$, respectively;[8,9] these values correspond to the excited-state stretching frequencies in the crystals under cryogenic conditions. The corresponding ground-state frequencies for the Re-Re stretch from resonance Raman (RR) spectroscopy are 274 and 275 cm^{-1}. In contrast to the excited-state Re-Re frequencies determined vibronically, recent TR^3 results have suggested a frequency of 204 cm^{-1} for the Re-Re stretch of the $^1\delta\delta^*$ excited state of $Re_2Cl_8^{2-}$ in CH_2Cl_2 solution.[11] A decrease in the frequency of the Re-Re stretching vibration upon $\delta \rightarrow \delta^*$ excitation is expected because of the decrease in formal Re-Re bond order. The vibronic and TR^3 results agree that this decrease occurs. However, the two approaches apparently yield values for this shift that differ by ca. 50 cm^{-1}; clearly this discrepancy needs to be resolved.

Aside from the issues related directly to the metal-metal bond, TR^3 spectroscopy may be applied to examine the question of torsional distortion in the $\delta\delta^*$ state. Because of the nodal character of the δ bond, there is a significant barrier to torsional distortion about the Re-Re axis in the ground state. With the elimination of the δ bond upon $\delta \rightarrow \delta^*$ excitation, the filled Re-Re bonding orbitals have cylindrical symmetry and the molecule is able to twist about the Re-Re axis away from its eclipsed-halide ground-state structure. The excited-state structure may then assume a staggered D_4 or D_{4d} structure. The extent to which this actually occurs in $Re_2X_8^{2-}$, under what conditions, and the torsional barrier imposed by the δ bond, however, remain as questions that are not adequately resolved. Theoretical studies support the view that the D_{4d} distortion may occur,[12] and experimental studies of the luminescence of quadruply bonded complexes suggest that this indeed occurs in solution.[13] In single crystals at low temperature, on the other hand, the mirror symmetry of the vibronically resolved absorption and emission spectra suggests that D_{4d} distortion does not occur under these conditions.[8,10] The question of the structure of the excited state in solution versus that in the crystals clearly merits further examination. The present study was undertaken to address these questions concerning the structure of the $\delta\delta^*$ excited state and to resolve the apparent discrepancy between the excited-state Re-Re stretching frequencies determined in the previous TR^3 and vibronic studies on the $Re_2Cl_8^{2-}$ complex.

Experimental Section

Sample Preparations. $(TBA)_2Re_2Cl_8$ and $(TBA)_2Re_2Br_8$ (TBA = tetrabutylammonium, $(n\text{-}C_4H_9)_4N^+$) were prepared by literature methods.[14] Methylene chloride and acetonitrile were dried over CaH_2, and nitromethane was dried over P_2O_5. The solvents were then distilled and degassed by freeze-pump-thaw cycles. For the Raman experiments, the appropriate solvent was vacuum-transferred to an NMR tube containing the sample. The tube was sealed under vacuum, with sample concentrations ranging from 3 to 10 mM.

Instrumentation. UV-visible absorption spectra were recorded before and after the TR^3 experiment on an IBM 9430 spectrophotometer. Transient difference absorption spectra were obtained by using the 355-nm line from a nanosecond-pulsed Nd:YAG laser to excite the sample and a shuttered, high-intensity xenon lamp to measure the absorbance before and after the excitation pulses. The measurement yielded the difference absorption spectrum between the ground and excited states.

Continuous-wave (CW) Raman spectra were obtained with either the 413.1-nm laser line of a Spectra-Physics 171-01 Kr$^+$ laser or the 501.7-nm line of a 171-19 Ar$^+$ laser. These wavelengths were chosen on the basis of their proximity to the probe wavelengths used in the TR^3 experiments. Typical CW laser power was 20 mW at the sample. Scattered light was collected with a 135° backscattering geometry into a SPEX 1403 spectrometer equipped with an RCA 31034A photomultiplier tube. The signal was processed with an ORTEC 9300 series photon counter and a Nicolet 1180E Raman data system.

The TR^3 experiment used the same SPEX 1403 scanning spectrometer and RCA 31034A photomultiplier tube as the CW experiments. A Stanford Research Systems Model SR250 gated integrator was used in place of the photon counter for signal processing. The SR250 instrument was triggered by the 10-Hz TTL synch output of the pulsed laser, and the Nicolet 1180E computer system controlled data storage and processing. Overlap of the integrator gate and the photomultiplier signal pulse was verified with a Hewlett-Packard 1741A oscilloscope.

Schematic diagrams of the experimental setups used for the TR^3 studies are shown in Figure 1. The excitation source for the TR^3 experiments was a pulsed Nd:YAG laser (Quanta-Ray DCR-2A). The Nd:YAG fundamental at 1064 nm was frequency-doubled and -tripled to obtain the second (532 nm) and third (355 nm) harmonics. In the $Re_2Br_8^{2-}$ experiment, the second harmonic was used to pump the pulsed dye laser (Quanta-Ray PDL-2) to obtain excitation pulses of 680 nm with Oxazine 725 dye (Exciton). The third harmonic pumped a stimulated Raman shift cell (Quanta-Ray RS-1) to produce probe pulses at 503 nm (second Stokes shift of H_2). An optical delay of 10-12 ns was employed between pump and probe pulses. The 680- and 503-nm pulses were then combined at a dichroic mirror and directed to the sample. The scattered photons were collected in a 180° backscattering geometry. The laser energy was 1-4 mJ/pulse at each wavelength, with a repetition rate of 10 Hz and a pulse width of 7 ns.

A similar setup was used to acquire the $Re_2Cl_8^{2-}$ TR^3 spectrum. In this case, the second harmonic from the Nd:YAG laser was directed through a beamsplitter, with approximately 20% of the 532-nm light sent to pump the Raman shift cell and the remainder sent to the dye laser. The 683-nm output (first Stokes shift of H_2) from the shift cell was used as the excitation source. The pulsed dye laser was set to produce 608-nm light with Rhodamine 640 (Exciton); the 608-nm light was then combined with the fundamental at a dichroic mirror and summed in a KD*P

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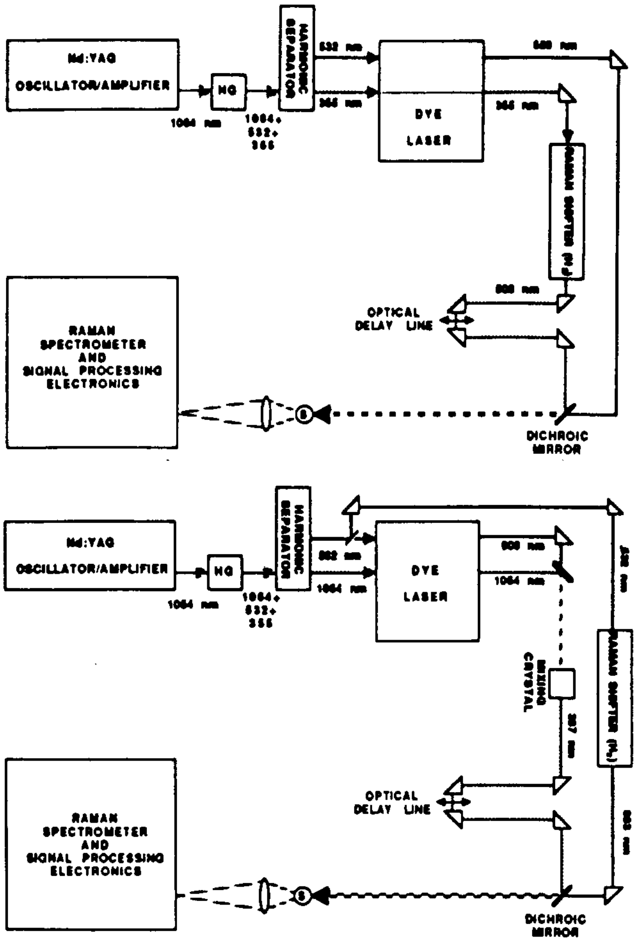

Figure 1. The TR^3 experimental apparatus as described in the Experimental Section. The top diagram illustrates the configuration used for the $Re_2Br_8^{2-}$ experiment, while the lower diagram represents the $Re_2Cl_8^{2-}$ configuration.

crystal to produce probe pulses at 387 nm.

Results

Absorption Spectra. The electronic absorption spectra of the ground states, together with the transient difference excited-state spectra of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ in CH_3CN, are shown in Figure 2. The lowest energy allowed electronic transition in the ground state of both complexes is the $^1(\delta \rightarrow \delta^*)$ absorption (centered at 685 nm for $Re_2Cl_8^{2-}$ and 715 nm for $Re_2Br_8^{2-}$),[15,17] while the next higher energy band in both cases has been assigned to the $\pi(X) \rightarrow \delta^*$ charge-transfer transition.[16] The transient absorption spectra were obtained with 355-nm excitation and are identical with those produced with 337- and 615-nm excitation in CH_3CN and CH_2Cl_2.[18] The excited-state $Re_2Cl_8^{2-}$ transient ($Re_2Cl_8^{2-}$) has an absorption maximum at 380 nm with a lifetime of 130 ns in CH_3CN. The $^*Re_2Br_8^{2-}$ transient absorption spectrum, obtained under the same conditions, exhibits two peaks centered at 500 and 555 nm and a lifetime of 90 ns. These excited-state absorption peaks have been attributed to the red-shifted $\pi(X) \rightarrow \delta^*$ charge-transfer transition of the $^1\delta\delta^*$ excited state.[18]

TR^3 Spectra. The TR^3 experiments utilized a pulse/probe technique. In the $Re_2Br_8^{2-}$ experiment, pulse or excitation laser pulses of 680 nm were used to generate the $\delta\delta^*$ excited state. Probe laser pulses were then selected to give resonance-enhanced Raman spectra of the transient species, using 503-nm probe wavelength for $^*Re_2Br_8^{2-}$ resonant with the excited-state absorption peak centered at 500 nm. For $^*Re_2Cl_8^{2-}$, 683-nm excitation pulses were used in conjunction with 387-nm probe pulses, which were close to resonance with the excited-state absorption peak at 380 nm (see Experimental Section for details).

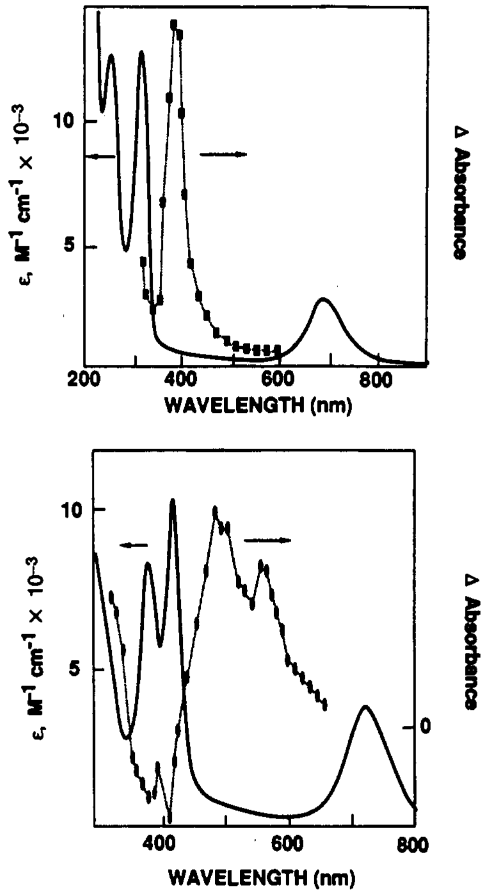

Figure 2. Upper trace: Absorption spectrum of the ground state of $Re_2Cl_8^{2-}$ in CH_3CN (solid line, ε) and the transient difference spectrum observed with 355-nm excitation (dashed line, ΔA). ε is measured in M^{-1} cm^{-1}, and ΔA is the difference between absorbance values of the excited and ground states. Lower trace: Ground-state absorption and transient difference spectra of $Re_2Br_8^{2-}$ in CH_3CN.

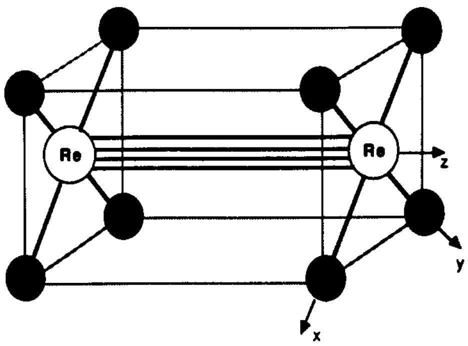

Figure 3. Schematic structure of the $Re_2X_8^{2-}$ (X = Cl, Br) molecule.

The ground-state structure of the $Re_2X_8^{2-}$ complexes consists of two approximately square-planar ReX_4 units held together cofacially by the quadruple bond with eclipsed-halide (D_{4h}) structure (Figure 3). Group-theoretical analysis of this structure predicts nine Raman-active modes ($3A_{1g} + 2B_{1g} + B_{2g} + 3E_g$). The three totally symmetric (A_{1g}) modes, which may be identified by their characteristic polarized scattering ($\rho < {}^3/_4$) in the Raman spectra, are the Re–Re stretch, the Re–X stretch, and the metal–metal–halide deformation. In the excited state, the molecule may retain the D_{4h} structure of the ground state or may rotate about the Re–Re axis, since the δ bond, which is responsible for the ground-state eclipsed structure, is eliminated upon excitation.

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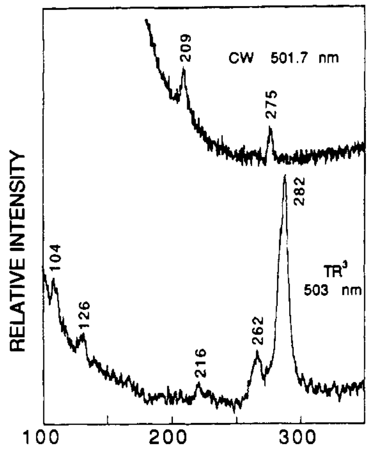

Figure 4. Lower trace: TR³ spectrum of $Re_2Br_8^{2-}$ in CH_2Cl_2 obtained by using 680-nm pump and 503-nm probe pulses. Upper trace: CW Raman spectrum of $Re_2Br_8^{2-}$ in CH_3NO_2 obtained by using 501.7-nm excitation.

One possible excited-state configuration is a staggered (dihedral X–M–M–X angle = 45°) D_{4d} geometry, which has Raman-active modes described as $3A_1 + 3E_1 + 3E_2$. The same three symmetric vibrations as in the ground state are Raman active. An intermediate torsional geometry (D_4) is also possible in the excited state. In this conformation there are four symmetric (A_1) vibrations: the Re–Re and Re–X stretches, the metal–metal–halide deformation, and the X–Re–Re–X torsion.[11]

The TR³ spectrum of $^*Re_2Br_8^{2-}$ in CH_2Cl_2, obtained by using 680-nm excitation pulses and 503-nm probe pulses, is shown in Figure 4. The continuous-wave Raman spectrum in CH_3NO_2 recorded with the 501.7-nm line of an Ar^+ laser is also shown. The CW spectrum shows ground-state frequencies at 275 and 209 cm^{-1} for the symmetric Re–Re and Re–Br stretches, respectively. The pulsed spectrum shows an intense solvent peak at 282 cm^{-1} and four Raman lines located at 104, 126, 216, and 262 cm^{-1}, which are attributable to $^*Re_2Br_8^{2-}$. The 104-, 216-, and 262-cm^{-1} features are polarized. The 216-cm^{-1} peak can be readily assigned to the symmetric Re–Br stretch and the 262-cm^{-1} line to the symmetric Re–Re stretch in the excited state. The remaining polarized peak at 104 cm^{-1} is attributed to the symmetric bending motion. The depolarized peak at 126 cm^{-1} is assigned to an asymmetric deformation.

Little frequency change is expected for the Re–Br vibration upon creation of the $\delta\delta^*$ excited state, since the $\delta \rightarrow \delta^*$ transition is largely localized along the Re–Re axis. In fact, this frequency is higher in the excited state than in the ground state, a phenomenon that is also observed in $^*Re_2Cl_8^{2-}$. The Re–Re stretching frequency is expected to decrease in the excited state, due to the reduction in bond order and accompanying bond lengthening. This decrease is observed (275 to 262 cm^{-1}) experimentally. The 262-cm^{-1} excited-state Re–Re stretching frequency observed in the solution TR³ experiment differs significantly, however, from the 252-cm^{-1} progression observed in the vibronically resolved single-crystal absorption spectrum.[8]

The Raman peak due to the symmetric Re–Re–Br bending motion of $Re_2Br_8^{2-}$ has not been definitively observed in the ground state. Utilizing a resonance condition with the $\pi(Br) \rightarrow \delta^*$ transition at low temperature, Clark and Stead observed weak features at 65, 88, 111, and 123 cm^{-1}.[19] With the exception of the 123-cm^{-1} peak, which was depolarized and assigned to a B_{1g} or B_{2g} bending motion, they could not obtain depolarization measurements of these weak features.[19] Our 126-cm^{-1} peak in the TR³ spectrum is depolarized and is attributed to an asymmetric bending motion in the excited state, analogous to the 123-cm^{-1} ground-state mode. Our observation of polarized scattering in the 104-cm^{-1} excited-state peak leads us to assign this as the symmetric M–M–X deformation (vide supra) and suggests that the 111-cm^{-1} peak observed by Clark and Stead represents this motion in the ground state. The Raman data for the ground and excited states of $Re_2Br_8^{2-}$, including assignments, are presented in Table I.

Table I. Resonance Raman, TR³, and Vibronic Frequencies (cm^{-1})[a]

coordinate	ground-state res Raman[a,b]	ground-state vibronic[c]	$\delta\delta^*$ TR³ [a,d]	$\delta\delta^*$ vibronic[e]
		$Re_2Br_8^{2-}$		
δ_{sym}(MMX)	111		104 (p)	98
δ_{asym}(XMX)	123 (dp)		126 (dp)	
ν(MM)	275 (p)		262 (p)	252
ν_{sym}(MX)	209 (p)		216 (p)	
		$Re_2Cl_8^{2-}$		
δ_{sym}(MMX)	154	158	146	137
δ_{asym}(XMX)	188 (dp)		201 (dp)	
ν(MM)	274 (p)	275	262	249
ν_{sym}(MX)	359 (p)		365 (p)	
		$Mo_2Cl_4(PMe_3)_4$		
ν(MM)	355 (p)		331	329
ν_{sym}(MX)	274 (p)			

[a] Polarizations indicated where measured. Polarized = p; depolarized = dp. [b] Reference 19 and present work. [c] Reference 10. [d] Present work. [e] References 8 and 9.

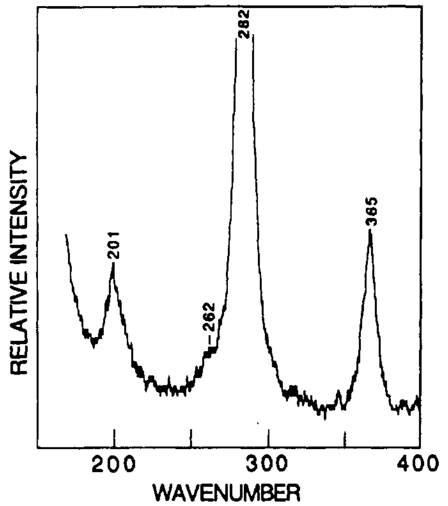

Figure 5. TR³ spectrum of $Re_2Cl_8^{2-}$ in CH_2Cl_2 obtained by using 683-nm pump and 387-nm probe pulses.

The TR³ spectrum of $^*Re_2Cl_8^{2-}$ in CH_2Cl_2 (obtained by using 640-nm excitation pulses and 416-nm probe pulses) has been reported[11] and shows three Raman peaks at 138, 204 and 366 cm^{-1}. These bands all appeared to be polarized, although a poor signal-to-noise ratio made polarization measurements difficult. The 366-cm^{-1} peak was assigned to the symmetric Re–Cl stretch and the peak at 138 cm^{-1} was attributed to the symmetric Re–Re–Cl bend in the excited state. The 204-cm^{-1} peak remained to be assigned to the symmetric Re–Re stretch, primarily due to the polarization result. In the present work, probe pulses of 387 nm (in direct resonance with the excited-state $\pi(Cl) \rightarrow \delta^*$ absorbance) were used to give optimum resonance enhancement of the Raman scattering of $^*Re_2Cl_8^{2-}$. The previously reported spectrum[11] utilized a 416-nm probe wavelength, well removed from the absorption maximum at 380 nm. The improved signal-to-noise ratio of the present spectra yields more reliable frequency and polarization data.

A TR³ spectrum of $Re_2Cl_8^{2-}$ in CH_2Cl_2 with 683-nm excitation pulses and 387-nm probe pulses is shown in Figure 5. This spectrum is the result of extensive signal averaging with the purpose of establishing whether a weak feature assignable to the excited-state Re–Re stretch may be observed between 240 and 280 cm^{-1}. This spectrum exhibits intense $^*Re_2Cl_8^{2-}$ peaks at 201 and 365 cm^{-1}, in close agreement with the earlier study.[11] In addition, the very intense CH_2Cl_2 peak observed at 282 cm^{-1} has

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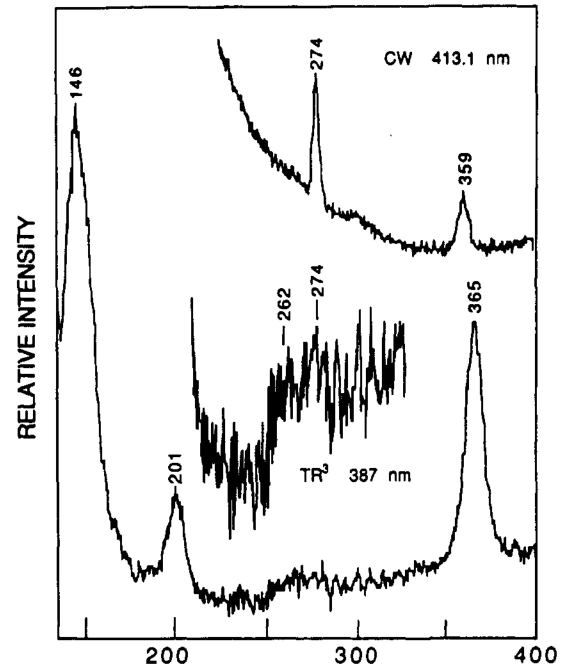

Figure 6. Lower trace: TR³ spectrum of $Re_2Cl_8^{2-}$ in CH_2Cl_2 obtained by using 683-nm pump and 378-nm probe pulses, with the Raman peak due to the solvent and the dye laser ASE background subtracted. Upper trace: CW Raman spectrum of $Re_2Cl_8^{2-}$ in CH_3NO_2 obtained by using 413.1 nm excitation.

a weak shoulder at approximately 260 cm^{-1}. Subtraction of the 282-cm^{-1} solvent peak (Figure 6) shows this shoulder to be a weak peak located at 262 cm^{-1} and, in addition, reveals a peak at 274 cm^{-1}. The 274-cm^{-1} peak is due to the Re–Re stretching vibration of $Re_2Cl_8^{2-}$ molecules remaining in the ground electronic state. This occurs because the pump pulse does not saturate the excited state and because there is a 15-ns time delay between the pump and probe pulses. The baseline compensation in the subtracted spectrum also emphasizes an intense Raman peak at 146 cm^{-1}, which corresponds to the 138-cm^{-1} feature reported earlier.[11]

Depolarization ratio measurements demonstrate the 365-cm^{-1} peak to be a polarized vibration, which supports its assignment as the symmetric Re–Cl stretch. The 262-cm^{-1} peak is not of sufficient intensity to obtain a depolarization ratio measurement, but its frequency strongly suggests an assignment as the symmetric Re–Re stretch. Its feeble intensity results from weak resonance enhancement by the $\pi(Cl) \rightarrow \delta^*$ transition at 380 nm. The peak at 146 cm^{-1} was located on the sharply rising amplified stimulated emission (ASE) background from the dye laser, making accurate depolarization ratio measurements impossible. It is, however, in the correct frequency region to be assigned to the M–M–X bending mode. The 201-cm^{-1} peak is observed to be depolarized in the present study, in contrast to the polarized assignment suggested earlier.[11] This precludes its assignment as the symmetric Re–Re stretch; this peak must then be due to an asymmetric deformation.

In the ground-state resonance Raman spectrum obtained by using 337.4-nm radiation, Clark and Stead reported peaks at 117, 154, 176, 188, and 334 cm^{-1} for $Re_2Cl_8^{2-}$.[19] The depolarized peak at 188 cm^{-1} was assigned to either a B_{1g} or a B_{2g} bending vibration, analogous to the mode in $(TBA)_2Re_2Br_8$ reported at 123 cm^{-1}. We favor the assignment of these peaks to an X–Re–X deformation because of the large frequency shift (from 188 to 123 cm^{-1}) when the halide is changed from Cl to Br. By analogy, the depolarized peaks in the TR³ spectra at 201 cm^{-1} ($Re_2Cl_8^{2-}$) and 126 cm^{-1} ($Re_2Br_8^{2-}$) are assigned to the asymmetric X–Re–X deformation in the excited state. The 146-cm^{-1} $^*Re_2Cl_8^{2-}$ peak is then assigned to the symmetric M–M–X bending motion in the excited state by analogy to the TR³ spectrum of the bromo complex.

Figure 6 also shows the ground-state Raman spectrum obtained with the 413.1-nm line of a Kr$^+$ laser. The Re–Re and Re–Cl stretches are located at 274 and 359 cm^{-1}, respectively, as compared to the excited-state values (assigned above) of 262 and 365 cm^{-1}. Again, the symmetric bending mode in the ground state was not observed. Analogy to the $^*Re_2Cl_8^{2-}$ and the $^*Re_2Br_8^{2-}$ assignments suggests that the 154-cm^{-1} ground-state peak represents this motion. The Raman results for the ground and excited states of $Re_2Cl_8^{2-}$ are summarized in Table I.

Discussion

Studies of the resolved vibronic absorption spectra[8,9] of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ have been reported, as have resolved emission spectra[10] of $Re_2Cl_8^{2-}$. The latter account pointed out the mirror relationship between the vibronic progressions observed in the absorption and emission spectra of the chloro complex. This was presented as strong evidence that the $\delta\delta^*$ excited state of this complex is not greatly distorted from its ground-state nuclear coordinates, in particular that no symmetry-breaking torsional distortion occurs. These conclusions apply specifically, however, to the crystalline solid. In $Re_2Cl_8^{2-}$, both ground-state (emission) and excited-state (absorption) progressions were observed, with two prominent progression frequencies in each. These were assigned to the Re–Re stretch (275 cm^{-1} in emission and 249 cm^{-1} in absorption) and the Re–Re–Cl symmetric angle bend (158 cm^{-1} in emission and 137 cm^{-1} in absorption). The $Re_2Br_8^{2-}$ spectra were more complicated to interpret and only absorption (excited-state) data were reported. However, an excited-state Re–Re stretching frequency of 252 ± 4 cm^{-1} appears consistent with both studies.[8,9] In addition, a progression at 98 cm^{-1} was reported[9] and assigned as the excited-state Re–Re–Br symmetric angle bend. These vibronic frequencies are summarized along with the Raman data in Table I.

Since the same three symmetric vibrations are Raman active in both staggered (D_{4d} or D_4) and eclipsed (D_{4h}) geometries, the excited-state structure cannot be elucidated definitively from the number and polarization of the Raman-active modes in the TR³ spectra. However, the vibrational frequencies provide clear evidence for a difference between the ground- and excited-state structures involving both torsion about the Re–Re bond and changes in the Re–Re distance. The symmetric Re–Re stretch of the excited state is seen at 262 cm^{-1} in both $^*Re_2Cl_8^{2-}$ and $^*Re_2Br_8^{2-}$, intermediate between the vibronic excited-state frequencies of 249 cm^{-1} (Cl) and 252 cm^{-1} (Br) and the ground-state frequencies of 274 and 275 cm^{-1} for the two complexes. The differences between the values for the Re–Re stretch for $^*Re_2X_8^{2-}$ determined by TR³ spectroscopy and by the vibronic analyses[8,10] are definitely experimentally significant. In previous TR³ studies of d^8 dimer systems, the TR³ and vibronic results agreed within 1–2 cm^{-1}.[4,5] When interpreting the difference between the TR³ and vibronic Re–Re stretching frequencies in the $\delta\delta^*$ excited state, one must realize that the vibronic experiment takes place in a single-crystal environment at cryogenic temperatures, where crystal constraints may preclude torsional distortion. Indeed, the mirror symmetry observed between the resolved absorption and emission spectra[10] suggests that such distortion does not occur in crystals of $Re_2Cl_8^{2-}$. The TR³ experiment, on the other hand, allows nanoseconds to pass between creation of the $\delta\delta^*$ state and Raman scattering by the excited state. Accordingly, the vibrational spectrum recorded by TR³ spectroscopy belongs to the fully relaxed (equilibrium) nuclear coordinates of the excited-state molecule unconstrained by the crystalline environment. Therefore, the vibronic experiment might probe the eclipsed-halide geometry of the excited state, while in the TR³ experiment the complex has had a chance to distort toward a staggered position—if indeed it does so. In the $Mo_2Cl_4(PMe_3)_4$ complex (Table I), which is sterically precluded by the bulky alternating phosphine ligands from undergoing torsional distortion in crystal or solution, both the TR³ and vibronic experiments probe the same (eclipsed) structure.

We interpret the TR³ and vibronic results as evidence that the torsional distortion does in fact occur in the relaxed $\delta\delta^*$ state of the Re dimers. This interpretation is consistent with earlier conclusions from fluorescence measurements.[13] We suggest that the Re–Re frequencies in the vibronic experiment (249 and 252 cm^{-1}) are lower than in the TR^3 experiment (262 cm^{-1}) because the eclipsed halides maintained by crystal constraints in the former case sterically prevent the metal atoms from assuming a metal–metal distance as short as they are permitted to in the staggered conformation allowed by the solution conditions and the time scale of the latter. The frequencies reflect these differing bond distances. Using Woodruff's rule,[20,21] we can calculate the changes in the Re–Re bond length for *Re$_2$Cl$_8^{2-}$ compared to the ground state.[22] The ground-state, TR^3, and vibronic metal–metal frequencies of 274, 262, and 249 cm^{-1} yield bond distances of 2.239, 2.276, and 2.320 Å, respectively. Thus, we estimate that the relaxed, staggered (solution TR^3) excited-state metal–metal distance is 0.037 Å longer than the ground-state distance, while the eclipsed (single-crystal vibronic) excited-state distance 0.081 Å longer than that of the ground state. In our view, the eclipsed halides constrain the excited-state bond distance to be approximately 0.04 Å longer than it is in the relaxed, staggered structure.

The decrease in formal Re–Re bond order from 4 to 3 upon $\delta \rightarrow \delta^*$ excitation has the expected effect of increasing the Re–Re bond distance. A similar effect of diminished bond order is noted in the Mo dimer (Table I). In this complex, however, the excited-state Mo–Mo frequencies are the same whether measured by TR^3 spectroscopy or by vibronic methods. This fact is consistent with the Re$_2$X$_8^{2-}$ results in that, because the Mo dimer is sterically prevented from undergoing torsional distortion, the TR^3 and vibronic experiments probe essentially the same structure and therefore give the same excited-state Mo–Mo stretching frequency.

The vibronic and TR^3 frequencies of the $\delta\delta^*$ excited states of the two Re$_2$X$_8^{2-}$ complexes are summarized in Table I, along with the ground-state resonance Raman frequencies and the ground-state vibronic frequencies (Re$_2$Cl$_8^{2-}$ only). The systematic differences between the vibronic and TR^3 excited-state frequencies are evident not only in the Re–Re stretch but in the Re–Re–X angle bend as well. The Re–Re–X frequencies provide essentially the same information as the Re–Re stretches; indeed, these two quantities are approximately linearly related for all of the observations tabulated (δ(MMX)/ν(MM) $\approx$ 0.40 for Re$_2$Br$_8^{2-}$ and 0.56 for Re$_2$Cl$_8^{2-}$), as expected for stretching and angle bending vibrations belonging to the same Re–Re–X structure. While the vibronic data on Re$_2$Cl$_8^{2-}$ suggest an eclipsed-halide (D_{4h}) excited-state structure in the crystal, the TR^3 data suggest that the relaxed structure of the excited state in solution differs from that in the crystal. The arguments presented above lead us to infer that substantial torsional distortion, probably to D_4 or D_{4d} symmetry, occurs upon excitation in solution. The quadruply bonded complexes appear to be systems in which the environment strongly influences excited-state structure and, inferentially, affects the photochemistry that the excited state may undergo. The importance of TR^3 spectroscopy in probing these excited-state structures under chemically relevant conditions is clearly demonstrated by this work.

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High-Pressure Micro-Raman Study of Crystalline Tricarbonyl(η^5-cyclopentadienyl)rhenium(I), (η^5-C$_5$H$_5$)Re(CO)$_3$

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Micro-Raman spectra of crystalline CpRe(CO)$_3$ (Cp = η^5-C$_5$H$_5$) have been recorded at several different pressures up to 40 kbar. The discontinuities observed for most of the fundamentals at about 9 kbar in the slopes of the wavenumber/pressure (ν_i/P) plots suggest the occurrence of a phase transition. The pressure dependences of the CO and Re–CO stretching modes indicate that the back-bonding interactions between the Re atom and the CO groups are appreciably strengthened by increasing external pressure in the low-pressure phase, most probably due to increased charge transfer from the Cp ring to the metal. The effects of pressure on several of the fundamental modes are discussed in terms of intra- and intermolecular interactions.

Introduction

The use of pressure as an independent variable to examine the phase behavior of organometallic carbonyl compounds is of particular importance, since many of these compounds do not exhibit phase transitions on lowering the temperature but may do so when high external pressures are applied.[1-5] These pressure studies are usually performed by using diamond-anvil cells in which the samples are squeezed together between the parallel faces of two diamonds. Diamond-anvil cell Raman spectroscopy is an extremely useful technique for studying this class of compounds because the CO stretching region (ca. 2000 cm^{-1}) is free from interference from the background fluorescence arising from the diamonds. This is an important spectral region for pressure work because it has recently been shown that metal–CO interactions and the molecular geometry of metal carbonyl compounds are

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