making instrumental modifications permitting the infrared MCD measurements on IrF_6^{2-} and for much additional help, to Dr. Hans Güdel for the loan of infrared gratings, to Drs. R. O. Allen and S. Williams for performing the neutron activation analyses, and to Dr. E. Sinn for an X-ray determination of the crystal orientation of Cs_2GeF_6:Os^{4+}. Last, but not least, we thank Dr. Warren C. Yeakel for many helpful discussions and for the use of his computer programs to calculate the tetragonal distortion parameter. L.C.W. wishes to acknowledge support of NDEA and Governor's fellowships. This work was supported by a grant from the National Science Foundation.

Registry No. OsF_6^{2-}, 38966-66-4; IrF_6^{2-}, 21265-41-8; Cs_2GeF_6, 16919-21-4; Cs_2IrF_6, 16923-82-3; H_2OsCl_6, 27057-71-2.

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(16) In our discussion of the MCD spectra of OsF_6^{2-} and IrF_6^{2-}, there will be frequent reference to the Faraday $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ terms, and to the dipole strength, $\mathcal{D}$. We use these symbols without subscript in a generic sense and append subscripts to designate explicit mathematical expressions. We follow the new conventions outlined by Stephens (ref 2a, especially Appendix II). The specific parameters of interest are [2a] $\mathcal{A}_1$, $\mathcal{B}_0$, $\mathcal{C}_0$, $\mathcal{D}_0$ which are related to our previous parameters (ref 8) as follows: $\mathcal{D}_0 = D/3$, $\mathcal{A}_1 = 2A/3\beta$, $\mathcal{B}_0 = -2B/3\beta$, $\mathcal{C}_0 = -2C/3\beta$. $\mathcal{A}_1$ is associated with a first-derivative MCD line shape and is *defined* to be positive (negative) if the line shape goes first negative (positive) and then positive (negative) going to higher energy. $\mathcal{B}_0$ and $\mathcal{C}_0$ are associated with absorption-like line shapes and are *defined* as positive (negative) if their accompanying MCD is positive (negative). $\mathcal{D}_0$ is proportional to the (zero-field) absorption band area, $\int(\epsilon/\nu)\,d\nu$. The specific definitions and physical significance of these parameters have been discussed elsewhere.[2a]

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Electronic Raman Spectra of Hexahalogenoosmate(IV) Ions in the Resonant Condition

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Electronic Raman spectra of OsX_6^{2-} (X = Cl, Br, and I) ions were obtained in aqueous solutions and were assigned to the T_{1g}, T_{2g}, and E_g spin–orbit levels derived from the lowest $^3T_{1g}$ term of Os(IV). Striking resonance effect was observed for $OsBr_6^{2-}$ which has intense absorption bands in the region of Ar^+ laser lines. The $OsBr_6^{2-}$ spectrum in a low-temperature solid showed some structures assignable to vibroelectronic Raman transitions.

Introduction

In recent years, there has been considerable interest in the Raman spectroscopic investigation of low-lying electronic states of rare earth and transition-metal ions.[1–10] Since the electronic Raman scattering is usually extremely diffused at room temperature, the reported spectra were mostly observed for low-temperature crystalline samples, and few attempts have been made to investigate the resonance Raman effect, which has been a matter of great concern in recent vibrational spectroscopy. In the preceding paper,[11] we reported the observation of a resonance Raman spectrum associated with the low-lying spin–orbit states of $OsBr_6^{2-}$ in aqueous acid solution. The observed electronic Raman lines were extremely broad as expected, showing the widths more than 10 times broader than the vibrational ones, but the scattered intensity was great enough to be clearly measured at room temperature owing to the resonance enhancement. In the present paper, we report the result of further investigation on $OsBr_6^{2-}$ in solution as well as in solid at 77 K, along with the essentially similar but less strikingly resonant spectra of $OsCl_6^{2-}$ and OsI_6^{2-}.

Experimental Section

K_2OsX_6 (X = Cl, Br, and I) was prepared from OsO_4, HX, and KX according to the methods of Turner et al.[12] and Fenn et al.[13] The solution spectra were measured by 1 M HX solutions of K_2OsX_6 for $OsCl_6^{2-}$ and $OsBr_6^{2-}$, but rather unstable K_2OsI_6 was dissolved in a 2 M $HClO_4$ solution saturated with KI to avoid decomposition during the spectral observation. A rotating cell was used throughout the solution measurements. The low-temperature spectra of $OsBr_6^{2-}$ were obtained for the solid formed by quenching the above acid solution with liquid nitrogen. Details of the spectroscopic measurements were the same as reported before, except that a He–Cd laser and a CW dye laser (Rhodamine 6G) were additionally employed for excitation and that the photomultiplier was replaced by the one (HTV R 649) with a higher sensitivity in the long wave region.

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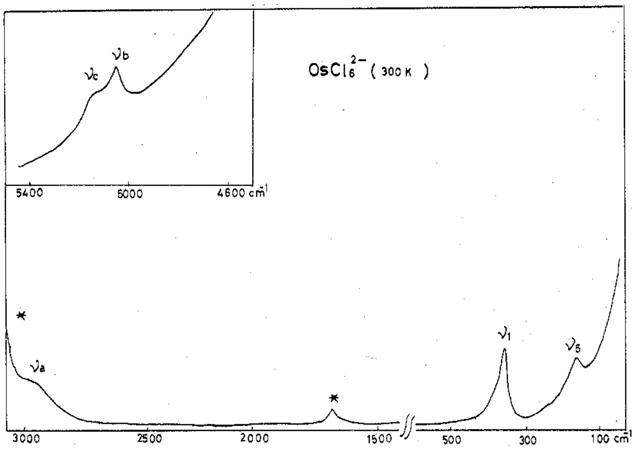

Figure 1. Raman spectrum of $OsCl_6^{2-}$ in 1 M HCl, taken with 454.5-nm excitation. The lines marked * are due to the solvent.

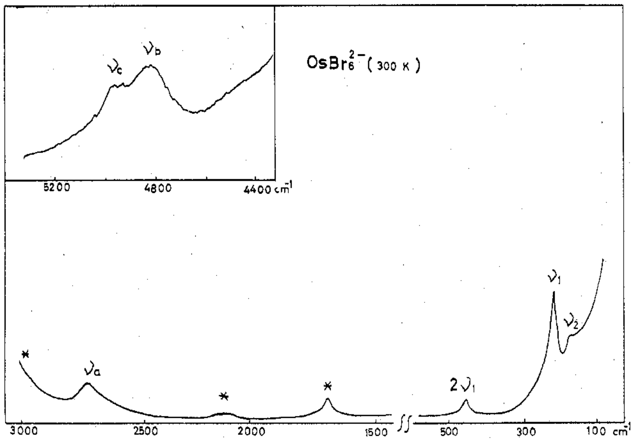

Figure 2. Raman spectrum of $OsBr_6^{2-}$ in 1 M HBr, taken with 488.0-nm excitation. The lines marked * are due to the solvent.

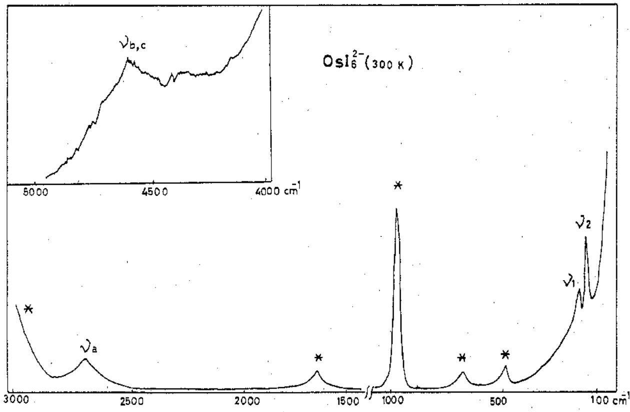

Figure 3. Raman spectrum of OsI_6^{2-} in 1 M $HClO_4$ saturated with KI, taken with 514.5-nm excitation. The lines marked * are due to the solvent.

Results and Discussion

The Raman spectra of three OsX_6^{2-} ions in solutions are shown in Figures 1–3 for the frequency range up to 5000 cm^{-1}. The vibrational lines of $OsCl_6^{2-}$ and $OsBr_6^{2-}$ are in good agreement with the more exhaustive results by Bosworth and Clark,[14] while those of OsI_6^{2-} unknown hitherto have been assigned as shown in Figure 3 (ν_1 128 cm^{-1} and ν_2 118 cm^{-1}) on the basis of observed depolarization ratios and correspondence of frequencies to the other homologues. Besides those vibrational lines at low frequencies, very broad scattering features are present near 2700 and 5000 cm^{-1} as denoted by ν_a, ν_b, and ν_c in the figures. They are definitely assignable to the electronic Raman transitions associated with the lower spin–orbit levels of OsX_6^{2-} as described in the following.

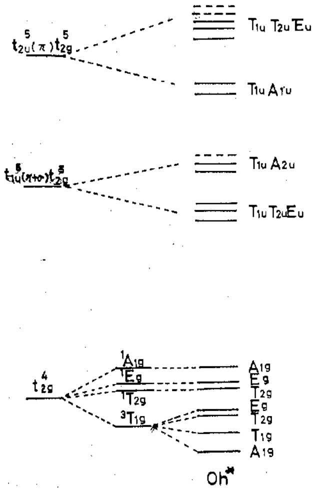

Figure 4. The schematic electronic energy levels of OsX_6^{2-} considering spin–orbit interaction.

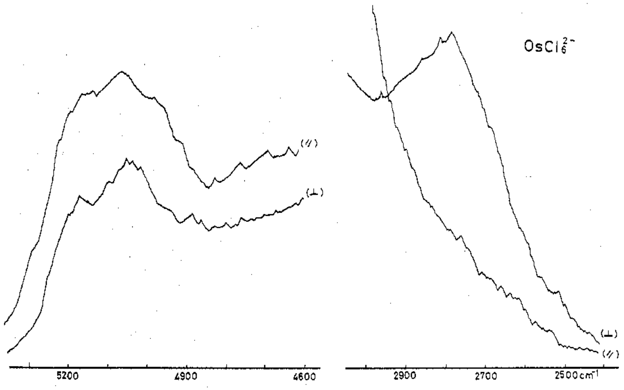

Figure 5. Polarization electronic Raman spectrum of $OsCl_6^{2-}$.

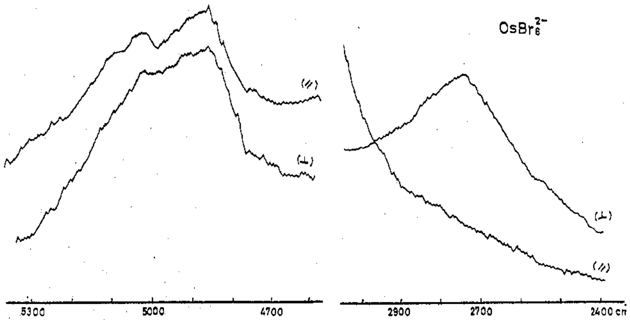

Figure 6. Polarization electronic Raman spectrum of $OsBr_6^{2-}$.

The energy levels of octahedral OsX_6^{2-} are schematically shown in Figure 4.[15] The Raman transitions from the A_{1g} ground state are all allowed for the six components of the spin–orbit states arising from the lowest $(t_{2g})^4$ configuration of Os(IV). The depolarization ratios in solution spectra are predicted from the character of scattering tensors as follows.

$$
\begin{aligned}
A_{1g}\text{ (ground state)} &\rightarrow A_{1g}\text{ (isotropic tensor)} \quad \rho_l = 0\\
&\rightarrow E_g\text{ (symmetric tensor)} \quad \rho_l = 3/4\\
&\rightarrow T_{1g}\text{ (antisymmetric tensor)}\\
&\qquad \rho_l = \infty\\
&\rightarrow T_{2g}\text{ (symmetric tensor)} \quad \rho_l = 3/4
\end{aligned}
$$

Figures 5–7 show the polarization Raman spectra of the frequecy regions under consideration, which indicate the depolarized character ($\rho_l \approx {}^3/_4$) of ν_b and ν_c but the nearly

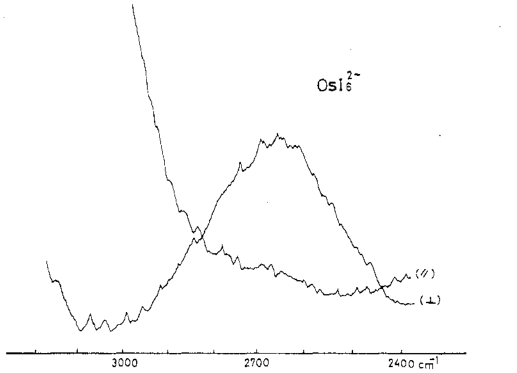

Figure 7. Polarization electronic Raman spectrum of OsI_6^{2-}.

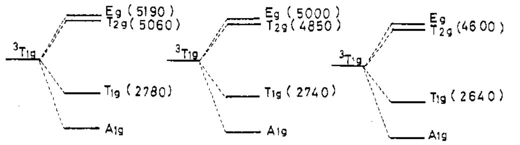

Figure 8. The splittings of the lowest $^3T_{1g}$ terms for OsX_6^{2-} (numerical values are in cm^{-1} units).

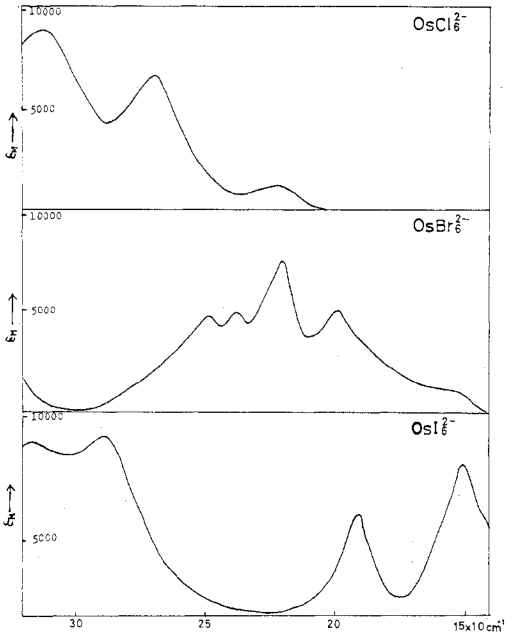

Figure 9. The visible and ultraviolet absorption spectra of OsX_6^{2-}.

perfect inverse polarization of ν_a in all three species. Then it turns out that ν_a is definitely assignable to the lowest excited T_{1g} state while ν_b and ν_c are most probably attributed to the T_{2g} and E_g states originating from the lowest $^3T_{1g}$ term. Allen et al.[16] measured the diffuse reflectance spectra of all four hexahalogenoosmate ions by the potassium salts between 4000 cm^{-1} and 20 000 cm^{-1} and assigned the bands observed at 5620, 5120, 4900, and 4620 cm^{-1} for X = F, Cl, Br, and I to the lump of $T_{2g}(^3T_{1g})$ and $E_g(^3T_{1g})$ levels of respective ions. On the other hand, Nims et al.[15] observed the sharp-line luminescence and absorption spectra of $OsBr_6^{2-}$ doped in a Cs_2ZrBr_6 single crystal between 10 000 and 16 500 cm^{-1} and derived the energy of lower levels to be 2759 cm^{-1} (T_{1g}), 4803 cm^{-1} (T_{2g}), and 4966 cm^{-1} (E_g). The observed Raman frequencies are in good agreement with those previous data of the $^3T_{1g}$ term as shown in Figure 8. Slight diminution of the splitting intervals toward the heavier ligands may be interpreted in terms of the increasing covalent character of Os–X bonds in the same order, as was discussed in detail by Allen et al.[16]

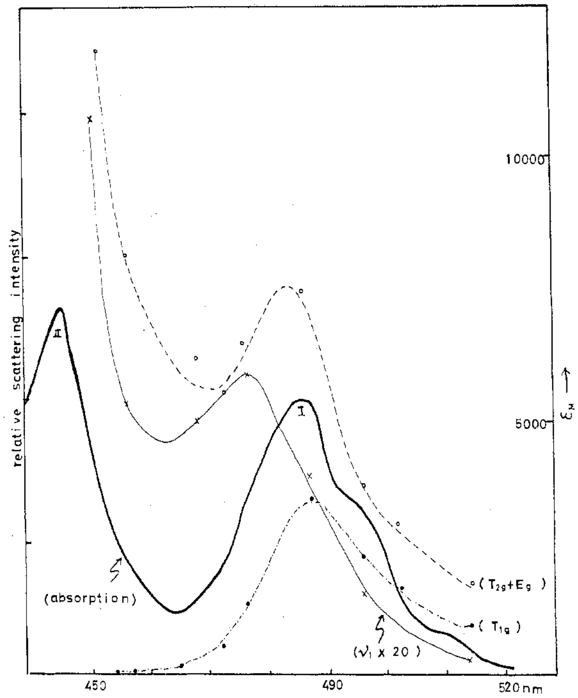

Figure 10. The Raman excitation profiles and visible absorption spectrum of $OsBr_6^{2-}$. Two peaks of absorption bands are denoted as I and II (see text).

Figure 9 shows the visible and near-ultraviolet absorption spectra of OsX_6^{2-} in solutions. The main features attributed to the ligand–metal charge-transfer transitions are sufficiently intense so that there is a good chance of observing the resonance effect in either vibrational or electronic Raman spectra by using appropriate exciting radiations. Since the wavelengths of a conventional Ar^+ laser are distributed over the first and second absorption bands of $OsBr_6^{2-}$, we investigated the dependence of scattered intensity on exciting wavelengths for this ion. The result is shown in Figure 10, where it is noted that the electronic Raman intensities are by far greater than that of the vibrational ν_1 line, which is also considerably resonant in the same region so that the electronic Raman bands are enhanced.

It is remarkable that in the region of the second absorption band, inversely polarized $\nu_a(T_{1g})$ undergoes no resonance enhancement in contrast to the lump of $\nu_b(T_{2g})$ and $\nu_c(E_g)$, which is enhanced more pronouncedly than in the first band. Now, the standard theory based on the dispersion formula gives the following expression for the scattering tensor.[2]

$$
\begin{aligned}
(\alpha\rho\sigma)_{\mathrm{gv,fv'}} = {} & \frac{1}{h}\sum_{\mathrm{e,v''}} \frac{1}{\nu_{\mathrm{ev'',gv}} - \nu}[\langle \mathrm{g}|m_\sigma|\mathrm{e}\rangle\langle \mathrm{e}|m_\rho|\mathrm{f}\rangle \times \\
& (\mathrm{v}|\mathrm{v''})(\mathrm{v''}|\mathrm{v'}) + \sum_i \sum_{s\neq \mathrm{e}} h_{\mathrm{se}}^{(i)} \{\langle \mathrm{g}|m_\sigma|\mathrm{e}\rangle\langle \mathrm{s}|m_\rho|\mathrm{f}\rangle(\mathrm{v}|\mathrm{v'}) \times \\
& (\mathrm{v''}|Q_i|\mathrm{v'}) + \langle \mathrm{g}|m_\sigma|\mathrm{s}\rangle\langle \mathrm{e}|m_\rho|\mathrm{f}\rangle(\mathrm{v}|Q_i|\mathrm{v''})(\mathrm{v''}|\mathrm{v'})\} + \\
& \sum_i \sum_{s\neq \mathrm{f}} h_{\mathrm{sf}}^{(i)}\langle \mathrm{g}|m_\sigma|\mathrm{e}\rangle\langle \mathrm{e}|m_\rho|\mathrm{s}\rangle(\mathrm{v}|\mathrm{v''})(\mathrm{v''}|Q_i|\mathrm{v'}) + \\
& \sum_i \sum_{s\neq \mathrm{g}} h_{\mathrm{sg}}^{(i)}\langle \mathrm{s}|m_\sigma|\mathrm{e}\rangle\langle \mathrm{e}|m_\rho|\mathrm{f}\rangle(\mathrm{v}|Q_i|\mathrm{v''})(\mathrm{v''}|\mathrm{v'})] + \\
& \frac{1}{h}\sum_{\mathrm{ev''}} \frac{1}{\nu_{\mathrm{ev'',fv'}} + \nu}[\rho \leftrightarrow \sigma, \mathrm{v} \leftrightarrow \mathrm{v'}]
\end{aligned}
$$

where $|\mathrm{g}\rangle$, $|\mathrm{e}\rangle$, and $|\mathrm{f}\rangle$ are the initial, intermediate, and final electronic states, and $|\mathrm{v})$, $|\mathrm{v''})$, and $|\mathrm{v'})$ are the corresponding vibrational states. Q_i is a normal coordinate of vibration and

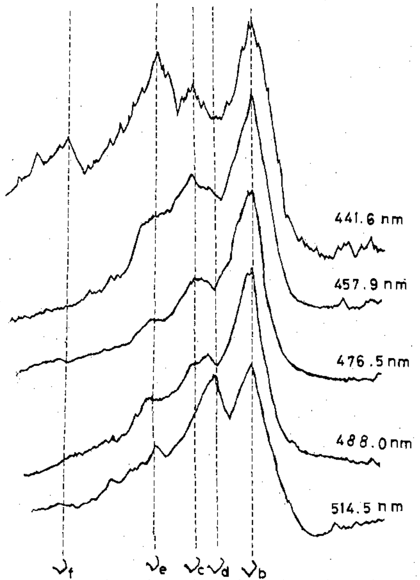

Figure 11. Exciting line dependency of vibroelectronic Raman lines of $OsBr_6^{2-}$ at 77 K.

$h_{se}^{(i)} = \langle s|(\partial H/\partial Q_i)_0|e\rangle/(E_e - E_s)$ etc. represent the vibronic coupling constants due to ith mode. The first term in brackets of the above equation is the Raman analogue of the Rayleigh scattering term, and this term contributes predominantly to electronic Raman intensity. Confining our attention to the first term, only the T_{1u} states of the octahedral ion can be active intermediate states, having a nonzero transition moment toward the A_{1g} ground state; the lowest ones are those of the resonant absorption bands considered above. Then, the scattered intensity of $\nu_a(T_{1g})$ may be typically represented by

$$I_{\rm I} \sim \sum_{\rho,\sigma} |\langle A_{1g}|m_\sigma|T_{1u}^{\rm I}\rangle\langle T_{1u}^{\rm I}|m_\rho|T_{1g}\rangle|^2$$

$$I_{\rm II} \sim \sum_{\rho,\sigma} |\langle A_{1g}|m_\sigma|T_{1u}^{\rm II}\rangle\langle T_{1u}^{\rm II}|m_\rho|T_{1g}\rangle|^2$$

for exciting wavelengths within the first (I) and second (II) bands. Since $|\langle A_{1g}|m|T_{1u}^{\rm I}\rangle|$ and $|\langle A_{1g}|m|T_{1u}^{\rm II}\rangle|$ are known to be comparable from the absorption spectrum, the observed excitation profile of $\nu_a(T_{1g})$ indicates that

$$|\langle T_{1u}^{\rm I}|m|T_{1g}\rangle| \gg |\langle T_{1u}^{\rm II}|m|T_{1g}\rangle| \approx 0$$

This result might be related to the difference in original charge-transfer configurations, which are $t_{1u}^5(\pi + \sigma)t_{2g}^5$ and $t_{2u}^5(\pi)t_{2g}^5$ for $|T_{1u}^{\rm I}\rangle$ and $|T_{1u}^{\rm II}\rangle$, respectively.[17] On the other hand, similar consideration on the lump of $\nu_b(T_{2g})$ and $\nu_c(E_g)$ indicates that there are fairly great transition moments toward either of the T_{1u} states. These observations give an example of probing the transition moment between excited states by means of electronic Raman scattering.

On $OsBr_6^{2-}$, the spectra were also measured at 77 K as shown in Figure 11, resulting in more conspicuous band contours slightly shifted to higher frequency from the room-temperature spectrum. Some rugged structures developed in the 5000-cm^{-1} region are noticeable. Since no electronic Raman transitions other than A_{1g}–T_{2g} and A_{1g}–E_g are expected in this region, observed extra maxima may probably be due to the vibroelectronic transitions associated with the above electronic ones. Figure 11 shows the spectra of the same region obtained by several exciting wavelengths, where the relative intensity of structure components changes remarkably for different exciting wavelengths. On the basis of the vibrational frequencies in the ground state, ν_1 210.6 cm^{-1} and ν_5 100 cm^{-1},[14] the most likely assignments may be $\nu_d = \nu_b(T_{2g}) + \nu_5$, $\nu_e = \nu_b(T_{2g}) + \nu_1$, and $\nu_f = \nu_b(T_{2g}) + 2\nu_1$.

The intensity behaviors of ν_e and ν_f are rather like those of ν_1 and $2\nu_1$ vibrational lines, and either case may be interpreted by the first term of the Franck–Condon type in the scattering formula given above. This is quite probable because equilibrium metal–ligand distance in the charge-transfer excited states is supposed to be appreciably greater than in the ground state. The source of intensity of ν_d may not be equal to the above totally symmetric case but possibly be related to the vibronic coupling effect represented by the second and following terms in the above formula. Particularly, $|T_{2g}\rangle$ and $|E_g\rangle$ can be coupled only through $\nu_5(t_{2g})$ vibration, and the coupling may become considerable because of the very small energy interval, causing the third term to be great. It is not quite obvious, however, why ν_d is relatively so intense at 514.5-nm excitation. This may conceivably be related to the observation by Bird et al.[17] that the low-frequency slope of the first absorption band is upheaved remarkably at low temperatures.

Registry No. K_2OsCl_6, 16871-60-6; K_2OsBr_6, 16903-69-8; K_2OsI_6, 12055-78-6.

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