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Contribution from the Christopher Ingold Laboratories,
University College London, London, England WC1H 0AJ

Resonance Raman and Electronic Spectral Study of the Octafluoro-, Octachloro-, Octabromo-, and Octaiododirhenate(III) Ions. Resonance Raman Spectra and Excitation Profiles at Resonance with the $\delta^* \leftarrow \delta$, $\delta^* \leftarrow (X)\pi$, and Putative $\pi^* \leftarrow \pi$ Bands

ROBIN J. H. CLARK* and MARTIN J. STEAD

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The effects on the resonance Raman spectra of excitation within the contours of the accessible $\delta^* \leftarrow \delta$, $\delta^* \leftarrow (X)\pi$, and putative $\pi^* \leftarrow \pi$ electronic transitions of the $[Re_2X_8]^{2-}$ species (where X = F, Cl, Br, I) are described. A progression in ν_1, the Re–Re stretching mode, dominates the resonance Raman spectrum of each ion at resonance with the $\delta^* \leftarrow \delta$ transition; a progression in ν_2, the Re–X symmetric stretching mode, dominates at resonance with the $\delta^* \leftarrow (X)\pi$ transition, while progressions in both ν_1 and ν_2 are clearly evident at resonance with the putative $\pi^* \leftarrow \pi$ transition. These results, together with Raman-band depolarization ratio measurements, confirm the conclusions of recent Xα–SCF scattered-wave calculations as to the assignments of the electronic bands of the $[Re_2Cl_8]^{2-}$ ion and lead to consistent band assignments for the $[Re_2F_8]^{2-}$, $[Re_2Br_8]^{2-}$, and $[Re_2I_8]^{2-}$ ions. The unusually large intensity of a band assigned to a non totally symmetric bending mode observed in the Raman spectra of the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions at resonance with the $\delta^* \leftarrow (X)\pi$ transition in each case is interpreted in terms of Jahn–Teller coupling between the components of the ^1E_u excited state.

Over the past 20 years a wide variety of homo- and heteronuclear metal–metal bonded complexes has been synthesized.[1] Much of the interest has focused on multiple bonds in simple molecules and ions, the $[Re_2Cl_8]^{2-}$ ion being a typical example. The structural features of this and related species have been investigated by using X-ray crystallography[2] and infrared,[3,5] Raman,[4,5] resonance Raman,[6] and single-crystal low-temperature electronic spectroscopy.[7] Theoretical approaches to the bonding in $[Re_2Cl_8]^{2-}$ came first from extended Hückel[8] and later from Xα–SCF scattered-wave calculations.[9] Early disagreements as to the assignments of the absorption bands in the electronic spectrum of $[Re_2Cl_8]^{2-}$[7,10] have now been resolved,[6,11] and work on the weaker bands in the electronic spectrum[11] has led to a fairly complete description of the electronic transitions in this complex ion. The SCF–Xα–SW relativistic work on the $[Re_2Cl_8]^{2-}$ ion gives greatly improved agreement between the observed and calculated electronic spectra of the ion,[12] as does the relativistic generalized valence-bond calculation using pseudopotentials for core orbitals.[13] Since the original Raman studies on the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions, an increase in the range of exciting radiation available and high-yielding and convenient syntheses of the analogous fluoride and iodide[14,15] have made it possible to extend considerably the vibrational spectroscopic data on these ions. The aim of the work is to obtain resonance Raman spectra of the $[Re_2X_8]^{2-}$ ions with excitation wavelengths in the regions of those of the lowest allowed transitions in each case and then to interpret the spectra in terms both of current theories of the resonance Raman effect and of the current theoretical model of the electronic structures and bonding in the complexes. A logical assignment to the electronic spectra of the $[Re_2F_8]^{2-}$ and $[Re_2I_8]^{2-}$ ions emerges from the analysis. Some features of the present study have appeared in preliminary form.[16]

Experimental Section

Preparative Details. The tetrabutylammonium salts were prepared by literature methods.[14,15,17] When the iodide was recrystallized under nitrogen, particular difficulties were experienced in removing any I_3^- present, and some traces of it were detected later during resonance Raman experiments. The I_3^- ion is an excellent resonance Raman scatterer when irradiated with blue or ultraviolet laser light, and even small quantities of it can obscure the spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$. Anal. Calcd for $[(n\text{-}C_4H_9)_4N]_2[Re_2F_8]$: C, 38.0; H, 7.10; N, 2.78. Found: C, 37.9; H, 6.71; N, 2.69. Calcd for $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$: C, 33.6; H, 6.35; N, 2.46; Cl, 24.9. Found: C, 33.4; H, 6.42; H, 2.42; Cl, 24.5. Calcd for $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$: C, 25.7; H, 4.83; N, 1.87; Br, 42.7. Found: C, 25.4; H, 4.83; N, 1.85; Br, 42.1. Calcd for $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$: C, 20.5; H, 3.87; N, 1.49; I. 54.2. Found: C, 20.6; H, 3.89; N, 1.39; I, 54.0.

Instrumental Details. The Raman spectra were recorded with a Spex 1401 spectrometer for the red and near-infrared regions and a Spex 14018/R6 for the blue and ultraviolet regions. Observations of bands at less than 200 cm^{-1} were carried out with the Spex 14018/R6 spectrometer in the triple mode where necessary in order to minimize stray light. Exciting radiation was provided by Coherent Radiation Models CR3, CR500K, CR15UV, and CR3000K lasers and a CR 599 dye laser employing the dye LD 700. Resonance Raman excitation profiles for complexes pressed into potassium sulfate disks were obtained at a nominal 14 K using an Air Products Displex system in conjunction with a Leybold-Heraeus turbomolecular pump. It should be noted that the temperature measured on the cryotip will be lower than that at the point of focus of the laser beam on the sample. Raman-band wavenumber measurements were made on the complexes pressed into disks with the appropriate alkali halide and held at ca. 80 K. Depolarization ratios were based on single $I_\parallel$ and $I_\perp$ scans for intense bands but on up to 30 repeat scans for weak bands, the latter

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Table I. Infrared Spectral Data[a] for the Complexes $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ for X = F, Cl, Br, and I

X = F	X = Cl	X = Br	X = I	
568 vs	347 m			str modes
560 s	338 sh	232 vs	178 vs	
552 s	332 vs	220 m	162 wm	
	295 w		138 vw?	
243 m	165 m	112 m		bending modes
225 m	154 w			
	126 vw			
	95 w			

[a] Values are in cm^{-1}.

Table II. Band Maxima[a] Observed for the Electronic Spectra of the Complexes $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ for X = F, Cl, Br, and 1

assignt[b]	F	Cl	Br	I
$b_{1u}(\delta^*) \leftarrow b_{2g}(\delta)$ (z)	17 900	14 000	14 000	13 000
$b_{1u}(\delta^*) \leftarrow e_g((X)\pi)$ (x, y)	?	30 800	23 800	14 800
$e_g(\pi^*) \leftarrow e_u(\pi)$ (z)	?	39 200	26 000	19 400

[a] Values are in cm^{-1}. [b] Polarizations are indicated in parentheses.

measurements being carried out with a Nicolet 1180 computer.

Electronic spectra, with the complex pressed into an appropriate alkali halide disk, were recorded at ca. 14 and 295 K, with a Cary 14 spectrometer.

Infrared spectra were obtained with a Perkin-Elmer 225 spectrometer, the complexes being pressed into appropriate cesium halide disks, and with a Nicolet 7199 Fourier transform interferometer (courtesy of Dr. P. L. Goggin), the complexes being suspended in a Fluorolube or Nujol mull between thin polythene plates. All infrared measurements were performed on samples held at room temperature.

Results

Infrared Spectroscopy. Neither the analytical data nor the infrared spectrum of the fluoride provides any evidence for the presence of water in the complex, which is, therefore, contrary to the previous report,[14] believed to be anhydrous. The spectra are as previously reported for the chloride and bromide,[3,5] but in the case of the iodide,[15] two additional weaker bands were also observed. Unfortunately, no bending modes could be assigned for the iodide as observations were limited to the region above 70 cm^{-1}. The infrared data are given in Table I, together with proposed assignments.[5]

The wavenumbers for the Re–Cl and Re–Br asymmetric stretching vibrations are similar to those reported by Ware[18] for $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ (313 and 217 cm^{-1}, respectively). Bands attributable to bending modes were observed around 160 cm^{-1} for $[Re_2Cl_8]^{2-}$ and 112 cm^{-1} for $[Re_2Br_8]^{2-}$, which compare closely with values found for the bending frequencies of $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$ (172 and 118 cm^{-1}, respectively).[18] For $[Re_2I_8]^{2-}$, bands attributable to stretching vibrations were observed at 178, 162, and 138 cm^{-1}; they are close to the value of 186 cm^{-1} found for the $\nu_3(t_{1u})$ stretching vibration[19] of $[PtI_6]^{2-}$.

Table III. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of the Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2F_8]$ at 77 K by Using . 530.9-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
180.7	8	3	
231.6	8	3	
317.8	4	100	ν_1
501.5		1	$\nu_1 + 180.7$
623.5	4	3	ν_2
636.4	6	37	$2\nu_1$
769.5	6	3	
816		1	$2\nu_1 + 180.7$
941.2	6	3	$\nu_1 + \nu_2$
953.8	8	12	$3\nu_1$
1089.2		3	$\nu_1 + 769.5$
1108.9		5	$\nu_1 + \nu_2 + 180.7$
1130		2	$3\nu_1 + 180.7$
1256		2	$2\nu_1 + \nu_2$
1270.3	10	5	$4\nu_1$
1407		2	$2\nu_1 + 769.5$
1426		4	$2\nu_1 + \nu_2 + 180.7$
1446		2	$4\nu_1 + 180.7$
1571		3	$3\nu_1 + \nu_2$
1586	13	3	$5\nu_1$
1748		3	$3\nu_1 + \nu_2 + 180.7$

Table IV. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ at 77 K by Using 647.1-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
275	2	100	ν_1
362	6	8	ν_2
549	4	18	$2\nu_1$

Electronic Spectra. The electronic spectra of the $[Re_2X_8]^{2-}$ ions as disks at ca. 14 K are closely similar to those reported previously[11,14,15] (Figures 2–5). Surprisingly, that of the fluoride displayed no vibronic structure on the band at 17 900 cm^{-1}. The band at lowest energy is, in all cases, assigned to the $\delta^* \leftarrow \delta$ ($b_{1u} \leftarrow b_{2g}$) transition (Table II). The next lowest band has been assigned[9] in the chloride and bromide complexes to a $\delta^* \leftarrow (X)\pi$ transition ($b_{1u} \leftarrow e_g$), and here we extend the argument by analogy to include the iodide and assign the 14 800-cm^{-1} band of this ion to this transition. The assignments of the higher energy bands are far less certain. The 39 215-cm^{-1} band of $[Re_2Br_8]^{2-}$ and the 37 735-cm^{-1} band of $[Re_2Br_8]^{2-}$ have been assigned to the $\pi^* \leftarrow \pi$ ($e_g \leftarrow e_u$) transition.[9] However, the orbitals involved do have substantial (44% in the case of the chloride) halide character, and so such a transition might be expected to move rather more than the ca. 1500 cm^{-1} implied above on going from Cl to Br. Unfortunately, the alternative of assigning the 26 000-cm^{-1} band of $[Re_2Br_8]^{2-}$ to the $\pi^* \leftarrow \pi$ transition seems almost as unsatisfactory, since this would imply an excessive shift (~13 000 cm^{-1}) on going from Cl to Br. For $[Re_2I_8]^{2-}$, it is suggested that the 19 400-cm^{-1} band arises from the $\pi^* \leftarrow \pi$ transition.

Resonance Raman Spectra. Previous experiments on $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ were concerned in part with the controversy over the assignment of the lowest lying electronic band, this being resolved in favor of the $\delta^* \leftarrow \delta$ ($b_{1u} \leftarrow b_{2g}$) Laporte-allowed transition. This conclusion is now extended to include both the fluoride and the iodide. Excitation within the contours of all the electronic bands of the halide complexes listed in Table II was carried out, with the exception of the 39 000-cm^{-1} band of $[Re_2Cl_8]^{2-}$, for which no suitable excitation lines were available. Depolarization ratios, harmonic wavenumbers, and anharmonicity constants have also been obtained, wherever possible. The resonance Raman spectra obtained by irradiating within the contours of each of the electronic transitions of each ion are described in turn. The spectral data are presented in such a way as to try to show the possible analogies between particular bands of the different complex anions.

Irradiation within the Contour of the $\delta^* \leftarrow \delta$ ($b_{1u} \leftarrow b_{2g}$) Transition. The $\delta^* \leftarrow \delta$ electronic transition involves orbitals that are largely metal based, and so excitation should lead primarily to a change in the metal–metal bond length. On the Franck–Condon (FC) model for resonance Raman scat-

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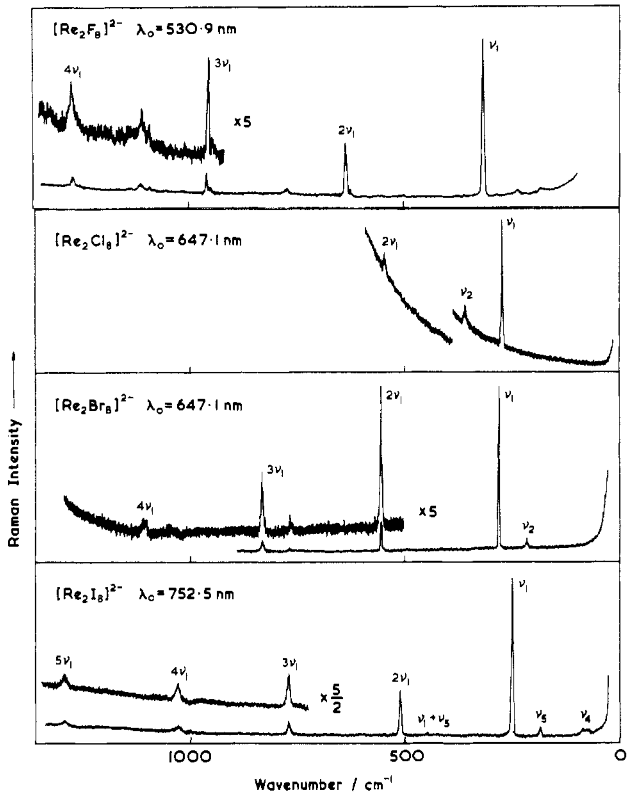

Figure 1. Resonance Raman spectra of the complexes $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ at ca. 80 K in the region of their $\delta^* \leftarrow \delta$ transitions: $[Re_2F_8]^{2-}$, KF disk, λ_0 = 530.9 nm (100 mW); $[Re_2Cl_8]^{2-}$, KCl disk, λ_0 = 647.1 nm (100 mW); $[Re_2Br_8]^{2-}$, KBr disk, λ_0 = 647.1 nm (150 mW); $[Re_2I_8]^{2-}$, CsI disk, λ_0 = 752.5 nm (100 mW).

Table V. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ at 77 K by Using 647.1-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
211	4	4	ν_2
276	3	100	ν_1
488	6	1	$\nu_1 + \nu_2$
552	5	16	$2\nu_1$
764	6	1	$2\nu_1 + \nu_2$
828	6	5	$3\nu_1$
1104	14	1	$4\nu_1$

Table VI. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$ at 77 K by Using 752.5-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
97	4	2	ν_4
152		1	ν_2
198	4	5	ν_5
257	3	100	ν_1
453	5	1	$\nu_1 + \nu_5$
514	5	25	$2\nu_1$
771	7	8	$3\nu_1$
1027	10	4	$4\nu_1$
1280	12	2	$5\nu_1$

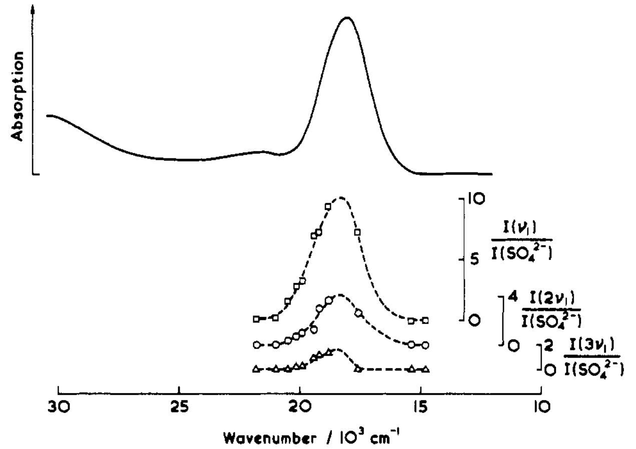

Figure 2. Electronic spectrum of the complex $[(n\text{-}C_4H_9)_4N]_2[Re_2F_8]$ as a $Cs[BF_4]$ disk at ca. 14 K, together with excitation profiles of the ν_1, $2\nu_1$, and $3\nu_1$ Raman bands of the anion.

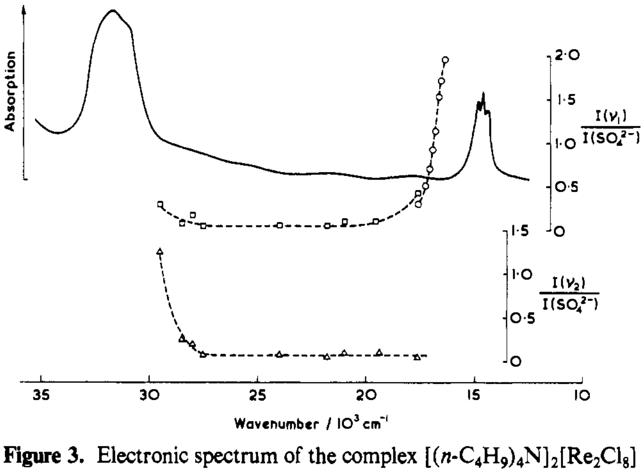

Figure 3. Electronic spectrum of the complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ as a KCl disk at ca. 14 K, together with excitation profiles of the ν_1 and ν_2 Raman bands of the anion.

tering, one would therefore expect the resonance Raman spectrum of $[Re_2X_8]^{2-}$ ions to be dominated by an overtone progression in ν_1, the metal–metal stretching vibration.

The spectra obtained for $[Re_2F_8]^{2-}$, $[Re_2Cl_8]^{2-}$, and $[Re_2Br_8]^{2-}$ were similar to those previously reported[6,15] (Figure 1) and clearly conform with the above expectations. It was noted that, when a sample of the bromide was cooled, the fluorescence background moves to the red and this allows a more well-defined overtone progression to be observed than that previously reported. The results are listed in Tables III–V for the fluoride, chloride, and bromide, respectively.

For $[Re_2I_8]^{2-}$ (for which resonance Raman spectra have not previously been reported), excitation with 13 287-cm^{-1} radiation gave an overtone progression $v_1\nu_1$ (where ν_1 is at 257 cm^{-1}) for all values of v_1 up to and including v_1 = 5 and a combination band $\nu_1 + \nu_5$, where ν_5 is at 198 cm^{-1} (see Table VI and Figure 1). A weak band at 97 cm^{-1}, labeled ν_4 by previous workers, was also observed with very low intensity. The band assigned to the metal–iodine stretching vibration, ν_2, at 152 cm^{-1} appeared only with very low intensity in the spectrum and did not form detectable combination bands with ν_1. This is in contrast to the behavior of ν_2 in the resonance Raman spectra of the fluoride, chloride, and bromide complexes, for which a short combination band progression $v_1\nu_1 + \nu_2$ is observed. No other bands at low wavenumber were observed.

No structure was observed in the excitation profiles of the ν_1, $2\nu_1$, ν_2, and ν_5 bands of the iodide, as expected, since the $\delta^* \leftarrow \delta$ band is itself unstructured.[15,21]

The excitation profiles of the ν_1, $2\nu_1$, and $3\nu_1$ bands of $[Re_2F_8]^{2-}$ (Figure 2), of the ν_1 band of $[Re_2Cl_8]^{2-}$ (Figure 3), of the ν_1 band of $[Re_2Br_8]^{2-}$ (Figure 4), and of the ν_1 and $2\nu_1$ bands of $[Re_2I_8]^{2-}$ (Figure 5) all maximize within the contours of the respective $\delta^* \leftarrow \delta$ bands, as expected in the *A*-term FC model for resonance Raman scattering. Very slight en-

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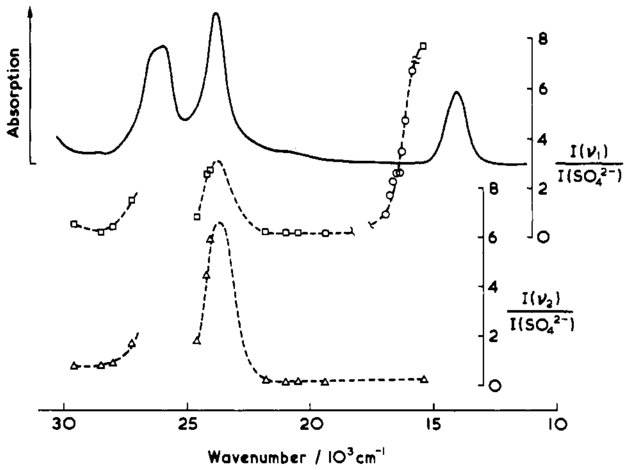

Figure 4. Electronic spectrum of the complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ as a KBr disk at ca. 14 K, together with excitation profiles of the ν_1 and ν_2 Raman bands of the anion.

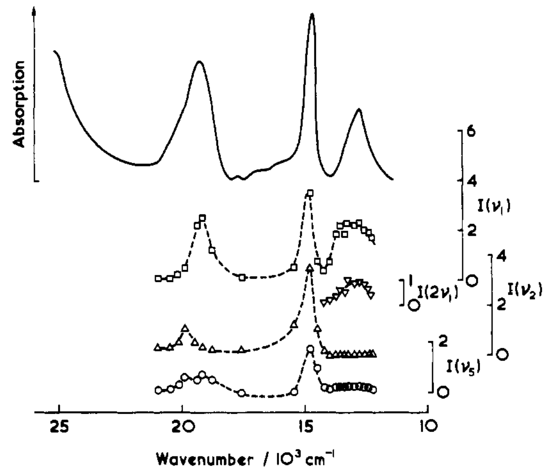

Figure 5. Electronic spectrum of the complex $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$ as a CsI disk at ca. 14 K, together with excitation profiles of the ν_1, $2\nu_1$, ν_2, and ν_5 Raman bands of the anion.

hancement to the ν_5 band of $[Re_2I_8]^{2-}$ is also observed for excitation in the vicinity of the $\delta^* \leftarrow \delta$ band.

Depolarization ratios (ρ) of totally symmetric modes associated with an electronic transition between nondegenerate states are expected to be 1/3 at resonance.[22,23] In agreement with this, the ρ value of the band assigned to the totally symmetric metal–metal stretching vibration ν_1 of $[Re_2F_8]^{2-}$ in dichloromethane was found to be 0.33 ± 0.03 for excitation with 18 837-cm^{-1} radiation, and for $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ in acetone they were found to be 0.29 ± 0.02 and 0.33 ± 0.02, respectively, for excitation with 15 453-cm^{-1} radiation.

Attempts to dissolve $[Re_2I_8]^{2-}$ in acetone gave a brown solution with an electronic absorption spectrum which was completely different from that of $[Re_2I_8]^{2-}$ in the solid state. However, when the solute was recovered by vacuum distillation in the cold, the product had a solid-state electronic absorption spectrum that was identical with that of $[Re_2I_8]^{2-}$. The nature of $[Re_2I_8]^{2-}$ in solution is therefore uncertain, and hence, no polarization studies have been carried out on the vibrational bands of this ion.

Irradiation within the Contour of the $\delta^* \leftarrow (X)\pi$ ($b_{1u} \leftarrow e_g$) Transition. The $\delta^* \leftarrow (X)\pi$ transition (x, y polarized) involves transfer of electron density from an orbital essentially localized on the ligands (X) (composed of p_π halogen orbitals) to an antibonding metal-based orbital.[9] One would therefore expect that the equilibrium geometry of the ion would change on $\delta^* \leftarrow (X)\pi$ excitation along the Q_2 (metal–halogen stretching) coordinate and thus (on the FC model for resonance Raman scattering)[21,22] that the Raman spectrum would be dominated by an overtone progression in ν_2. Depending on the metal–metal bonding nature of the LUMO (the δ^* orbital), some small structural change along the Q_1 coordinate might also be expected, leading, in addition, to a weak overtone progression in ν_1.

Table VII. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ at 77 K by Using 337.5-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
117	9	5	
154	7	4	
176	sh	6	
188	8	19	ν_7
274	6	12	ν_1
334		2	
361	8	100	ν_2
548	8	2	$2\nu_1/\nu_2 + \nu_7$
722	10	2	$2\nu_2$

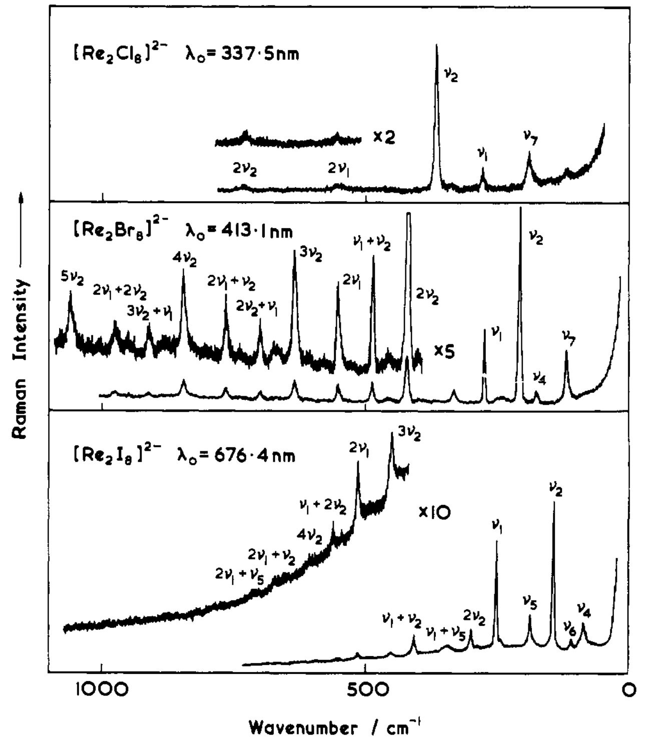

Figure 6. Resonance Raman spectra of the complexes $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ at ca. 80 K in the region of their $\delta^* \leftarrow (X)\pi$ transitions: $[Re_2Cl_8]^{2-}$, KCl disk, λ_0 = 337.5 nm (~20 mW); $[Re_2Br_8]^{2-}$, KBr disk, λ_0 = 413.1 nm (130 mW); $[Re_2I_8]^{2-}$, CsI disk, λ_0 = 676.4 nm (100 mW).

For $[Re_2Cl_8]^{2-}$, for which the $\delta^* \leftarrow (X)\pi$ transition lies at 30 800 cm^{-1}, excitation with 29 629-cm^{-1} radiation yielded only a short overtone progression in ν_2, as far as $2\nu_2$ (Table VII, Figure 6). However, the excitation profile of ν_2 shown in Figure 3 reveals that the enhancement of this band as resonance is approached is much greater than that of ν_1, in agreement with the FC model for resonance Raman scattering. In contrast to the spectrum obtained at resonance with the $\delta^* \leftarrow \delta$ transition, bands at 117, 154, 176, 188, and 334 cm^{-1} are also seen. Depolarization ratios of ν_2 and of the strong band observed at 188 cm^{-1}, which we shall call ν_7, were measured on exciting with 29 629-cm^{-1} radiation and found to be 0.15

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Table VIII. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ at 77 K by Using 413.1-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
65	4	1	
88	12	3	
111	sh	2	
123	8	25	ν_7
179	6	6	ν_4
211	5	100	ν_2
240	doublet	2	
250		3	$2\nu_7$
277	5	37	ν_1
335	9	6	$\nu_2 + \nu_7$
389	5	1	
400	5	2	$\nu_1 + \nu_7$
422	6	27	$2\nu_2$
458	16	2	$\nu_2 + 2\nu_7$
488	5	11	$\nu_1 + \nu_2$
526	13	0.7	$\nu_1 + 2\nu_7$
545	sh	1.7	$2\nu_2 + \nu_7$
553	6	8	$2\nu_1$
610	12	1.2	$\nu_1 + \nu_2 + \nu_7$
634	8	12	$3\nu_2$
670	13	1.0	$2\nu_1 + \nu_4/2\nu_2 + \nu_7$
700	7	0.5	$\nu_1 + 2\nu_2$
739	11	0.3	$\nu_1 + \nu_2 + 2\nu_7$
756	sh	0.3	$3\nu_2 + \nu_7$
765	8	6	$2\nu_1 + \nu_2$
830	sh	0.2	$3\nu_1$
846	10	4.0	$4\nu_2$
880	20	1.7	$2\nu_1 + \nu_2 + \nu_7$
913	10	2.4	$\nu_1 + 3\nu_2$
950	19	1.1	$3\nu_1 + \nu_7$
969	sh	0.7	$4\nu_2 + \nu_7$
976	13	2.9	$2\nu_1 + 2\nu_2$
1043	sh	0.2	$3\nu_1 + \nu_2$
1058	12	2.3	$5\nu_2$
1186	15	0.2	$2\nu_1 + 3\nu_2$
1267	17	0.3	$6\nu_2$

Table IX. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$ at 77 K by Using 676.4-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
50	sh	2	
73	sh	2	
84	sh	6	
97	8	17	ν_4
119	4	1	ν_6
151	4	100	ν_2
194	4	22	ν_5
257	3	76	ν_1
303	5	13	$2\nu_2$
347	doublet	6	$\nu_2 + \nu_5$
352		6	$\nu_1 + \nu_4$
409	5	14	$\nu_1 + \nu_2$
453	7	4	$3\nu_2/\nu_1 + \nu_5$
494	sh	1	$2\nu_2 + \nu_5$
515	5	4	$2\nu_1$
547	sh	0.05	
562	6	0.15	$\nu_1 + 2\nu_2$
604	10	0.10	$4\nu_2$
669	8	0.05	$2\nu_1 + \nu_2$
709	8	0.05	$2\nu_1 + \nu_5$

± 0.01 and 0.78 ± 0.05, respectively. The depolarization ratio of ν_2 at resonance is close to the value 1/8 as expected for a totally symmetric mode involved in a transition to a doubly degenerate (^1E_u) excited state, and this is consistent with the proposed electronic band assignment. ν_7 is assigned, on the basis of its depolarization ratio, to a non totally symmetric bending mode.

The non totally symmetric mode ν_7 could have gained intensity from Herzberg–Teller (HT) coupling with another excited state or by Jahn–Teller (JT) coupling within the doubly degenerate state. Since the nearest excited state to which there is an allowed electronic transition is 9000 cm^{-1} away, the HT mechanism is not likely to be very important, and the dominant effect ought to be due to JT coupling.[23] This would give intensity to $\Gamma_{e_u} \otimes \Gamma_{e_u} \supset a_{1g} + a_{2g} + b_{1g} + b_{2g}$ vibrational modes, but only the b_{1g} and b_{2g} ones would be JT active (a D_{4h} M_2X_8 system does not possess an a_{2g} fundamental). A vibrational analysis of the $[Re_2X_8]^{2-}$ unit shows that there are two stretching modes, one of e_g and one of b_{1g} symmetry, and four bending modes, two of e_g, one of b_{1g}, and one of b_{2g} symmetry, remaining to be assigned. ν_7 is therefore assigned, on the basis of its wavenumber and depolarization ratio, to either a b_{1g} or a b_{2g} bending vibration. The remaining bands cannot be assigned in the absence of depolarization ratio measurements.

For $[Re_2Br_8]^{2-}$, excitation within the contour of the band maximizing at 23 800 cm^{-1} using 24 205-cm^{-1} radiation gives a complex resonance Raman spectrum (see Figure 6 and Table VIII), which is dominated by a strong overtone progression in the metal–bromine stretching vibration ν_2 (211 cm^{-1}) up to $6\nu_2$, a weaker progression in ν_1 (277 cm^{-1}), the totally symmetric metal–metal stretch up to $3\nu_1$, and a strong band observed at 123 cm^{-1}, which we shall call ν_7. The excitation profiles of ν_1 and ν_2 are included in Figure 4; both appear to maximize under the peak of the $\delta^* \leftarrow (X)\pi$ band, with ν_2 showing the greater enhancement. HT coupling should be greater than for the corresponding case in $[Re_2Cl_8]^{2-}$, as the nearest state to which there is a strongly allowed transition is only 2200 cm^{-1} away; however, the dominant effects are still expected to arise from JT coupling within the ^1E_u excited state itself.

Measurement of the depolarization ratios of the bands observed for $[Re_2Br_8]^{2-}$ in acetone solution gave the following values: ν_1, 0.09 ± 0.01; ν_2, 0.12 ± 0.01; the 179-cm^{-1} band, ν_4, 0.74 ± 0.02; the 123-cm^{-1} band, ν_7, 0.77 ± 0.01 for excitation with 24 205-cm^{-1} radiation. A value of 1/8 is expected for a totally symmetric mode coupled to an electronic transition between a nondegenerate ground state and a doubly degenerate excited state, while a value of 0.75 is expected for non totally symmetric modes involved in such a transition.[22,23] These values confirm our assignment of ν_1 and ν_2 to totally symmetricd modes and also support the assignment of the resonant electronic transition. Thus, ν_7 is assigned to either a b_{1g} or a b_{2g} metal–bromine bending mode, its intensity being derived from JT coupling (cf. $[Re_2Cl_8]^{2-}$), while the band at 179 cm^{-1}, ν_4, is assigned to a b_{1g} stretching vibration. The other weaker bands account for the remaining vibrations, but no positive assignment can be made as they are too weak to obtain reliable depolarization measurements thereon.

Simple extension of the above arguments to the iodide leads to the assignment of the electronic absorption band at 14 800 cm^{-1} to the $\delta^* \leftarrow (X)\pi$ transition. This extension appears to be borne out by the experimental observation of an overtone progression $v_2\nu_2$, for all values of v_2 up to and including v_2 = 4, a short $v_1\nu_1$ progression, and a series of combination bands of the type $v_1\nu_1 + v_2\nu_2 + v_5\nu_5$ (where ν_5 is at 194 cm^{-1}). The spectrum (see Figure 6) is similar to those observed when excitation is within the contours of the analogous transitions of the chloride and bromide complexes. The excitation profiles of ν_1, $2\nu_1$, ν_2, and ν_5 all maximize at 14 800 cm^{-1} (see Figure 5). A complete list of all bands observed for excitation with 14 783-cm^{-1} radiation is shown in Table IX. Again, JT coupling is thought to be a more important intensity-giving mechanism than is HT coupling to the lower lying $^1A_{2u}$ excited

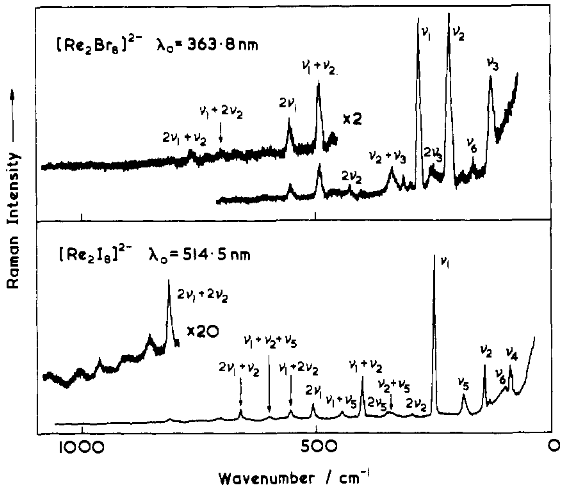

Figure 7. Resonance Raman spectra of the complexes $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ at ca. 80 K in the region of their higher energy (possibly $\pi^* \leftarrow \pi$) transitions: $[Re_2Br_8]^{2-}$, KBr disk, $\lambda_0 = 363.8$ nm (75 mW); $[Re_2I_8]^{2-}$, CsI disk, $\lambda_0 = 514.5$ nm (100 mW).

state 1800 cm^{-1} away. Previous workers[20] assigned the weakest band at 119 cm^{-1}, ν_6, to an e_g stretching mode; this is reasonable if one invokes weak HT coupling to $^1A_{2u}$ state since $\Gamma_{a_{2u}} \otimes \Gamma_{e_u} \supset e_g$. The stronger band at 97 cm^{-1} is assigned to a b_{1g} stretching vibration, which gains intensity via JT coupling. No attempt has been made to assign modes observed below 90 cm^{-1}, as they are probably strongly mixed with the lattice modes.

The strong band observed at 194 cm^{-1}, labeled ν_5, is difficult to assign. Others[20] had assigned it to a first overtone of the 97-cm^{-1} mode, ν_4. This is difficult to accept for two reasons; first, overtones of non totally symmetric modes are normally expected to be very weak,[22,23] and second, the band appears on exciting within the contour of the $\delta^* \leftarrow \delta$ transition, conditions under which ν_4 itself is very weak.

Assignments of the weaker bands must be regarded as tentative where no depolarization ratios can be obtained.

Irradiation within the Contour of the Band Tentatively Assigned to the $\pi^* \leftarrow \pi$ ($e_g \leftarrow e_u$) Transition. Since the $e_u(\pi)$ orbital is Re–Re π bonding and Re–Cl is σ antibonding, whereas the $e_g(\pi)$ orbital is Re–Re π antibonding and (probably) Re–Cl is nonbonding,[9] the $e_g \leftarrow e_u$ transition is expected to be associated with an increase in the Re–Re bond length and a decrease in the Re–Cl bond length. Thus, Raman progressions in both ν_1 and ν_2 are expected to be observed at resonance.

For $[Re_2Br_8]^{2-}$, excitation within the contour of the band maximizing at 26 000 cm^{-1} leads to the development of short overtone progressions in ν_1 as well as ν_2 and to combination bands of the type $v_1\nu_1 + v_2\nu_2 + v_7\nu_7$. Additionally, weaker bands were seen at 310, 296, 194, and 162 cm^{-1}, but these bands formed neither overtone nor combination band progressions. A full list of bands observed in the resonance Raman spectrum obtained by irradiating with 27 488-cm^{-1} radiation is given in Table X, and the complete spectrum is shown in Figure 7. Thus, both ν_1 and ν_2 are, as expected, strongly enhanced at resonance (Figure 4).

The depolarization ratios of the bands assigned to the ν_1 and ν_2 modes of $[Re_2Br_8]^{2-}$ in acetone are as follows: ν_1, 0.18 ± 0.02; ν_2, 0.16 ± 0.02. However, the $\pi^* \leftarrow \pi$ transition gives rise only to nondegenerate excited states, $^1A_{2u}$, $^1A_{1u}$, $^1B_{1u}$, and $^1B_{2u}$, of which only the transition to the $^1A_{2u}$ state is expected to be strongly allowed. The depolarization ratios of totally symmetric modes coupled to a $^1A_{2u} \leftarrow {}^1A_{1g}$ transition are expected to be 1/3. The measured values for the bands assigned to ν_1 and ν_2 are thus closer to those expected for an electronic transition involving a doubly degenerate excited state. From this one might infer either that the electronic assignment is incorrect or that the ρ value has been determined too far from rigorous resonance to give the expected value. In fact, measurement of ρ for ν_2 using 28 511-cm^{-1} radiation, which is even further from resonance, reveals a reduction in the value of ρ for $[Re_2Br_8]^{2-}$ to 0.05 ± 0.01, suggesting that polarization dispersion might indeed account for the unusually low value of ρ.[23] However, the matter is complicated since the appearance of the 123-cm^{-1} band, ν_7, suggests that JT coupling is present and, hence, that the transition involves a doubly degenerate excited state. To explain the appearance of new bands, HT coupling to the excited state nearby or to the more distant ^1E_u state could be invoked. Vibrational modes that are HT coupled to ^1E_u state, to which there is an allowed electronic transition, are more likely to be resonance Raman active than vibrational modes HT coupled to states to which electronic transitions are forbidden. On this basis one would expect to see $\Gamma_{a_{2u}} \otimes \Gamma_{e_u} \supset e_g$ modes enhanced; thus, we tentatively assign the 162-cm^{-1} band, ν_6, to an e_g stretching mode.

Table X. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ at 77 K by Using 363.8-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
124	10	49	ν_7
162	12	10	ν_6
194	16	4	
212	10	100	ν_2
248	18	12	$2\nu_7$
277	8	98	ν_1
296	10	4	
310	4	8	
335	18	14	$\nu_2 + \nu_7$
400	8	5	$\nu_1 + \nu_7$
424	16	5	$2\nu_2$
463	sh	4	$\nu_2 + 2\nu_7$
489	10	21	$\nu_1 + \nu_2$
524	8	2	$\nu_1 + 2\nu_7$
552	10	9	$2\nu_1$
677	6	3	$2\nu_1 + \nu_7/2\nu_2 + 2\nu_7$
700	14	4	$\nu_1 + 2\nu_2$
765	14	2	$2\nu_1 + \nu_2$
887	15	2	$2\nu_1 + \nu_2 + \nu_7$
975	14	2	$2\nu_1 + 2\nu_2$

For $[Re_2I_8]^{2-}$, excitation with 19 435-cm^{-1} radiation gives a strong resonance Raman spectrum with short progressions in ν_1, ν_2, and ν_5 and a series of combination bands of these fundamentals. These results are similar to those obtained for the bromide for excitation with 27 488-cm^{-1} radiation. Weaker bands at 118, 99, and 84 cm^{-1} are also observed. The appearance of the band at 99 cm^{-1} assigned[20] to a b_{1g} metal–iodine stretching mode suggests that JT coupling may also be important for this ion. Table XI presents a full list of all bands observed for excitation with 19 435-cm^{-1} radiation, and part of the spectrum is included in Figure 7. The assignments are different from those of the previous workers[20] and they do not require the unusual intensity patterns in the band progressions involving totally symmetric modes that have been proposed.

The resonance Raman excitation profiles of $[Re_2I_8]^{2-}$ are included in Figure 5, and these seem to suggest that there are two electronic transitions occurring in the 19 000–20 000-cm^{-1} region, one involving the metal–metal bond and the other involving the metal–iodine bonds. The 19 400-cm^{-1} band is plainly asymmetric. The excitation profile of the band assigned to ν_1 maximizes under the main band while the excitation profile of the ν_2 band maximizes under the shoulder at 19 800 cm^{-1} on the 19 400-cm^{-1} absorption band. The behavior of the ν_5 band is somewhat unusual, as it appears to have a local minimum between the main band and the shoulder; this could

Table XI. Assignments, Intensities, and Full-Width Half-Maxima (Fwhm) of Bands Observed in the Raman Spectrum of the Complex $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$ at 77 K by Using 514.5-nm Radiation

wavenumber/ cm^{-1}	fwhm/ cm^{-1}	peak height	assignt
84	sh	4	
99	8	16	ν_4
118		6	ν_6
153	5	27	ν_2
196	9	13	ν_5
258	5	100	ν_1
303	7	2	$2\nu_2$
346	doublet	3	$\nu_2 + \nu_5$
353		3	$\nu_1 + \nu_4$
389	sh	1	$2\nu_5$
409	5	22	$\nu_1 + \nu_2$
452	9	4	$\nu_1 + \nu_5$
514	5	7	$2\nu_1$
561	7	4	$\nu_1 + 2\nu_2$
604	doublet	2	$\nu_1 + \nu_2 + \nu_5$
610		1	$2\nu_1 + \nu_4$
648	sh	0.7	$\nu_1 + 2\nu_5$
665	7	6	$2\nu_1 + \nu_2$
710	12	1	$2\nu_1 + \nu_5$
755	doublet	0.4	$\nu_1 + 2\nu_2 + \nu_5$
764		0.4	$3\nu_1$
818	8	2.0	$2\nu_1 + 2\nu_2$
860	16	0.7	$2\nu_1 + \nu_2 + \nu_5$
905	doublet	0.4	$2\nu_1 + 2\nu_5$
918		0.5	$3\nu_1 + \nu_2$
967	15	0.4	$3\nu_1 + \nu_5$
1013	20	0.3	$2\nu_1 + 2\nu_2 + \nu_5$

be caused by interference between the two adjacent electronic transitions.[24]

In the absence of depolarization ratios, no firm assignment of the 19 400-cm^{-1} electronic band can be made except to say that it appears to be similar in nature to the 26 000-cm^{-1} band of $[Re_2Br_8]^{2-}$ and involves both metal- and iodine-based orbitals.

Anharmonicity Constants. $[Re_2F_8]^{2-}$. The overtone progression observed by exciting with 18 837-cm^{-1} radiation, i.e. within the contour of the $\delta^* \leftarrow \delta$ transition, gives a value for ω_1 of 318.5 ± 0.3 cm^{-1} and for x_{11} of −0.24 ± 0.08 cm^{-1}.

$[Re_2Cl_8]^{2-}$. The overtone progressions observed were too short to permit the determination of any harmonic frequencies or anharmonicity constants.

$[Re_2Br_8]^{2-}$. Measuring the wavenumbers of the overtone progression of ν_1 produced by exciting with 15 453-cm^{-1} radiation gives values of $\omega_1 = 276.0\ cm^{-1}$ and $x_{11} = 0.00 \pm 0.04\ cm^{-1}$. These values differ slightly from those found previously (276.2 and −0.39 cm^{-1}, respectively),[6] but it should be noted that the present measurements were made at ca. 80 K rather than at room temperature and that, in the previous work, the wavenumber determination had to be made on a spectrum with a rapidly rising fluorescence background. Analogous results were found for ν_2, viz. $\omega_2 = 211.0\ cm^{-1}$ and $x_{22} = 0.00 \pm 0.04\ cm^{-1}$, from the data obtained by irradiating within the contour of the $\delta^* \leftarrow (X)^*$ transition.

$[Re_2I_8]^{2-}$. The overtone progression observed by exciting with 13 287-cm^{-1} radiation, i.e. within the contour of the $\delta^* \leftarrow \delta$ transition, gives a value for ω_1 of 257.5 ± 0.2 cm^{-1} and for x_{11} of −0.2 ± 0.05 cm^{-1}. Exciting within the contour of the $\delta^* \leftarrow (X)\pi$ transition with 14 783-cm^{-1} radiation allows calculation, from the $v_2\nu_2$ progression, of a value for ω_2 of 151.5 ± 0.1 cm^{-1} and for x_{22} of −0.15 ± 0.05 cm^{-1}.

Discussion

The foregoing interpretation of the electronic spectra of the $[Re_2X_8]^{2-}$ ions is based on a simple FC view of resonance Raman scattering. The assignment of the lowest electronic transition of the fluoride and iodide to the $\delta^* \leftarrow \delta$ transition is firmly based, since the resonance Raman spectra of these ions with 18 837- and 13 287-cm^{-1} excitation, respectively, is very similar to those obtained for the chloride and bromide complexes when being excited within the contour of their $\delta^* \leftarrow \delta$ transitions. The assignment is confirmed by the fact that the depolarization ratios of the a_{1g} bands are 1/3 at resonance. The assignment of the band occurring at 198 cm^{-1} in the spectrum of the iodide is, however, not certain, but the initial proposal[20] that it be assigned to the first overtone of the 97-cm^{-1} band is seen to be unlikely.

The tentative assignment for the 30 800-cm^{-1} band of $[Re_2Cl_8]^{2-}$ by Mortola et al.[9] to a $\delta^* \leftarrow (X)\pi$ ligand-to-metal charge-transfer transition is confirmed. Again the simple FC view of resonance Raman scattering explains the main features of the spectra obtained; that is, the strong overtone progressions based on the metal–halogen stretching vibration ν_2, but the appearance of an intense non totally symmetric mode, ν_7, cannot be so explained and must result from JT coupling. The measured depolarization ratios of the a_{1g} modes at resonance of approximately 1/8 are in agreement with the resonant excited state being degenerate (^1E_u). The depolarization ratio of 3/4, measured for the ν_7 band indicates that this band arises from a non totally symmetric mode.

The striking feature of the resonance Raman spectrum of the bromide is the appearance of a strong band at 123 cm^{-1} which is assigned to a non totally symmetric mode on the basis of its depolarization ratio of 3/4. The intensity of this band results from JT coupling within the excited state. The first overtone of this band is weak, about one-tenth the intensity of the fundamental, as is characteristic of the behavior of non totally symmetric modes.[22,23]

Without depolarization ratio measurements for the iodide the assignment of the electronic absorption band at 14 800 cm^{-1} to the $\delta^* \leftarrow (X)\pi$ transition is tentative, but the assignment is supported by the observation that the resonance Raman spectrum of the ion is similar to those obtained for $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ with excitation resonant with their analogous electronic transitions.

The resonance Raman spectra obtained by excitation within the contour of the band that has been tentatively assigned to the $\pi^* \leftarrow \pi$ transition of $[Re_2Br_8]^{2-}$ and $[Re_2I_8]^{2-}$ are similar to one another in having short progressions in both ν_1 and ν_2; although this is the expected behavior at resonance with a transition involving orbitals that have substantial metal as well as ligand character, as occurs for other dinuclear molybdenum and ruthenium systems,[25-28] the assignments remain uncertain in this region.

Raman spectra of the ions have also been obtained in the regions of Laporte- and/or spin-forbidden bands,[11] but only very slight Raman-band enhancements occur at these wavelengths.

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Registry No. $[(n\text{-}C_4H_9)_4N]_2[Fe_2F_8]$, 72931-85-2; $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, 14023-10-0; $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$, 14049-60-6; $[(n\text{-}C_4H_9)_4N]_2[Re_2I_8]$, 67815-33-2.

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