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The Vibrational Spectra and Structures of Perbromyl and Perchloryl Fluorides[1]

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Raman and infrared spectra of BrO_3F gas and the Raman spectrum of ClO_3F gas are reported. The ClO_3F results confirm the tetrahedral C_{3v} symmetry indicated by earlier work, and the BrO_3F results support a similar structure for it. The fundamental frequencies of BrO_3F are 875.5, 605.0, and 359.8 cm^{-1} for species a_1 and 976.5, 382.0, and 286 cm^{-1} for species e.

Introduction

Perbromyl fluoride, BrO_3F, has recently been synthesized for the first time,[2] and we have undertaken to study its infrared and Raman spectra in order to establish its molecular structure. In the course of our study it became evident that reliable band assignments could only be made by comparison with the spectra of the analogous molecule ClO_3F, perchloryl fluoride. The infrared spectrum of gaseous perchloryl fluoride has been very thoroughly investigated by Lide and Mann,[3] and a portion of the spectrum has been studied at high resolution by Madden and Benedict.[4] The Raman spectrum of perchloryl fluoride, however, has only been reported in the liquid phase, and the study contains some puzzling observations.[5] We have therefore examined the Raman spectrum of gaseous ClO_3F.

Experimental Section

Materials.—Perbromyl fluoride was prepared by the reaction of potassium perbromate with antimony pentafluoride in anhydrous hydrogen fluoride.[2] The HF was subsequently absorbed in sodium fluoride.[2] The potassium perbromate was synthesized by methods that have been described in detail elsewhere.[6]

The principal impurity in the perbromyl fluoride was elemental bromine, which we reduced to quite low levels by using only the vapor in equilibrium with the liquid BrO_3F. The less volatile Br_2 concentrated in the liquid phase. In some cases the bromine concentration was reduced still further by treating the BrO_3F at room temperature with 10–100 Torr of fluorine. This converted the Br_2 to BrF_3, which was left behind when the BrO_3F was distilled at −80°. However, this procedure introduced some HF into the sample. Furthermore, traces of Br_2 were continually formed in the BrO_3F, most likely in the course of its fluorination of the surfaces with which it came in contact.

Perchloryl fluoride was prepared from potassium perchlorate by the method of Wamser, *et al.*[7]

Spectral Measurements.—The Raman spectra were obtained with a Carson argon ion laser, a Spex 1401 monochromator linear in wave number, an ITT FW-130-S20 detector, Hamner photon-counting electronics, and a TI recorder. The method of obtaining polarization data was No. IV of those described by Claassen, Selig, and Shamir.[8]

The perchloryl fluoride was contained in a Pyrex ampoule for the Raman experiment. Perbromyl fluoride reacts with glass, however, and its Raman spectrum was obtained in a cell machined out of Kel-F and fitted with clamped-on sapphire windows. Inasmuch as these windows were optically active, the resulting polarization measurements are only qualitative.

The infrared spectrum of perbromyl fluoride was obtained with a Beckman IR-12 spectrophotometer, using a 10-cm nickel cell with clamped-on windows. The window material was silver chloride for measurements above 400 cm^{-1} and polyethylene for measurements at lower wave number.

Results and Discussion

Perchloryl Fluoride.—Figure 1 shows the Raman spectrum of gaseous perchloryl fluoride. If we had no other information than this spectrum, we could immediately assign the three sharp, polarized bands to totally symmetric modes, while the presence of only three broad, depolarized bands would indicate that the symmetry can be no lower than C_{3v}. We therefore assign the 1062-, 716-, and 549-cm^{-1} bands to species a_1 and the 1314-, 573-, and 414-cm^{-1} bands to species e, for tetrahedral C_{3v} symmetry. This agrees well with the earlier work.[3,5]

Our results are in essential agreement with the Raman spectrum of liquid ClO_3F,[5] but we have made one important improvement. In the liquid an unexpectedly broad band was observed between 695 and 724 cm^{-1}, while in the gas this band is resolved to show the isotope shift. The insets in Figure 1 show this band and the intense 1062-cm^{-1} band at high resolution. It is interesting to note that the four peaks between 704.1 and 716.8 cm^{-1} all coincide to within less than 1 cm^{-1} with the four Q branches seen in the infrared spectrum.[3] The isotope shift for this band must be 10.3 cm^{-1}, with two Q branches showing for each isotopic molecule. The isotope shift indicated in the other inset is 2.1 cm^{-1}. Madden and Benedict[4] reported an isotope shift of 0.9 cm^{-1} for the band at 549 cm^{-1}, but our Raman work did not resolve this band.

We see, then, that the vibrational spectra of perchloryl fluoride are well characterized, and they should provide reliable guidance for assigning the spectral bands of perbromyl fluoride.

Perbromyl Fluoride.—The Raman spectrum of

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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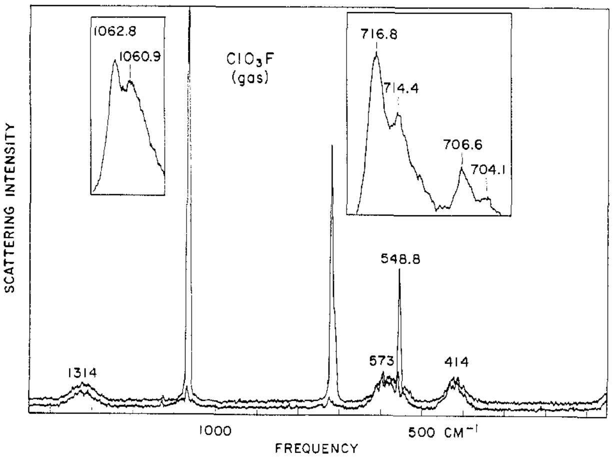


Figure 1.—Raman spectrum of gaseous perchloryl fluoride at ~900 Torr pressure and room temperature. The upper trace is with the electric vector perpendicular to the plane of the sample and slit length, while the lower trace is with the electric vector parallel to this plane. Main traces were made with a 4-cm^{-1} slit width, the small inset was made with a 0.7-cm^{-1} slit width, and the large inset was made with a 1.7-cm^{-1} slit width.

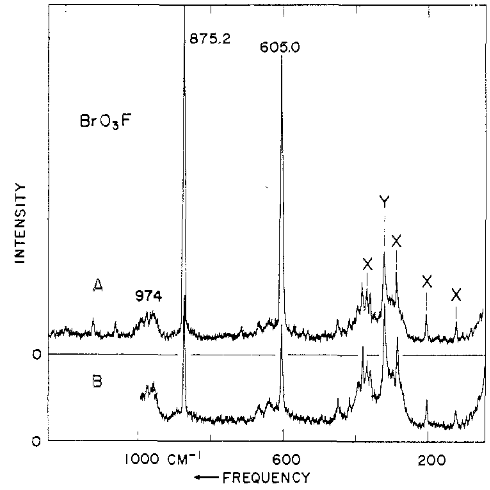


Figure 2.—Raman spectrum of gaseous perbromyl fluoride at *ca.* 2 atm pressure and room temperature. The polarization differs between traces A and B, but the optical activity of the sapphire cell windows prevents quantitative interpretation. Bands marked "X" and "Y" belong to HF and Br_2, respectively.

BrO_3F appears in Figure 2. The sharp, intense bands at 875.2 and 605.0 cm^{-1} are definitely polarized, and they can therefore be assigned to species a_1. The band at 974 cm^{-1} is depolarized, and we assign it to species e. At lower frequencies, however, the spectrum is complicated by HF lines and by the fluorescence of Br_2.

The infrared spectrum of perbromyl fluoride is shown in Figure 3. In addition to intense bands at frequencies near to those found in the Raman spectrum, there are infrared bands centered at 382.0 and 286 cm^{-1}, and there is a spike at 359.8 cm^{-1} that is probably a Q branch.

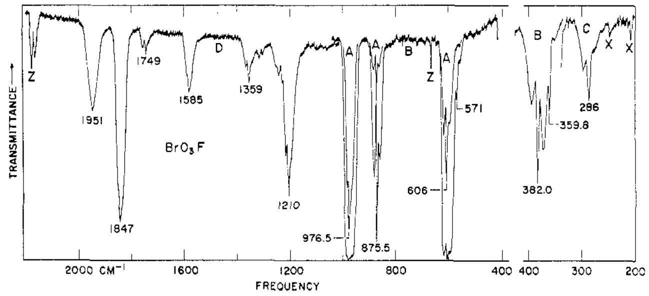
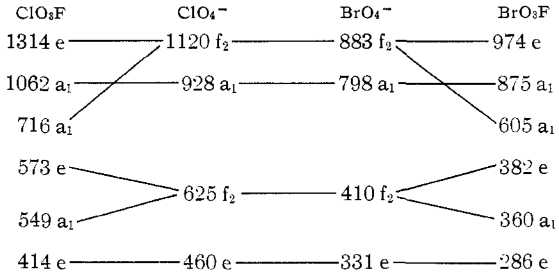


Figure 3.—Infrared spectrum of gaseous perbromyl fluoride; cell length 10 cm; sample pressures: A, ~6 Torr; B, ~20 Torr; C, ~200 Torr; D, ~600 Torr. Bands marked "X" and "Z" belong to HF and CO_2, respectively.

To assign these bands to species is not easy. We may obtain guidance by making comparisons with ClO_4^-, and BrO_4^-, as is suggested in Table I. From this table it appears that the two bands of BrO_3F that split from the BrO_4^- band at 410 cm^{-1} should be near each other at about 350 cm^{-1}. This supports the identification of the infrared band at 359.8 cm^{-1} as a fundamental. Then, of the bands at 359.8 and 382.0 cm^{-1}, one must belong to species a_1 and the other to species e. Careful examination of the Raman spectrum shows two small peaks at approximately these frequencies. The one at 354 cm^{-1} appears somewhat weaker in the lower trace relative to nearby peaks, suggesting that it is polarized. We therefore assign the 359.8-cm^{-1} infrared band to species a_1 and the 382.0-cm^{-1} band to species e. This

TABLE I

VIBRATIONS OF RELATED MOLECULES AND IONS[a]



[a] Frequencies in cm^{-1}. Values for ClO_4^- from ref 9 and 10; values for BrO_4^- from ref 6.

TABLE II

OBSERVED SPECTRAL BANDS OF PERCHLORYL AND PERBROMYL FLUORIDES[a]

ClO_3F		BrO_3F		
Ir	Raman	Ir	Raman	Assignment
1061 s	1062.8 1060.9 vs^b	875.5 s	875.2 vs^b	ν_1 (a_1)
717 s 707 m	716.8 706.6 s^b	606 vs	605.0 vs^b	ν_2 (a_1)
549 w	548.8 m^b	359.8 m	354? w^b	ν_3 (a_1)
1315 vs	1314 w	976.5 vs	974 w	ν_4 (e)
589 m	573 w	382.0 s	376? w	ν_5 (e)
405 w	414 w	286 w	296? vw	ν_6 (e)
809 w		571 w		$2\nu_6$
1412? 1430 w		1210 w		$2\nu_2$
1897 w		1359 vw		$\nu_4 + \nu_5$
2030 w		1585 vw		$\nu_2 + \nu_4$
2115 w		1749 vw		$2\nu_1$
Ca. 2350 w		1847 w		$\nu_1 + \nu_4$
2630 w		1951 vw		$2\nu_4$

[a] Frequencies in cm^{-1}. Infrared frequencies for ClO_3F from ref 3. [b] Polarized.

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assignment gives the best agreement with the analogy suggested by Table I, and it is also supported by the fact that Lide and Mann[3] found the e infrared band of perchloryl fluoride at 589 cm^{-1} to be more intense than the a_1 band at 549 cm^{-1}.

The infrared bands at 382.0 and 286 cm^{-1} have rather different contours, although both are assigned to species e. This is not surprising, because the Coriolis interactions commonly produce different band shapes for degenerate bands of the same species.

Table II lists and assigns all the observed bands of BrO_3F and the corresponding bands of ClO_3F. The seven combination bands observed in the infrared spectrum of BrO_3F can all be accounted for as overtones or binary sums.

In conclusion, the results of this study establish that perbromyl fluoride is isostructural with perchloryl fluoride; *i.e.*, it is a tetrahedral molecule of C_{3v} symmetry, with three oxygen atoms and one fluorine atom bonded to the central bromine atom.

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Spectroscopic and Chemical Properties of the Cyanotrihydroborate Anion

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The preparation of the potassium salt of the cyanotrihydroborate anion (KBH_3CN) is reported and a procedure for obtaining high-purity cyanotrihydroborate salts is outlined. The infrared and Raman spectra of BH_3CN^- and cyanotrideuterioborate (BD_3CN^-) are reported and the fundamental frequencies are assigned. The nmr and infrared data for this species are used to make qualitative comparisons of the bonding and structures of BH_3CN^- and other BH_3X adducts. The behavior of KBH_3CN in strongly acidic and neutral aqueous solutions is examined. K_b for hydrolysis of KBH_3CN is found to be approximately 10^{-10}. Attempted reductions of the cationic species Ag^+, Hg^{2+}, Cu^{2+}, and $Fe(CN)_6^{3-}$ by BH_3CN^- are discussed. A tentative mechanistic model for metal ion reduction is proposed and contrasted with that proposed for H^+.

Introduction

Several authors[2–9] have investigated BH_3 adducts in recent years. The interest in this area has ranged from investigations into the behavior of BH_3 as related to its isoelectronic analog O[3,4] to the general study of BH_3X compounds and attempts to correlate their chemical and structural properties.[2,5–8] Work in this latter area has been somewhat hampered by the lack of detailed information on a large number of BH_3X adducts. Recent reports by Parry and coworkers[3,4] and Keller[6] have contributed substantially to the available information on BH_3 adducts.

Wittig[10] first isolated BH_3CN^- as the lithium salt. His report gave limited solubility and stability data. More recent work by Borch[11] and others[12] has established the utility of $LiBH_3CN$ as a selective reducing agent for organic reductions. Also, Kreevoy[13] has published preliminary kinetic data for the acid (H^+) hydrolysis of $LiBH_3CN$ and proposed a mechanism for its decomposition. The possibility of coordination of BH_3CN^- by transition metal ions is obvious, but, to date, the only report on BH_3CN^-–M^+ complexes has been Shriver's[14] report that a solution of $Fe(phen)_2(CN_2)$ takes up B_2H_6. He found that the structure of the complexes formed from the metal cyanides was $M–CN–BH_3$. With BH_3CN^- the borane group is already carbon bound, and, if $M–CN–BH_3$ complexes are to form, linkage isomerization must take place. This possibility is intriguing and well worth our further investigation.

We wish to report, here, complete spectral data for BH_3CN^- and a brief discussion of some unusual properties of BH_3CN^-. Also, we use the spectral data to make qualitative comparisons between BH_3X adducts. Later reports will deal with the nature of the force field in BH_3CN^- and related molecules and give more complete data on several aspects of the transition metal chemistry of BH_3CN^-.

Experimental Section

Cation Exchange, Deuteration, and Purification Procedures for MBH_3CN and MBD_3CN Salts.—$LiBH_3CN$, purchased from Alfa Inorganics, was purified by precipitation of $LiBH_3CN \cdot$dioxane from ether solution.[10]

In a typical preparation of KBH_3CN, 0.10 mol of $LiBH_3CN \cdot$dioxane in 50 ml of H_2O was added to 0.12 mol of $KF \cdot 2H_2O$ (Fisher Scientific) in 25 ml of H_2O. The resulting solution was cooled in an ice bath (0°) and the LiF precipitate was collected

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