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# Vibrational Spectra and Force Fields of the Tetrafluorooxohalate(V) Anions $ClF_4O^-$, $BrF_4O^-$, and $IF_4O^-$

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Improved syntheses are described for $BrF_4O^-$ and $IF_4O^-$ salts, and their vibrational spectra are reported. The spectra of $CsBrF_4O$ are simpler than those previously reported for $KBrF_4O$ and thus allow more reliable assignments. For comparison, the low-temperature Raman spectrum of $CsClF_4O$ has also been recorded. Normal-coordinate analyses have been carried out for the $ClF_4O^-$, $BrF_4O^-$, and $IF_4O^-$ anions and are compared to those of the structurally related $HalF_4^-$ anions and $HalF_5$ molecules and those of $XeF_4$, $XeF_4O$, and $XeF_5^+$.

## Introduction

The existence of $KBrF_4O$, a salt containing a novel bromine oxyfluoride anion, has recently been reported both by Bougon and co-workers[1] and by Gillespie and Spekkens.[2] It was obtained either by the reaction[1] of $KBrO_3$ with a large excess of $BrF_5$ at 80 °C in the presence of $F_2$ or by the reaction[2] of $KBrF_6$ with $KBrO_3$ in $CH_3CN$ solution. Both methods have drawbacks. Although Bougon's method[1] can yield a pure product, the course of the reaction is difficult to control and frequently $KBrF_4$ is obtained as the only product (see below). Gillespie's method[2] produces a mixture of $KBrF_2O_2$ and $KBrF_4O$ which must be separated by numerous extractions with $CH_3CN$. In view of these difficulties, an improved synthetic method for the synthesis of $BrF_4O^-$ was desirable.

Although the crystal structure of $CsIF_4O$ has been reported,[3] only a small amount of the material had been obtained accidentally during unsuccessful attempts to crystallize $CsIF_6$ from $CH_3CN$ solution. Furthermore, products containing mixtures of $MIF_4O$ and $MIF_2O_2$ salts have been prepared[4] by the interaction of $MIO_3$ or $MIO_2F_2$ with $IF_5$ or by the controlled hydrolysis of $MIF_6$ in $CH_3CN$. However, no suitable method for the preparation of pure $MIF_4O$ has previously been reported.

The vibrational spectra of these $HalF_4O^-$ anions were also of interest. For $IF_4O^-$ only spectra of mixtures of $IF_4O^-$ and $IF_2O_2^-$ salts were known,[4] and for $KBrF_4O$ the previously reported[1,2] Raman spectra exhibited more bands than permitted for an isolated six-atom species. Interionic dynamic coupling was suggested[1] to account for the large number of bands observed for $KBrF_4O$. However, in view of their similar relative intensities, the bands occurring in the 530–390-cm$^{-1}$ region could not be reliably assigned.

In this paper we report improved syntheses for $BrF_4O^-$ and $IF_4O^-$ salts and their vibrational spectra which allow more reliable assignments for these ions. These assignments are supported by normal-coordinate analyses of 12 structurally closely related species.

## Experimental Section

**Materials.** Bromine pentafluoride (Matheson Co.) was treated with 35 atm of $F_2$ at 200 °C for 24 h prior to its use. Fluorine (Rocketdyne) was passed through a NaF scrubber for removal of HF. The alkali metal perbromates[5] and $CsClF_4O$[6] were prepared as previously described. Potassium bromate (Baker AR) was used as received. Iodine pentafluoride was purified by distillation and $I_2O_5$ was prepared from $I_2$ and $HNO_3$. The KF was dried by fusion in a platinum crucible.

**Apparatus.** Volatile materials were manipulated in a well-passivated (with $ClF_3$ and $BrF_5$) 304 stainless-steel vacuum line equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded on Perkin-Elmer Model 283 and 577 spectrophotometers. For gases a Monel cell with AgCl windows was used. The spectrum of $CsBrF_4O$ was recorded as a dry powder between AgBr windows in the form of a pressed disk. The pressing operation was carried out using a Wilks minipellet press. The spectrum of $KIF_4O$ was recorded as a Nujol mull between CsI windows. Raman spectra were recorded on Cary Model 82 and 83 spectrometers using the 4880-Å exciting line, a Claassen filter[7] for the elimination of plasma lines, and melting-point capillaries or Kel-F tubes as sample containers. For the low-temperature spectra a previously described[8] device was used.

**Synthesis of $KIF_4O$.** A mixture of KF and $I_2O_5$ in a mole ratio of 5:1 was treated with a large excess of $IF_5$ for 1 h at 25 °C. Volatile products were pumped off, first at 25 °C and then at 100 °C. The white crystalline residue was identified by elemental and spectroscopic analyses as $KIF_4O$. Anal. Calcd for $KIF_4O$: K, 15.2; I, 49.2. Found: K, 15.1; I, 49.0.

**Syntheses of $BrF_4O^-$ Salts.** In a typical experiment, $CsBrO_4$ (2.044 mmol) was placed into a sapphire reaction tube ($^1/_2$ in. o.d. × 12 in. length, Tyco) which contained a Teflon-coated magnetic stirring bar and was attached to a valve through a Swagelok compression fitting using a Teflon front ferrule and a steel back ferrule. Bromine pentafluoride (14.1 mmol) and $F_2$ (2.4 mmol) were added at −78 °C. The mixture was stirred at 25 °C for 30 h and then cooled to −196 °C. The products volatile at −196 °C were pumped off and those volatile at 25 °C were separated by fractional condensation through a series of traps kept at −64, −95, and −196 °C, respectively. On the basis of their infrared and Raman spectra, they consisted of $FBrO_2$, $BrF_5$, and $FBrO_3$, respectively. On the basis of its infrared and Raman spectrum, the white solid residue (623 mg) consisted of $CsBrF_4O$ (weight calculated for 2.044 mmol of $CsBrF_4O$ was 623 mg). Similar results were obtained when the reaction was carried out at 70 °C. However, if the reaction was carried in the absence of $F_2$, the conversion of $CsBrO_4$ to $CsBrF_4O$ was very low, even after prolonged heating to 80 °C. The influence of HF on this reaction was also studied. The addition of 5 mol % (based on $MBrO_4$) HF did not produce significant amounts of $BrF_4O^-$ in the reaction of $CsBrO_4$ with $BrF_5$ in the absence of $F_2$ at 25–50 °C.

For the $KBrO_4$–$BrF_5$–$F_2$ reaction system, when studied in the same manner as described above for $CsBrO_4$, higher reaction temperatures were required. For example, at 45 °C for 19 h, essentially all of the $KBrO_4$ starting material was recovered unchanged. Heating of the starting materials to 80 °C for 95 h resulted in a conversion of $KBrO_4$ to $KBrF_4O$ of about 70%.

A sample of $KBrF_4O$ was also prepared from $KBrO_3$ and $BrF_5$ by closely following the procedure published[1] by Bougon. However, when the reaction conditions or the scale of the reaction were slightly modified, several experiments produced $KBrF_4$ in almost quantitative yield, even when the $BrF_5$ was prefluorinated with 35 atm of $F_2$ at 200 °C. No evidence was found for the formation of significant amounts of $FBrO_3$ in these reactions.

**The $CsClF_4O$–$ClF_3$ System.** A weighed sample of $CsClF_4O$ in a tenfold excess of $ClF_3$ was stirred for 24 h at 25 °C. The volatile products were pumped off and consisted of unreacted $ClF_3$ and $ClF_3O$. On the basis of its weight and vibrational spectra,[9] the white solid

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residue consisted exclusively of $CsClF_4$.

## Results and Discussion

**Synthesis of $XF_4O^-$ Salts.** The reaction of $I_2O_5$ with a large excess of $IF_5$ in the presence of a stoichiometric amount of KF affords essentially pure $KIF_4O$ in a one-step reaction according to

$$I_2O_5 + 3IF_5 + 5KF \rightarrow 5KIF_4O$$

This synthesis is based on the previous report[10] of Aynsley et al. that the reaction of $I_2O_5$ with $IF_5$ produces $IF_3O$.

The $KIF_4O$ prepared in this manner is a white, crystalline solid. It is stable up to about 200 °C and hydrolyzes according to

$$KIF_4O + 2H_2O \rightarrow KIO_3 + 4HF$$

Attempts to synthesize $K_2IF_5O$ by changing the $KF{:}I_2O_5$ ratio in the above synthesis were unsuccessful. On the basis of its vibrational spectra, the resulting product was shown to be $KIF_4O{\cdot}KF$.

For the synthesis of $BrF_4O^-$ salts, the reactions of $MBrO_4$ with $F_2$ in $BrF_5$ solution were found to be most reproducible. Whereas $CsBrO_4$ is fluorinated even at ambient temperature, the reaction of $KBrO_4$ requires heating to about 80 °C. Although the formation of $BrF_4O^-$ salts in these reactions was shown to be reproducible and quantitative, the amount of the volatile by-products $FBrO_2$ and $FBrO_3$ varied and was never sufficient to account for all of the missing oxygen. The remaining oxygen was probably in the form of $O_2$ which was pumped off at −196 °C together with the unreacted $F_2$. Furthermore, it is remarkable that under the given conditions the reactions did not proceed in the absence of $F_2$. This implies that $F_2$ participates in these reactions and does not merely serve the purpose of suppressing a possible reduction of $BrF_5$ to $BrF_3$, as was previously suggested[3] for the bromate–$BrF_5$ system. It was also shown that, contrary to a previous report on the $KBrO_3$–$BrF_5$ system, the addition of small amounts of HF did not significantly catalyze the $CsBrO_4$–$BrF_5$ reaction between 20 and 50 °C.

Although the reaction of $KBrO_3$ with $BrF_5$ to form $KBrF_4O$ which was previously reported[1] by Bougon and co-workers was successfully duplicated in our laboratory, it was difficult to accomplish. Frequently, quantitative conversion to $KBrF_4$ was obtained. Since the $BrF_5$ used in our experiments had been thoroughly prefluorinated with $F_2$ at 200 °C, it could not have contained sufficient $BrF_3$ for a quantitative displacement reaction, such as

$$KBrF_4O + BrF_3 \rightarrow KBrF_4 + BrF_3O$$

That such a displacement reaction of $HalF_4O^-$ by $HalF_3$ can indeed proceed quantitatively was demonstrated in this study for the system

$$CsClF_4O + ClF_3 \rightarrow CsClF_4 + ClF_3O$$

In view of the possibility of such a displacement reaction and the known[11] thermal instability of $BrF_3O$, the presence of a small amount of $BrF_3$ might be sufficient to catalyze the decomposition of $BrF_4O^-$ to $BrF_4^-$ according to

$$\begin{tikzcd} BrF_4O^- + BrF_3 \arrow[r] & BrF_4^- + BrF_3O \arrow[dl, "\Delta T"] \\ BrF_3 + {}^1/_2O_2 \arrow[u] & \end{tikzcd}$$

Our finding that $BrF_4^-$ can be readily formed in this system confirms the original report[12] by Schmeisser and Pammer but is inconsistent with the recent report[2] of Gillespie and Spekkens.

From a mechanistic point of view, the reactions of $BrF_5$ with $BrO_3^-$ or $BrO_4^-$ are very interesting since they involve an oxygen–fluorine exchange. On the basis of the observed quantitative yields of $BrF_4O^-$, a free-radical mechanism involving the addition of oxygen atoms to bromine fluorides is extremely unlikely. Furthermore, the increased reactivity of the thermally more stable $CsBrO_4$ relative to that of $KBrO_4$ suggests an alkali metal salt catalyzed reaction. A mechanism involving the addition of $BrF_5$ or $BrF_6^-$ across a Br=O double bond of $BrO_4^-$ or $BrO_3^-$ followed by $FBrO_3$ or $FBrO_2$ elimination with $BrF_4O^-$ formation appears plausible but requires additional experimental support.

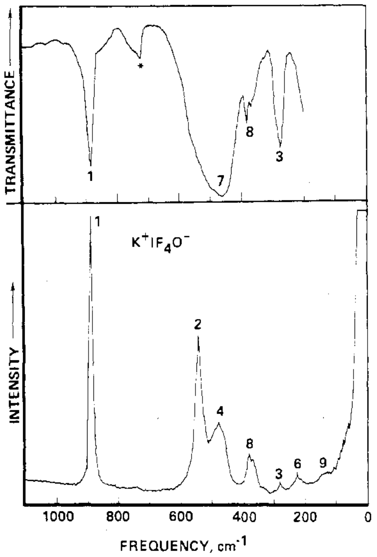

**Figure 1.** Vibrational spectra of $KIF_4O$: upper trace, infrared spectrum of a Nujol mull between CsI windows; lower trace, Raman spectrum. The band marked by an asterisk is due to Nujol. The numbers 1–9 designate the assignments to the corresponding fundamentals.

**Vibrational Spectra.** Vibrational spectra were recorded for $KIF_4O$, $CsBrF_4O$, $KBrF_4O$, and $CsClF_4O$. The spectra of $KIF_4O$ (see Figure 1 and Table I) are in fair agreement with those[4] previously assigned to the $MIF_4O$ part of $MIO_2F_2$–$MIF_4O$ mixtures, except for the relative intensities of the 280- and 365-cm$^{-1}$ infrared bands. This discrepancy is caused by the fact[4] that $IO_2F_2^-$ possesses a strong infrared band at 360 cm$^{-1}$.

The vibrational spectra of $CsBrF_4O$ are shown in Figure 2. The spectra of $KBrF_4O$ were in excellent agreement with those[1,2] previously reported and, hence, are not reiterated. Surprisingly, the vibrational spectra of $CsBrF_4O$ significantly differed from those of $KBrF_4O$. Since in the $HalF_4$ stretching frequency region the room-temperature Raman spectrum of $CsBrF_4O$ was more similar to that[13] of $CsClF_4O$ than to that[1,2] of $KBrF_4O$, we have also reexamined the Raman spectrum of $CsClF_4O$ (see Figure 3).

By analogy with the previous report[2] on $KBrF_4O$, it was found that cooling of the samples resulted in much better resolved Raman spectra. The observed frequencies of $CsBrF_4O$ and $CsClF_4O$ are summarized in Table I. Attempts to obtain the Raman spectrum of $CsBrF_4O$ in anhydrous HF solution failed owing to the displacement reaction

$$CsBrF_4O + HF \rightarrow CsHF_2 + BrF_3O$$

The observed spectrum was in excellent agreement with that recently reported[11] for $BrF_3O$.

The previously reported[1,2] Raman spectra of $KBrF_4O$ are very complex and contain more bands than expected for an isolated six-atom species. Furthermore, the relative intensities of many bands are too similar to allow conclusive assignments. In view of these complications and in the absence of additional structural data on $BrF_4O^-$, the proposed[1,2] $C_{4v}$ structure for $BrF_4O^-$ had to be considered tentative, although very likely.

Table I. Vibrational Spectra of $KIF_4O$, $CsBrF_4O$, and $CsClF_4O$ and Assignments for $CsBrF_4O$: Observed Frequencies ($cm^{-1}$) and Relative Intensities[a]

| $KIF_4O$ | | $CsBrF_4O$ | | | $CsClF_4O$ | |
|---|---|---|---|---|---|---|
| | | | Raman | | Raman | |
| IR | Raman | IR | 25 °C | −120 °C | 25 °C | −120 °C |
| 885 s | 887 (10) | 934 vs | 931 (4.8) | 929 (5.5) $\nu_1$ | 1223 (0.3) | 1228 (0.4) |
| 540 sh | 540 (5.8) | | 500 (10) | 499 (10) $\nu_2$ | 1213 sh | 1215 sh |
| 480 vs | | | | 482 (2.9) $\nu_7$ | 1200 (0.6) | 1202 (0.7) |
| | 478 (2.3) | 570–460 vs | 472 (4.4) | 471 (4.2) $\nu_7$ | 1189 (0.2) | 1191 (0.4) |
| 383 m | 381 (1.3) | | 444 (3) | 444 (3.2) $\nu_7$ | | 1182 sh |
| 366 mw | 368 (1) | | | 421 (5.9) $\nu_8$ | | 605 (0.2) |
| 279 ms | 283 (0.3) | | 413 (6.8) | 417 (7.9) $\nu_4$ | 585 (0.6) | 588 (0.9) |
| | 224 (0.5) | 399 } m | 400 sh | 401 (2.7) $\nu_8$ | 556 (0.3) | 559 (0.5) |
| | 140 (0+) | 389 } | | 390 (1.5) $\nu_8$ | 465 sh | 470 (5) |
| | | 301 vs | 299 (1.5) | 303 (1.6) $\nu_3$ | 455 (10) | 459 (9) |
| | | | | 291 (0.2) $\nu_3$ | | 452 (10) |
| | | 240 sh | 236 (1.7) | 234 (2.1) $\nu_6$ | | 435 (0.3) |
| | | | 218 sh | 225 sh $\nu_6$ | | 419 sh |
| | | | 202 (0+) | 205 (0.2) $\nu_5$ | 412 (2.4) | 414 (3.5) |
| | | | 178 (0.5) | 179 (0.5) $\nu_9$ | 395 sh | 395 (1.2) |
| | | | | 164 (0.2) $\nu_9$ | | 370 sh |
| | | | | 80 | 353 (5.5) | 358 (6.6) |
| | | | | 62 | | 345 (5) |
| | | | | | 335 sh | 334 (3.7) |
| | | | | | | 320 sh |
| | | | | | | 290 sh |
| | | | | | 276 (0.5) | 278 (0.6) |
| | | | | | | 258 (0.2) |
| | | | | | | 215 sh |
| | | | | | | 200 sh |
| | | | | | 196 (1.0) | 194 (1) |
| | | | | | | 185 sh |
| | | | | | 82 | 89 |
| | | | | | 70 | 73 |

[a] Uncorrected Raman intensities (peak heights).

Table II. Comparison of the Frequencies ($cm^{-1}$) of the Fundamental Vibrations of the $HalF_4O^-$ Anions with Those of Similar Molecules and Ions

| Approx description of mode for $XF_4Y$ in point group $C_{4v}$ | | | $ClF_4O^-$ | $ClF_4^-$ | $ClF_5$ | $BrF_4O^-$ | $BrF_4^-$ | $BrF_5$ | $IF_4^-$ | $IF_4O^-$ | $IF_5$ | $XeF_4$ | $XeF_4O$ | $XeF_5^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | $\nu_1$ | $\nu(XY)$ | 1203 | | 708 | 930 | | 682 | | 887 | 710 | | 926 | 679 |
| | $\nu_2$ | $\nu_{sym}(XF_4)$ | 456 | 505 | 539 | 500 | 523 | 587 | 522 | 537 | 616 | 543 | 576 | 625 |
| | $\nu_3$ | $\delta_{sym}$(out-of-plane $XF_4$) | 339 | 425 | 495 | 302 | 317 | 369 | 271 | 279 | 318 | 291 | 294 | 355 |
| $B_1$ | $\nu_4$ | $\nu_{sym}$(out-of-phase $XF_4$) | 356 | 417 | 480 | 417 | 449 | 535 | 455 | 480 | 604 | 502 | 527 | 610 |
| | $\nu_5$ | $\delta_{asym}$(out-of-plane $XF_4$) | | | | 205 | | | | | | | | 261 |
| $B_2$ | $\nu_6$ | $\delta_{sym}$(in-plane $XF_4$) | 278 | 288 | 375 | 235 | 246 | 312 | 195 | 219 | 276 | 235 | 233 | 300 |
| E | $\nu_7$ | $\nu_{asym}(XF_4)$ | 578 | 590 | 725 | 505 | 478 | 644 | 448 | 482 | 631 | 586 | 608 | 652 |
| | $\nu_8$ | $\delta(YXF_4)$ | 414 | | 484 | 395 | | 415 | | 374 | 372 | | 361 | 410 |
| | $\nu_9$ | $\delta_{asym}$(in-plane $XF_4$) | 194 | | 299 | 179 | [183] | 237 | | 140 | 200 | | 161 | 218 |

Consequently, a detailed analysis of the simpler $CsBrF_4O$ spectrum and its comparison with those of $ClF_4O^-$ and $IF_4O^-$ were expected to provide additional support for the proposed $C_{4v}$ model.

**Assignments for $BrF_4O^-$.** For an isolated $BrF_4O^-$ anion of symmetry $C_{4v}$ nine fundamental vibrations should be observed. These are classified as 3 $A_1$ + 2 $B_1$ + $B_2$ + 3 E. All nine modes should be Raman active, whereas only the $A_1$ and E modes should be infrared active. For a solid salt, such as $CsBrF_4O$, the actual site symmetry of the anions is expected to be lower than $C_{4v}$. This symmetry lowering can cause a splitting of the E modes into their degenerate components and violations of the above given selection rules. Furthermore, if the unit cell contains more than one anion, the number of internal modes can increase by a factor Z, where Z is the number of anions per unit cell. On the basis of tentative unit-cell dimensions reported[1] by Bougon for $KBrF_4O$, Z is estimated to be about 32. Assuming that $CsBrF_4O$ has a similar crystal structure, each mode could be split into many components. However, only a much lower number of bands are usually observed since these correlation splittings are relatively small and usually do not exceed 1–2% of the mode frequency.

Assignments for $BrF_4O^-$ can be made by comparison with the known vibrational spectra of the structurally related species $ClF_4O^-$,[13] $ClF_4^-$,[9] $ClF_5$,[14-17] $BrF_4^-$,[18] $BrF_5$,[14,16] $IF_4^-$,[19] $IF_5$,[14,16] $XeF_4$,[19,20] $XeF_4O$,[14] and $XeF_5^+$.[21] All of these species are pseudooctahedral with an approximately square-planar $XF_4$ group. A summary of the frequencies of their fundamental vibrations is given in Table II.

On the basis of its high frequency and relative intensity, the Br=O stretching mode $\nu_1$ ($A_1$) must be assigned to the band at 930 $cm^{-1}$. Of the remaining bands, the symmetric in-phase $BrF_4$ stretching mode $\nu_2$ ($A_1$) should be the most intense Raman band and by comparison with the known assignments for $ClF_4^-$, $ClF_4O^-$, $BrF_4^-$, $IF_4^-$, and $IF_4O^-$ should have a frequency in the vicinity of about 500 $cm^{-1}$. It therefore must be assigned to the Raman band at 500 $cm^{-1}$. The symmetric out-of-phase $BrF_4$ stretching mode $\nu_4$ ($B_1$) should be the second most intense Raman band and, by comparison with the known frequencies of the closely related $BrF_4^-$ anion (see Table II), is predicted to occur about 80 $cm^{-1}$ below $\nu_2$ ($A_1$). Conse-

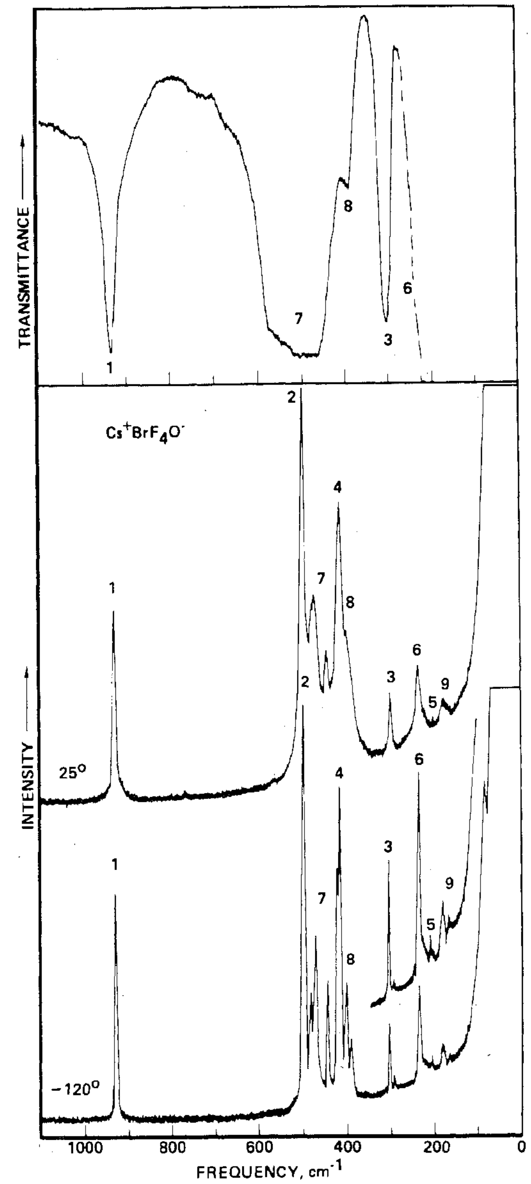

**Figure 2.** Vibrational spectra of CsBrF$_4$O: upper trace, infrared spectrum of the dry powder in an AgBr disk, the broken line indicating absorption due to the window material; lower traces, Raman spectra recorded at different temperatures and gain settings with a spectral slit width of 2 cm$^{-1}$.

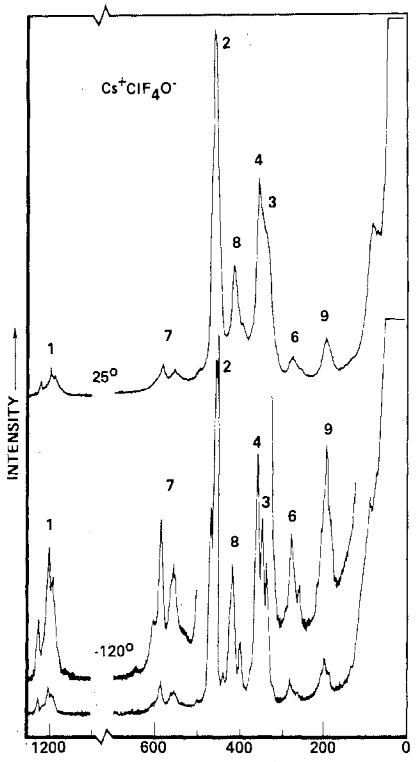

**Figure 3.** Raman spectra of CsClF$_4$O recorded at different temperatures and gain settings with a spectral slit width of 2 cm$^{-1}$.

quently, this mode must be assigned to the band at about 417 cm$^{-1}$. The last stretching mode, the antisymmetric BrF$_4$ stretch, $\nu_7$ (E), is expected to result in a very strong and broad infrared band in the 450–550-cm$^{-1}$ frequency region. Such an infrared band has been observed (see Figure 2) and is consequently assigned to $\nu_7$. In the Raman spectrum, there are three bands at 482, 471, and 444 cm$^{-1}$, respectively, which are assigned to the degenerate $\nu_7$ (E) mode for the following reasons. Their frequencies are too high for a deformation mode and differ by too much from those of the nondegenerate $\nu_2$ and $\nu_4$ modes in order to be accounted for by correlation splittings of the latter. The splitting of $\nu_7$ into three components can be explained by Fermi resonance (see below).

The assignments for the BrF$_4$O$^-$ deformation modes can be made by comparison with those of BrF$_5$ and BrF$_4^-$. In this type of molecule, the umbrella deformation mode $\nu_3$ (A$_1$) always results in a very intense infrared band and, consequently, is assigned to the strong infrared band at 301 cm$^{-1}$. Then the 236- and 178-cm$^{-1}$ bands must be due to the symmetric and the antisymmetric in-plane XF$_4$ deformation modes, $\nu_6$ (B$_2$) and $\nu_9$ (E), respectively, with $\nu_6$ (see Table II) always having the higher frequency. The OBrF$_4$ deformation mode $\nu_8$ (E) is assigned to the remaining Raman bands at 421, 401, and 390 cm$^{-1}$ which show the expected counterparts of medium intensity in the infrared spectrum. The last yet unassigned deformation mode is the antisymmetric out-of-plane XF$_4$ deformation $\nu_5$ (B$_1$). This mode is expected to be of very low intensity and usually is not observed for similar species. Of the compounds listed in Table II, it has only been observed for XeF$_5^+$ at 261 cm$^{-1}$. Since the related $\nu_3$ (A$_1$) mode of XeF$_5^+$ exhibits a frequency higher by 53 cm$^{-1}$ than that of $\nu_3$ of BrF$_4$O$^-$, the frequency of $\nu_5$ of BrF$_4$O$^-$ might be expected to occur around 210 cm$^{-1}$. A careful inspection of the Raman spectrum of CsBrF$_4$O shows indeed a very weak band at 205 cm$^{-1}$ which is therefore assigned to $\nu_5$ (B$_1$) of BrF$_4$O$^-$. The two bands at 80 and 62 cm$^{-1}$, respectively, observed in the Raman spectrum of CsBrF$_4$O occur at too low a frequency for internal BrF$_4$O$^-$ vibrations and must be assigned to lattice modes.

The splittings, best observed in the low-temperature Raman spectrum of CsBrF$_4$O, can be readily accounted for by assuming a splitting into two components for each of the three doubly degenerate E modes. The additional splittings observed for $\nu_7$ and $\nu_8$ can be readily explained by Fermi resonance of $\nu_7$ and $\nu_8$ with the E mode combination bands ($\nu_3 + \nu_9$) and ($\nu_6 + \nu_9$), respectively. Similarly the splitting observed for $\nu_3$ might be explained by Fermi resonance with a combination band of a lower frequency mode and a lattice vibration. Since bromine contains two naturally occurring isotopes ($^{79}$Br and $^{81}$Br) in almost equal abundance, we have computed the approximate isotopic splittings to be expected for BrF$_4$O$^-$. In all cases the computed isotopic splittings were considerably smaller than those observed and the relative intensities did not exhibit the correct 1:1 ratio. Consequently, the observed splittings cannot be attributed to the bromine isotopes.

The assignments proposed for CsBrF$_4$O are summarized in Tables I and II. When compared to those of the related

**Table III.** Assumed Molecular Parameters for $ClF_4O^-$, $BrF_4O^-$, and $IF_4O^-$

| Parameter | $ClF_4O^-$ | $BrF_4O^-$ | $IF_4O^-$ |
|---|---|---|---|
| $R$, Å (ax) | 1.42 | 1.56 | 1.72 |
| $r$, Å (eq) | 1.75 | 1.88 | 1.965 |
| $\beta$, deg (<OXF) | 90 | 90 | 90 |
| $\alpha$, deg (<FXF) | 90 | 90 | 90 |

compounds of Table II, these assignments for $BrF_4O^-$ result in very satisfactory frequency trends. Additional support for the assignments comes from the results of a normal-coordinate analysis (see below).

On the basis of the above assignments for $CsBrF_4O$, the previously reported[1,2] vibrational spectrum of $KBrF_4O$ can be reassigned in the following manner (cm$^{-1}$): 930 ($\nu_1$); 529 ($\nu_2$); 506, 486, 481, 459 ($\nu_7$); 434 ($\nu_4$); 421, 409, 399 ($\nu_8$); 314 ($\nu_3$); 248, 239 ($\nu_6$); 196, 184, 161 ($\nu_9$).

**Assignments for $ClF_4O^-$ and $IF_4O^-$.** The assignments previously proposed[13] for $ClF_4O^-$ have been confirmed by this study. In view of the low-temperature splittings observed for $BrF_4O^-$, we have examined the low-temperature Raman spectrum of $CsClF_4O$ for similar effects. In general, the assignments for chlorine fluorides are more difficult than those of the corresponding bromine and iodine compounds. This is caused by a well-documented[22] overlap of the frequency ranges of the stretching and the deformation modes. This frequently results in coincidences of fundamental vibrations and, if they belong to the same symmetry species, in their mixing.

Although the room-temperature Raman spectra of $CsBrF_4O$ (see Figure 2) and $CsClF_4O$ (see Figure 3) in the $HalF_4$ stretching frequencies region appear at first glance to be quite analogous, this first impression is somewhat misleading. For $ClF_4O^-$, the antisymmetric $ClF_4$ stretching mode $\nu_7$ has a frequency considerably higher than those of the two symmetric stretching modes $\nu_2$ and $\nu_4$, whereas for $BrF_4O^-$ the frequency of $\nu_7$ falls between those of $\nu_2$ and $\nu_4$. Therefore, for $ClF_4O^-$ the bands belonging to $\nu_7$ are well isolated and can be assigned with confidence. The remaining assignment of the $ClF_4O^-$ spectrum has previously been discussed in detail[13] and, therefore, is not reiterated.

For $IF_4O^-$, the assignments[4] proposed by Milne and Moffett have been adopted, except for $\nu_9$ (E). This mode results in a very weak and broad Raman band. On the basis of frequency correlations with related molecules and force constant arguments, a frequency of about 140 cm$^{-1}$ appears more plausible than the value of 124 cm$^{-1}$ previously proposed.[4]

Table II lists the frequencies of 12 species containing an approximately square-planar $XF_4$ group. The given assignments are all consistent with each other, thus rendering any gross misassignments for any of these species highly unlikely. The trends observed within this group of 12 species will be discussed in terms of their force constants (see below) rather than in terms of their frequencies since the frequencies of some of the modes are strongly influenced by the mass of the central atom.

**Force Constants.** The plausibility of the above assignments for the $XF_4O^-$ anions was examined by computations of modified valence force fields and by their comparison with those of the structurally related $XF_4$ and $XF_5$ species. The required potential and kinetic energy metrics were computed by a machine method[23] using the geometries listed in Table III. For $BrF_4O^-$ and $ClF_4O^-$ the exact geometries are unknown and therefore idealized bond angles of 90° were assumed. The bond lengths of $BrF_4O^-$ were estimated by comparison with those known for the related species $BrF_4^-$,[24] $BrF_5$,[25] and $BrO_4^-$.[26] For $ClF_4O^-$ the previous estimates[13] were adopted. For $IF_4O^-$ the exact geometry is known.[3] Since the observed OIF bond angle of 89° is very close to the 90° estimates used for $ClF_4O^-$ and $BrF_4O^-$ and since the OXeF bond angle in $XeOF_4$ was found to be larger than 90° (91.8°),[27] we have also used a 90° bond angle for $IF_4O^-$. This simplifies the computations and makes the resulting force fields more comparable. The force constant definitions used are those[14] of Begun et al. Literature values, for which the deformation coordinates had been weighted by unit (1 Å) distance, were converted back to unweighted values to allow a better comparison. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. The potential energy distribution showed that for the $XF_4O^-$ anions all of the vibrations were highly characteristic (99–100%), except for the E block. However, introduction of small $F_{78}$ terms resulted in the E-block vibrations also becoming highly characteristic (91% or higher). The resulting force fields are summarized in Table IV.

As can be seen from Table IV, the force constants are all very reasonable. A few very minor deviations can be readily explained. For example, $f_{rr}$ of $BrF_4^-$ appears somewhat high. This is caused by using for the antisymmetric stretching mode the relatively low frequency value of 478 cm$^{-1}$ observed for the solution spectrum.[19] For the solid, the band due to this vibration is extremely broad[18] with its band center being closer

**Table IV.** Comparison of the Symmetry and Internal Force Constants[a] of 12 Species Containing an Approximately Square-Planar $XF_4$ Group Using the Assignments and Frequency Values of Table II

| | | $ClF_4O^-$ | $ClF_4^-$ [b] | $ClF_5$ [c] | $BrF_4O^-$ | $BrF_4^-$ [b] | $BrF_5$ [c] | $IF_4^-$ [b] | $IF_4O^-$ | $IF_5$ [c] | $XeF_4$ [b] | $XeF_4O$ [d] | $XeF_5^+$ [e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | $F_{11} = f_R$ | 9.38 | | 3.51 | 6.70 | | 4.02 | | 6.56 | 4.82 | | 7.08 | 4.35 |
| | $F_{22} = f_r + 2f_{rr} + f_{rr'}$ | 2.33 | 2.853 | 3.24 | 2.80 | 3.06 | 3.81 | 3.052 | 3.23 | 4.22 | 3.302 | 3.60 | 4.38 |
| | $F_{33} = f_\beta + 2f_{\beta\beta} + f_{\beta\beta'}$ | 0.415 | 0.630 | 1.20 | 0.470 | 0.577 | 0.805 | 0.514 | 0.575 | 0.72 | 0.597 | 0.601 | 0.875 |
| $B_1$ | $F_{44} = f_r - 2f_{rr} + f_{rr'}$ | 1.38 | 1.946 | 2.59 | 1.95 | 2.258 | 3.21 | 2.319 | 2.58 | 4.08 | 2.822 | 3.11 | 4.17 |
| | $F_{55} = f_\beta - 2f_{\beta\beta} + f_{\beta\beta'}$ | | | | 0.682 | | | | | | | | 0.764 |
| $B_2$ | $F_{66} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$ | 0.216 | 0.232 | 0.389 | 0.154 | 0.169 | 0.271 | 0.106 | 0.134 | 0.217 | 0.155 | 0.152 | 0.260 |
| E | $F_{77} = f_r - f_{rr'}$ | 1.81 | 1.86 | 2.43 | 1.91 | 1.794 | 2.97 | 1.755 | 2.01 | 3.39 | 3.048 | 3.16 | 3.65 |
| | $F_{88} = f_\beta - f_{\beta\beta'}$ | 0.494 | | 0.772 | 0.386 | | 0.635 | | 0.444 | 0.526 | | 0.418 | 0.595 |
| | $F_{99} = f_\alpha - f_{\alpha\alpha'}$ | 0.157 | | 0.382 | 0.142 | 0.143 | 0.249 | | 0.091 | 0.192 | | 0.122 | 0.232 |
| | $F_{78} = f_{r\beta} - f_{r\beta'}$ | 0.246 | | 0.185 | 0.128 | | | | 0.087 | | | | |
| $f_R$ | | 9.38 | | 3.51 | 6.70 | | 4.02 | | 6.56 | 4.82 | | 7.08 | 4.35 |
| $f_r$ | | 1.838 | 2.13 | 2.674 | 2.142 | 2.227 | 3.24 | 2.221 | 2.458 | 3.77 | 3.055 | 3.258 | 3.968 |
| $f_{rr}$ | | 0.238 | 0.23 | 0.161 | 0.213 | 0.20 | 0.15 | 0.183 | 0.163 | 0.035 | 0.120 | 0.123 | 0.053 |
| $f_{rr'}$ | | 0.028 | 0.27 | 0.244 | 0.232 | 0.433 | 0.27 | 0.466 | 0.447 | 0.38 | 0.007 | 0.098 | 0.318 |
| $f_\alpha$ [f] | | 0.187 | ~0.2 | 0.385 | 0.148 | 0.156 | 0.260 | ~0.1 | 0.113 | 0.205 | ~0.13 | 0.137 | 0.246 |
| $f_\beta$ [g] | | 0.46 | ~0.6 | 0.98 | 0.428 | ~0.5 | 0.720 | ~0.46 | 0.510 | 0.623 | ~0.49 | 0.509 | 0.735 |

[a] All values in mdyn/A. [b] Data from ref 19. [c] Data from ref 16. [d] Data from ref 14. [e] Data from ref 21; values of $f_{rr}$ and $f_{rr'}$ in Table V of ref 21 should be exchanged. [f] Assuming $f_{\alpha\alpha} = 0$. [g] Assuming $f_{\beta\beta} = 0$.

to 500 cm$^{-1}$. If this higher frequency value is chosen, $f_{rr}$ of $BrF_4^-$ becomes more similar to those of $BrF_4O^-$ and $BrF_5$. Similarly for the lighter central atoms, the off-diagonal symmetry force constants in the E block become more important, thus increasing the uncertainties in these numbers which were obtained from underdetermined force fields.

**General Trends.** Inspection of Table IV reveals the following trends. Whereas the values of the XF stretching force constants either are similar (within the $XF_4^-$ series) or increase in the direction Cl < Br < I (for $XF_4O^-$ and $XF_5$), the XO stretching force constant in $ClF_4O^-$ is much higher than those in both $BrF_4O^-$ and $IF_4O^-$. Since the values of the XO force constants within the $ClO_4^-$, $BrO_4^-$, $IO_4^-$ series (8.24, 6.05, 5.90 mdyn/Å)[28] exhibit the same trend, this seems to reflect a general characteristic of XO bonds. In the $XO_4^-$ series, the central X atom does not possess any free valence electron pair or fluorine ligands, and therefore no special resonance or bonding effects should be invoked. The bond-weakening effect of a formal negative charge in the anions and the bond-strengthening effect of a positive charge in the cations are as expected. The negative charge increases the $X^{\delta+}$—$F^{\delta-}$ polarity of the $XF_4$ bonds, thus weakening them. The reverse is true for a positive charge. This effect can also account for most of the observed increase in the force constants when going from an iodine species to the corresponding isoelectronic xenon species which differ by one formal charge.

A comparison of the $XF_4^-$–$XF_4O^-$ pairs for each halogen shows that for X being chlorine, an oxygen substituent releases electron density to the more electronegative $ClF_4$ group, thus increasing the polarity of the $ClF_4$ bonds and decreasing the Cl–F stretching force constant. For X being bromine, there is little change in the X–F stretching force constant indicating comparable electronegativities for oxygen and the $BrF_4$ group. For X being iodine, oxygen becomes more electronegative than the $IF_4$ group, thus withdrawing electron density from $IF_4$ and increasing the covalency of the $IF_4$ bonds.

The $XF_4$ deformation constants $f_\alpha$ show the expected trend. With decreasing size of the central atom, the mutual repulsion among the ligands increases and the bonds become more difficult to deform. The FXO angle deformation constant, $f_\beta$, does not appear to change significantly when going from chlorine to iodine. However, for a given halogen atom, $f_\beta$ appears to follow the same trends exhibited by the corresponding $XF_4$ stretching force constants, $f_r$.

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**Registry No.** $CsClF_4O$, 39018-38-7; $CsBrF_4O$, 65391-03-9; $KIF_4O$, 59654-71-6; KF, 7789-23-3; $I_2O_5$, 12029-98-0; $IF_5$, 7783-66-6; $CsBrO_4$, 33259-95-9; $BrF_5$, 7789-30-2; $F_2$, 7782-41-4; $KBrF_4O$, 60995-34-8; $ClF_3$, 7790-91-2; $CsClF_4$, 15321-04-7; $ClF_5$, 13637-63-3; $BrF_4^-$, 19702-38-6; $IF_4^-$, 19702-40-0; $XeF_4$, 13709-61-0; $XeF_4O$, 13774-85-1; $XeF_5^+$, 42879-72-1.

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# A Spectroscopic Reexamination of a Series of Bis($\beta$-diketonato)copper(II) Complexes

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ESR and optical absorption studies of a series of bis($\alpha$-substituted $\beta$-diketonato)copper(II) complexes (the substituent is the alkyl or trifluoromethyl group) in toluene or cyclohexane have been carried out systematically. ESR spectra have been analyzed by computer simulation. The coordination bondings as well as the energies and intensities of the metal ← ligand charge-transfer transitions of $B_{3u}$ and $B_{2u} \leftarrow B_{1g}$ in $D_{2h}$ and those of d–d transitions have been fully discussed, with special attention to the correlation of them with the p$K_a$ of the ligands, and their mutual relationships have been explained satisfactorily in terms of covalency in the $\sigma$ bonding.

## Introduction

Many studies on the ultraviolet and visible spectra of bis($\beta$-diketonato)copper(II) complexes have been carried out primarily in order to assign spectral bands.[2-11] Various ambiguities, however, still remain because conclusive data have not been available. On the other hand, many ESR studies of the complexes also have been done since Maki and McGarvey's excellent work in 1958.[12-16] The ESR results so far obtained not only for the complexes but also for many other planar copper(II) complexes, however, do not seem entirely satisfactory. This is because there have not been many cases in which direct comparison among the planar complexes in their ESR results is of significance. Inaccuracies in some data may also be responsible for this situation.

One method for improving the situation is to reinvestigate systematically a series of planar copper(II) complexes of