which is being obtained for the first time through the application of resonance Raman spectroscopy to visual pigments.[1–5,7]

Note Added in Proof. As mentioned in the text of the paper, ground-state resonance structures are important in predicting the ground-state vibrational frequencies observed but not the observed intensities. Our recent data on unprotonated Schiff bases support this hypothesis. These results show, for example, that the C—CH_3 vibrational frequencies move from 1005 cm^{-1} in crystalline *all-trans*-retinal (which has an electron-withdrawing terminal carbonyl) to 1012 cm^{-1} in crystalline *all-trans-N*-retinylidene-*n*-butylamine in which the terminal oxygen has been replaced by an *n*-butylamine group. The *n*-butylamine group has a reduced electron affinity relative to oxygen. This reduces the δ^+ character on C_5, C_9, and C_{13} by making resonance structures II–IV less likely (see Figure 4), thus increasing the C-CH_3 vibrational frequencies.

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Resonance Raman Spectra of Tetra(*n*-butylammonium) Salts of the Octachlorodirhenate(III) and Octabromodirhenate(III) Ions

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Abstract: The metal-metal bonded species $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$ both display a resonance Raman spectrum when irradiated in the solid state with exciting lines which approach the wavenumber (ca. 14 000 cm^{-1}) of the $\delta^* \leftarrow \delta$ electronic band maximum of each anion. Two overtone progressions in the metal-metal stretching frequency, ν_1(Re–Re)a_{1g}, have been observed for each ion; these reach $4\nu_1$ for the first and $\nu_2 + 2\nu_1$ for the second, where ν_2 is the ν_2(Re–X)a_{1g} fundamental (X = Cl or Br). Further members of these progressions were obscured by strong underlying fluorescence. The results indicate that the resonant electronic transition is electric dipole allowed. The members of each overtone progression are seen to decrease in intensity and increase in half-bandwidth with increase in the vibrational quantum number of the ν_1 fundamental. The observation of overtone progressions permits the determination of the spectroscopic constants ω_1 and x_{11} for each anion. By use of a tunable dye laser, partial excitation profiles of various fundamentals of the octahalodirhenate ions have also been determined.

It is now well established that under conditions in which a molecule is excited with a laser line whose frequency corresponds or closely corresponds with the band maximum of an allowed electronic transition, a resonance Raman (RR) spectrum may be obtained. Such spectra are characterized by a large increase in the intensity of a totally symmetric fundamental of the scattering molecule, together with the appearance of high-intensity overtone progressions in this same fundamental.[1–6]

Metal-metal bonded complexes are known to display the RR effect, partly because of the highly polarizable nature of many metal-metal bonds, especially where multiple, and partly because of their generally low-lying, and therefore accessible, allowed electronic transitions. A previous RR study of the $Mo_2Cl_8^{4-}$ ion has shown[7,8] that long overtone progressions in the ν_1(Mo–Mo)a_{1g} fundamental may be observed by exciting a Raman spectrum of the ion with a laser line which corresponds in wavenumber (actually ca. 19 000 cm^{-1}) with that of the intense "metal-metal" transition $2b_{1u} \leftarrow 2b_{2g}$ ($\delta^* \leftarrow \delta$)[8–10] of the ion. The isoelectronic and isostructural $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions also possess an intense electronic transition in the visible region (at ca. 14 000 cm^{-1}).[11,12] This band was originally considered to arise from the $^1a_{2u} \leftarrow {}^1b_{2g}$ ($\sigma_n(1) \leftarrow \delta$) transition,[13] and thus be electric dipole forbidden, but recent single crystal electronic studies[12] and X_α scattered wave calculations[14] indicate that is is correctly assigned as the $2b_{1u} \leftarrow 2b_{2g}$ ($\delta^* \leftarrow \delta$) transition; the latter would be an electric dipole allowed transition of the Mulliken charge transfer type.[15] In so far as RR spectra have only been observed,[6] and are only ex-

Table I. Infrared and Raman Bands in the Spectra of $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$ in the Solid State (cm^{-1})[a,b]

	$[(C_4H_9)_4N]_2Re_2Cl_8$		$[(C_4H_9)_4N]_2Re_2Br_8$	
Assignment	R	Ir	R	Ir
ν(Re-Cl)	356.5 m			
		346 s		
		338 sh		
	327.7 w	332 s		(332 vw)?
	310.1 w			
	295.0 w	296 w		
	255.7 m			
ν(Re-Re)	271.9 vs		275.4 s	275 vw
ν(Re-Br)			240.6 m	234 vs
				220 m
			209.8 vs	
			191.6 m	
Skeletal bends and lattice modes	184.5 m		154.8 m	
		165 m		126 w(sh)
		155 w		112 m
		125 vw		82 w
		98 vw?		
		92 vw		
		68 w?		68 w?
		49 m		
		42 m		

[a] Qualitative intensities: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Other spectral bands due to fundamentals of the cation.

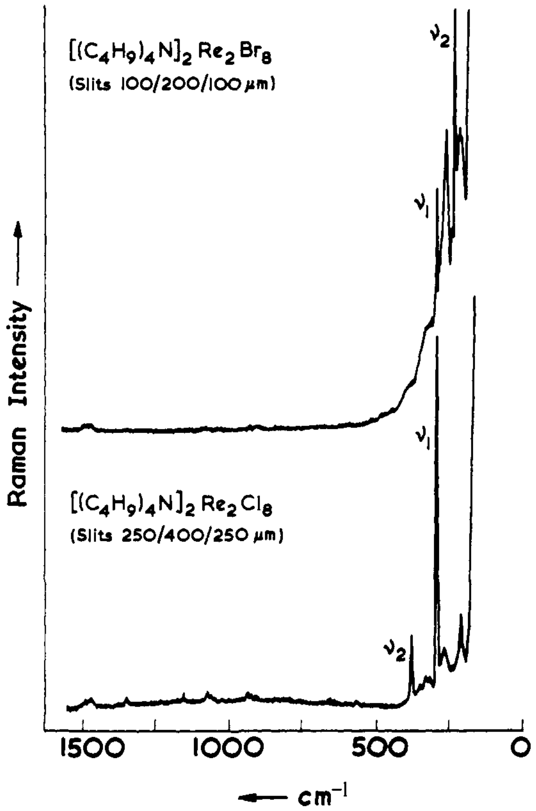

Figure 1. Raman spectra of $[(C_4H_9)_4N]_2Re_2Br_8$ and $[(C_4H_9)_4N]_2Re_2Cl_8$ obtained with Ar^+ 514.5-nm excitation, slit widths as shown.

pected to be observed[16] for scattering species in which the resonant electronic transition is electric dipole allowed, RR spectroscopy would thus appear to offer an unambiguous technique for the confirmation of the assignment of the 14 000-cm^{-1} band of these interesting ions. In the present investigation, therefore, the Raman spectra of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions have been investigated with a variety of different exciting lines in the vicinity of the 14 000-cm^{-1} electronic transition of each ion. RR spectra have been observed for each ion, specifically overtone progressions in the $\nu_1(Re-Re)a_{1g}$ fundamental. The observation of these overtone progressions thus (a) provides clear confirmation that the 14 000-cm^{-1} electronic transition is electric dipole allowed and (b) makes possible the determination of the spectroscopic constants ω_1 and x_{11} for the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions for comparison with those of the $Mo_2Cl_8^{4-}$ and other ions. Partial excitation profiles for several fundamentals have also been established.

Experimental Section

Preparation of Samples. The tetra-*n*-butylammonium salts were found suitable for Raman spectral investigation and were prepared by literature methods.[17]

Instrumental Details. The Raman spectra were recorded by use of a Spex 1401 spectrometer in conjunction with Coherent Radiation Model 52 Ar^+ and Kr^+ lasers, and a Coherent Radiation Model 490 dye laser equipped with rhodamine 6G. The scattered radiation was collected at 90° and focussed by a *f*/0.95 lens on to the entrance slit of the monochromator after having been passed through a polarization scrambler. The 0.75-m Czerny-Turner monochromator employed two 1200 lines/mm Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with a cooled, grade I, RCA C31034 phototube (linear display). The power available at 457.9, 488.0, 514.5, 568.2, and 647.1 nm was 300 mW, 1.5 W, 1.8 W, 100 mW, and 500 mW, respectively. Using the dye laser, exciting wavelengths between 580 and 630 nm were used for which the power lay in the 100–500-mW range (maximum at 605 nm). For all excitation wavelengths extraneous emission lines were removed by use of a Claassen filter and associated beam expander. The spectra were calibrated by reference to the emission lines of neon which were superimposed directly onto the spectra while they were recorded. The rotating sample technique[6,18,19] was used in order to minimize thermal decomposition of the sample at the beam focus.

Band areas were determined by the cut-and-weigh procedure and then corrected for the relative spectral response of the instrument as described previously.[20]

The diffuse reflectance spectra of the powdered solids were recorded by use of a Cary 14 spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer (to 200 cm^{-1}) as Nujol mulls, and on a R.I.I.C. interferometer (200–20 cm^{-1}) as paraffin wax disks (P.C.M.U. Service, Harwell). In the latter case, spectra were recorded for 10–21 mg of compound to 100–300 mg of paraffin wax in 13- or 25-mm disks.

Results and Discussion

Raman Spectra. The Raman spectrum of each complex is found to depend markedly on the wavenumber (ν_0) of the exciting line. With the 457.9, 488.0, and 514.5 nm exciting lines, which are all far removed from the lowest allowed electronic transition of both anions (ν_e),[11,12] a normal Raman spectrum is obtained (see Figure 1, Table I), similar to that reported by San Fillippo and Sniadoch[21] but differing substantially from that reported by Bratton et al.[22] However, the Kr^+ 647.1 nm exciting line approaches closely the first electronic band maximum of these compounds (electronic origins 14 183 cm^{-1} for $[(C_4H_9)_4N]_2Re_2Cl_8$ and 13 597 cm^{-1} for $[(C_4H_9)_4N]_2Re_2Br_8$).[12] Consequently, as indicated earlier, a RR spectrum might be expected to be observed with this exciting line. Unfortunately, the underlying fluorescence background is very intense from both ions

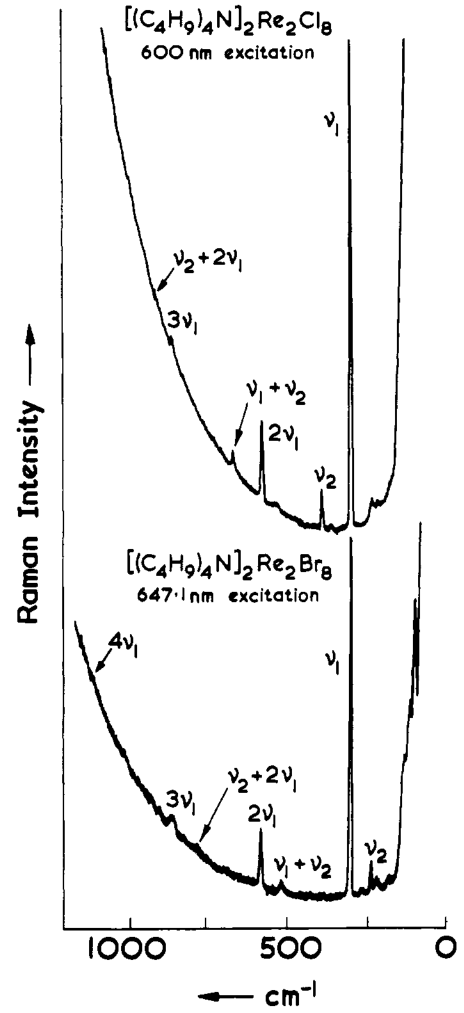

Figure 2. Resonance Raman spectra of $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$ obtained with 600.0-nm and 647.1-nm excitation, respectively, slit widths 300/400/300 μm.

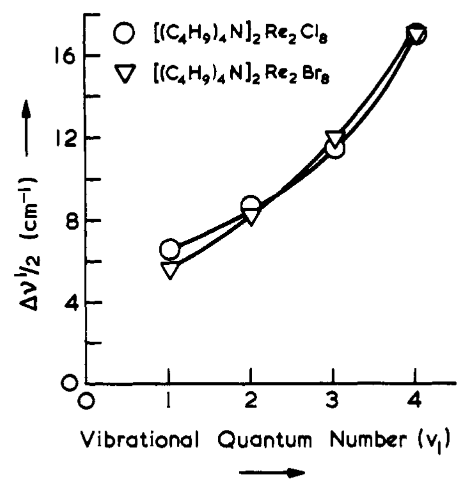

Figure 3. Half-bandwidths for the $\nu_1(a_{1g})$ fundamental and its overtones observed in the resonance Raman spectra of $[(C_4H_9)N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$.

Table II. Wavenumbers and Half-Bandwidths of the ν(Re–Re), $\nu_1(a_{1g})$ Fundamental and Its Overtones and the Members of the $\nu_2 + v_1\nu_1$ Progression in the RR Spectra of the Tetra-*n*-butylammonium Salts of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ Ions (cm^{-1})[a]

	$[(C_4H_9)_4N]_2Re_2Cl_8$		$[(C_4H_9)_4N]_2Re_2Br_8$	
Band	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$
ν_1	271.9	6.5	275.4	5.5
$2\nu_1$	542.7	8.5	549.9	8.5
$3\nu_1$	813.8	11.5	823.9	12
$4\nu_1$	1083	17	1097	17
ν_2	356.5	8.5	209.8	6.0
$\nu_2 + \nu_1$	629.3	10	485.2	10
$\nu_2 + 2\nu_1$	900	15.5	759	16

[a] Other bands of higher frequency observed in the spectra are due to fundamentals of the cation.

when excited with 647.1-nm excitation. Thus in the case of the $Re_2Cl_8^{2-}$ ion, no Raman spectrum could be observed with this line,[23] but in the case of the $Re_2Br_8^{2-}$ ion (for which ν_0-ν_e is greater) a RR spectrum was indeed observed. This spectrum was characterized by an enormous intensity enhancement in the rhenium-rhenium stretching fundamental, $\nu_1(a_{1g})$,[22] for which the depolarization ratio $\rho \approx 0.0$, and the appearance of an overtone progression in ν_1 as far as $4\nu_1$.

A RR spectrum of the $Re_2Cl_8^{2-}$ ion could only be obtained by use of a slightly shorter wavelength exciting line λ_0, i.e., perversely one for which ν_0-ν_e was greater than for 647.1-nm excitation. This was because the intensity of the underlying fluorescence background diminished by this change much more rapidly than that of the RR spectrum, which was accordingly then revealed. The appropriate exciting wavelength was obtained by use of a dye laser in conjunction with rhodamine 6G (pumped by an Ar^+ laser, all-wave power 4 W). By this procedure, RR spectra of the $Re_2Cl_8^{2-}$ ion have been obtained for the range λ_0 = 580–615 nm and of the $Re_2Br_8^{2-}$ ion for the range λ_0 = 580–630 nm and 647.1 nm. The RR spectra of the $Re_2Cl_8^{2-}$ ion (600-nm excitation) and $Re_2Br_8^{2-}$ ion (647.1-nm excitation) are illustrated in Figure 2, and the wavenumbers and half-bandwidths of the ν_1(Re–Re) fundamental and its overtones are given in Table II.

Measurements of the depolarization ratio indicate that it is a totally symmetric fundamental which displays the RR effect, in agreement with the theory of Nafie et al.,[2] and in addition the overtones in both cases display other characteristic features of the RR effect, i.e., continuous increase in half-bandwidth (as shown in Figure 3) and continuous decrease in band area with increase in vibrational quantum number. Similar effects have been observed recently for spectra of, for example, the $Mo_2Cl_8^{4-}$ ion,[8] the $AuBr_4^-$ ion,[24] and the S_3^- ion,[25] and the subject has been discussed theoretically by Kobinata.[26]

A second, much weaker, progression ($\nu_2 + v_1\nu_1$) is also evident in the RR spectra of both compounds as far as $v_1 = 2$. The frequencies and half-bandwidths for each member of this progression are also given in Table II. The fundamental ν_2 (356.5 cm^{-1} for the chloride, 210 cm^{-1} for the bromide) is polarized (ρ = 0.01 for both ions in acetone solution) and thus is correctly assigned as $\nu(ReX)a_{1g}$ in each case.

Harmonic Frequencies and Anharmonicity Constants. The observation of a number of overtones of the ν_1(Re–Re)a_{1g} fundamental in the RR spectrum of each compound makes it possible to determine the harmonic frequency (ω_1) and the anharmonicity constant (x_{11}). The observed wavenumber $\nu(v_1)$ of any overtone of an anharmonic oscillator is given by the expression[27]

$$\nu(v_1) = G(v_1) - G(0)$$

$$\nu(v_1) = v_1\omega_1 - x_{11}(v_1^2 + v_1) + \text{higher terms}$$

where $G(v_1)$ is the term value of the v_1th vibrational level.

Table III. Harmonic Frequencies[a] and Anharmonicity Constants for the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ Ions (cm^{-1})

$[(C_4H_9)_4N]_2Re_2Cl_8$		$[(C_4H_9)_4N]_2Re_2Br_8$	
ω_1	x_{11}	ω_1	x_{11}
272.6 ± 0.4	0.35 ± 0.05	276.2 ± 0.5	0.39 ± 0.06

[a] We have adopted the standard procedure for obtaining these parameters. It should be noted, however, that the harmonic frequencies will be slightly in error owing to the ignoring of cross terms in the potential function.

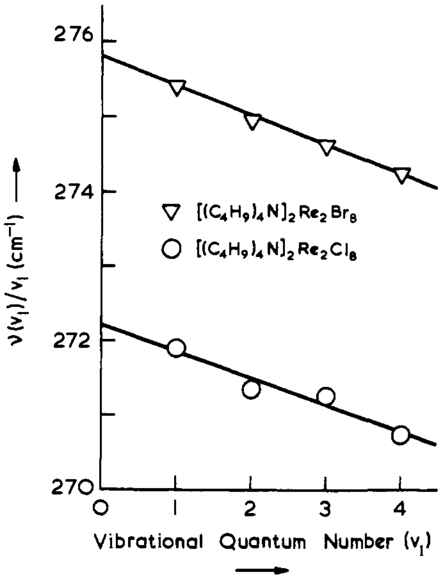

Figure 4. Plot of $\nu(v_1)/v_1$ vs. v_1 for the ν_1(Re-Re)a_{1g} fundamental and its overtones for $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$.

Hence ω_1 and x_{11} may be deduced from a plot of $\nu(v_1)/v_1$ vs. v_1. The experimental results for both compounds are shown in Figure 4 and the results of the least-squares analysis are shown in Table III.

The x_{11} values are both small, and thus as in the case of previous results on fundamentals displaying the RR effect,[6] the ν_1 mode is close to behaving as a harmonic oscillator. It should also be noted that these values are significantly smaller than those obtained for the ν_1(Mo-Mo)a_{1g} fundamental of the $Mo_2Cl_8^{4-}$ ion, which are in the range 0.59 ± 0.17 cm^{-1}. No attempt was made to determine values of ω_1 and x_{11} from the $\nu_2 + v_1\nu_1$ progression as insufficient data points were available.

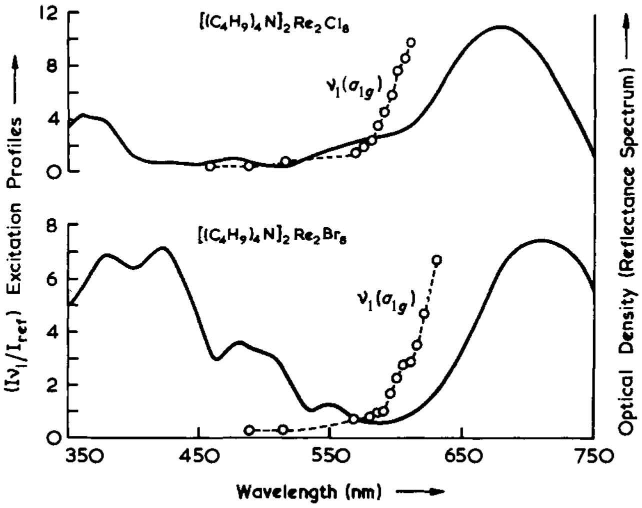

Figure 5. Diffuse reflectance spectra of $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2RE_2Br_8$ (full lines) together with the excitation profiles (dashed lines) for the ν_1(Re-Re)a_{1g} fundamental for each anion.

Band Intensities. The intensities of the four observed Raman-active stretching fundamentals of the $Re_2Br_8^{2-}$ ion were measured relative to that of the 980-cm^{-1} band of potassium sulfate as internal standard. The relative intensities of each band at each exciting frequency, after correction for the spectral response of the instrument, are given in Table IV. This table also gives the intensity of the ν_1(Re-Re)a_{1g} fundamental of the $Re_2Cl_8^{2-}$ ion relative to sulfate. In addition the intensity of the first overtone of the $\nu_1(a_{1g})$ fundamental was measured relative to that of the fundamental itself for both the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions for each exciting frequency used and these relative intensities are given in Table V. The results indicate that the intensity of the first overtone increases more rapidly than the fundamental

Table IV. Intensities of Raman Bands of the Complexes $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$ Relative to the 980-cm^{-1} Band of Sulfate as Internal Standard at Different Exciting Wavelengths[a]

	$[(C_4H_9)_4N]_2Re_2Br_8$				$[(C_4H_9)_4N]_2Re_2Cl_8$
Exciting wavelength, nm	$I[\nu_1(a_{1g})]/I_{SO_4^{2-}}$	$I[\nu_2(a_{1g})]/I_{SO_4^{2-}}$	$I[240.6\ cm^{-1}]/I_{SO_4^{2-}}$[b]	$I[191.6\ cm^{-1}]/I_{SO_4^{2-}}$[b]	$I[\nu_1(a_{1g})]/I_{SO_4^{2-}}$
457.9	0.2_5	0.7_5	0.0_5	0.1	0.5
488.0	0.2_5	0.8_5	0.0_5	0.1	0.6
514.5	0.2_5	0.6	0.1	0.1	0.9
568.2	0.7_5	1.1	0.1	0.1	1.5
580.0	0.7_5	0.6	0.1	0.1	2.5_5
585.0	0.9_5	0.9	0.1	0.1	3.5
590.0	0.9_5	0.8	0.1	0.1	4.6
595.0	1.7	1.1	0.1	0.1_5	5.7
600.0	2.2_5	1.2	0.1_5	0.2	7.7
605.0	2.6	1.2	0.1_5	0.4_5	8.5
610.0	2.6	1.0_5	0.2_5	0.5_5	9.8
615.0	3.5	0.9	0.2_5	0.6	
620.0	4.7	1.1	0.2	0.7	
630.0	6.7	0.9_5	0.2_5	0.5	

[a]Corrected for spectral response. [b] The 240.6- and 191.6-cm^{-1} bands are the b_{1g} and e_g rhenium-bromine stretching vibrations, although it is not clear which is which.

Table V. Intensity of First Overtone of ν_1(Re–Re)(a_{1g}) Relative to the Fundamental for $[(C_4H_9)_4N]_2Re_2Cl_8$ and $[(C_4H_9)_4N]_2Re_2Br_8$ as a Function of Exciting Wavelength[a]

Exciting wavelength, nm	$[(C_4H_9)_4N]_2$-Re_2Cl_8[b] $I(2\nu_1)/I(\nu_1)$	$[(C_4H_9)_4N]_2$-Re_2Br_8[c] $I(2\nu_1)/I(\nu_1)$
580.0	0.09	
585.0	0.14	0.12
590.0	0.16	0.14
595.0	0.18	0.13
600.0	0.17	0.13
605.0	0.20	0.15
610.0	0.21	0.15
615.0	0.22	0.16
620.0		0.17
630.0		0.20
647.1		0.31

[a] Corrected for spectral response. [b] The maximum of the $\delta^* \leftarrow \delta$ electronic band occurs at 14 500 cm^{-1} (ϵ = 1530) for a methanol solution of the complex $[(C_4H_9)_4N]_2Re_2Cl_8$: F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965). [c] The maximum of the $\delta^* \leftarrow \delta$ electronic band occurs at 14 100 cm^{-1} by diffuse reflectance for the complex $[(C_4H_9)_4N]_2Re_2Br_8$ (this work).

as ν_0 approaches ν_e, this being another common characteristic of the RR effect. The diffuse reflectance spectra of both complexes are shown in Figure 5, together with plots of the relative Raman intensity of the $\nu_1(a_{1g})$ fundamental at each exciting frequency used (excitation profiles).

It is clear from Table IV that the only band which shows any marked difference in intensity as the exciting frequency changes is that assigned to the ν_1(Re–Re)a_{1g} fundamental. Not even the ν_2(Re–Cl)a_{1g} vibration shows any enhancement when ν_0 approaches ν_e. Thus it is clear that in RR spectroscopy the fundamental displaying the RR effect is that associated with the bonds most affected by the electronic transition. The excitation profile of the $\nu_1(a_{1g})$ band is quite similar to the diffuse reflectance spectrum in the region studied but unfortunately it is not possible to carry out a detailed plotting of the excitation profile as at the moment no means of measuring the spectrum in the region 650–680 nm excitation is available in our laboratory. The use of the dyes cresyl violet and rhodamine B in conjunction with a powerful pump source should permit a more detailed investigation at a later date.

Conclusion

The quadruply bonded ions $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ are shown to display a striking RR spectrum when excited with radiation in the vicinity of the 14 000-cm^{-1} electronic transition, progressions in ν(ReRe) being the characteristic feature of each spectrum. The results indicate clearly that the resonant electronic transition is electric dipole allowed, in agreement with recent single crystal electronic spectral measurements and with X_α scattered wave calculations.

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