

**Table II.** Vibrational Modes ( $cm^{-1}$ ) for Interhalogen Molecules in Solid Argon

Mode	Cl-F species	Br-F species	I-F species
X-F str	Cl-F 770	Br-F 661	I-F 603 <sup>a</sup>
Antisym X-F	ClF <sub>2</sub> 578 <sup>b</sup>	BrF <sub>2</sub> 569	
Eq X-F	ClF <sub>3</sub> 754 <sup>c</sup>	BrF <sub>3</sub> 672 <sup>c</sup>	
Ax, antisym X-F	ClF <sub>3</sub> 683	BrF <sub>3</sub> 597	IF <sub>3</sub> 535
Ax, antisym X-F	Cl <sub>2</sub> F <sub>2</sub> 636	Br <sub>2</sub> F <sub>2</sub> 555	I <sub>2</sub> F <sub>2</sub> 526
X-F' str	ClF <sub>5</sub> 722 <sup>d</sup>	BrF <sub>5</sub> 681	IF <sub>5</sub> 704
Antisym X-F	ClF <sub>5</sub> 726	BrF <sub>5</sub> 636	IF <sub>5</sub> 634
X-F str	Cl <sub>2</sub> F 559	(Br <sub>2</sub> F 507)	(I <sub>2</sub> F 499)
X-X str	Cl <sub>2</sub> F 464		
X-X-F bend	Cl <sub>2</sub> F 270		

<sup>a</sup> Deduced from electronic spectra. <sup>b</sup> References 2 and 3.

<sup>c</sup> Reference 7. <sup>d</sup> G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

intermediate interhalogen species to be produced and trapped for spectroscopic study.

**Acknowledgment.** The Virginia study was supported by a grant from the National Science Foundation. The work done at Tennessee was supported by the Army Research Office and by the Air Force Office of Scientific Research. G.M. would like to thank W. N. Hubbard of the Argonne National Laboratory for a sample of purified fluorine.

**Registry No.** ClF, 7790-89-8; ClF<sub>3</sub>, 7790-91-2; Cl<sub>2</sub>F<sub>2</sub>, 37621-12-8; ClF<sub>5</sub>, 13637-63-3; Cl<sub>2</sub>F, 65516-29-2; BrF, 13863-59-7; BrF<sub>2</sub>, 64973-51-9; BrF<sub>3</sub>, 7787-71-5; Br<sub>2</sub>F<sub>2</sub>, 65414-56-4; BrF<sub>5</sub>, 7789-30-2; Br<sub>2</sub>F, 64973-52-0; IF<sub>3</sub>, 22520-96-3; I<sub>2</sub>F<sub>2</sub>, 65414-57-5; IF<sub>5</sub>, 7783-66-6;

I<sub>2</sub>F, 58751-33-0; F<sub>2</sub>, 7782-41-4; Cl<sub>2</sub>, 7782-50-5; Br<sub>2</sub>, 7726-95-6; I<sub>2</sub>, 7553-56-2.

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## Preparation and Photoelectrolytic Behavior of the Systems $WO_{3-x}$ and $WO_{3-x}F_x$

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Received August 27, 1977

A convenient method of preparing compounds in the system  $WO_{3-x}F_x$  is described and the photoelectrolytic behavior of  $WO_{3-x}$  and  $WO_{3-x}F_x$  anodes has been investigated. It was found that the substitution of small amounts of fluorine for oxygen in  $WO_3$  does not affect adversely its photoelectrolytic behavior. Moreover, substituted fluorine increases the stability of electrodes of  $WO_3$  when used for the photoelectrolysis of water.

### Introduction

There has been considerable interest recently in the search for stable electrode materials for use in photoelectrolysis. This process is one in which water is decomposed into hydrogen and oxygen when a suitable semiconductor, placed in an electrochemical cell, is illuminated with energy greater than the band gap, creating electron-hole pairs.<sup>1</sup> Under appropriate conditions, these electron-hole pairs can be separated and used as oxidizing and reducing species.<sup>2</sup>

The requirements of such a stable electrode material are indeed stringent. The material must be chemically inert and should have a band gap that utilizes an optimum of the solar spectrum ( $\sim 1.6$  eV). In addition, the semiconductor must be conducting and when placed in an electrolyte it should have sufficient band bending to separate the photogenerated electron-hole pairs. The position of bands relative to the electrochemical scale must be such that oxidation of  $O^{2-}/O_2$  and reduction of  $H^+/H_2$  can take place.

The degree of band bending and the position of the bands can be controlled to some degree by varying the pH of the electrolyte used in the cell and by the application of an external bias. It is known that the conductivity of such materials can

be altered by chemical substitution or doping procedures. Therefore, the properties which are most difficult to control and, thus, more critical are the magnitude of the band gap and the material's chemical stability.

To date, the only materials which have been used successfully have been broad-band oxides.<sup>3-6</sup> These oxides were made conductive by removing small amounts of oxygen. Since there is some question as to the long-term stability of these defect structures in a highly oxidizing environment,<sup>7</sup> it was of interest to compare the relative stability of defect oxides to those of oxyfluorides.

The use of  $WO_3$  as a stable electrode in photoelectrolysis has been reported by several investigators. Butler et al.<sup>8</sup> have indicated that  $WO_3$  is an n-type semiconductor with a band gap of 2.7 eV. Experiments performed with single crystals in a 1.0 M sodium acetate solution showed spontaneous photocurrent (i.e., no applied bias) with no decay in photocurrent or visible deterioration of the electrode surface even after passage of approximately 75 C/cm<sup>2</sup>. They indicated that an appreciable applied bias was necessary before photodecomposition of water was observed. Hodes et al.<sup>9</sup> found similar results with polycrystalline films of  $WO_3$  prepared by either

**Table I.** Structural Properties of  $\text{WO}_{3-x}\text{F}_x$ 

$x$	$a, \text{Å}$	$b, \text{Å}$	$c, \text{Å}$	$\alpha$	$\beta$	$\gamma$
0	7.306 (1)	7.527 (1)	3.854 (1)	$88^\circ 43' \pm 2'$	$90^\circ 17' \pm 2'$	$90^\circ 39' \pm 2'$
$0.0079 \pm 0.0005$	7.301 (1)	7.527 (1)	3.856 (1)	$88^\circ 48' \pm 2'$	$90^\circ 17' \pm 2'$	$90^\circ 35' \pm 2'$
$0.0177 \pm 0.001$	7.311 (1)	7.545 (1)	3.851 (1)	$90^\circ$	$90^\circ 51'$	$90^\circ$
$0.0663 \pm 0.005$	7.369 (1)	7.482 (1)	3.848 (1)	$90^\circ$	$90^\circ$	$90^\circ$

the oxidation of tungsten metal films or the decomposition of ammonium tungstate. Hardee and Bard<sup>10</sup> have prepared  $\text{WO}_3$  films by three different methods. Unlike Hodes et al., they found that the films prepared by the oxidation of the metal were not stable on repeated cycling of the electrode. Unfortunately, the electrode surfaces were deep blue rather than yellow-green. This color difference is indicative of either reduced  $\text{WO}_3$  or hydrogen bronzes of the type  $\text{H}_x\text{WO}_3$ .

It was therefore desirable to examine more closely the photoelectrolytic behavior of  $\text{WO}_{3-x}$  for various amounts of  $x$ . It was also of interest to determine the effect on stability of substituting fluorine for oxygen in  $\text{WO}_3$ , rather than creating defects.

### Experimental Section

Tungsten oxide was prepared by heating high purity (99.99%) tungsten foil (0.010 in.) under flowing oxygen for 24 h at 1000 °C. Defect tungsten oxide films were made by heating the  $\text{WO}_3$  samples in evacuated sealed silica tubes in the presence of freshly ground titanium at temperatures of 100–800 °C for 2–24 h.<sup>11</sup>

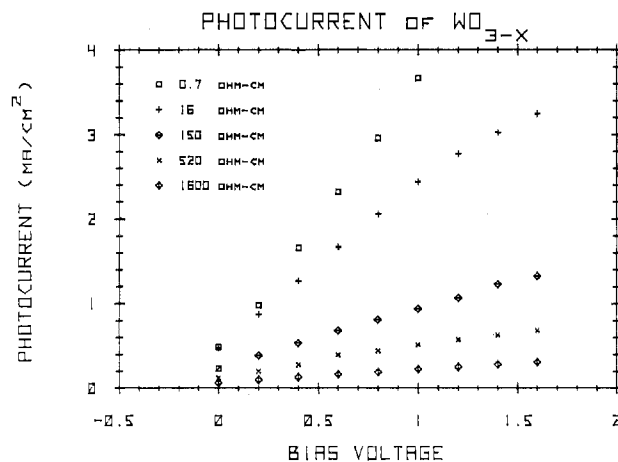
A convenient method for substituting fluorine has been used to synthesize members of the system  $\text{WO}_{3-x}\text{F}_x$ . In this process the freshly oxidized  $\text{WO}_3$  was placed on a pure tungsten foil which sits in a tungsten boat. The boat was then placed in one zone of a two-zone furnace. It was determined that the optimum temperature of this reaction zone should be 650 °C. Potassium bifluoride was placed in a nickel boat and inserted in the second zone of the furnace. This zone was maintained at 400 °C which was sufficient to allow for a slow thermal decomposition of the  $\text{KHF}_2$ . Variation in the fluorine content was achieved by varying the temperature of the reaction zone. The entire reaction chamber consisted of a nickel tube with stainless steel Swagelok fittings welded to both ends.

The reaction tube was purged initially with argon at room temperature. After 30 min the gas flow was stopped and the temperature of the two zones was raised to operating conditions. It was found that uniform samples were made under these static conditions. After 4 h the reaction tube was removed from the furnace and flushed again with argon until room temperature was achieved. During the purging procedures the argon was bubbled through a 9 M NaOH solution. All reactions were carried out in a well-ventilated hood.

The crystal structures of all of the samples were determined from powder x-ray diffraction spectra using either MgO or CaO as an internal standard. The scans were taken with a Philips Norelco diffractometer, using  $\text{Cu K}\alpha$  radiation (1.5405 Å) at a rate of  $1/4^\circ$   $2\theta$   $\text{min}^{-1}$ .

Resistivity measurements were made by ultrasonically soldering indium leads on the polycrystalline samples and using the standard four-probe van der Pauw technique.<sup>12</sup> Optical band gap measurements were made by making KBr windows which contained finely ground oxide or oxyfluoride intimately mixed and the absorption spectra were taken on a Cary 14 spectrophotometer.

Photoelectrolytic measurements were made by first soldering an oxide or oxyfluoride sample to a Pt wire which was sealed in a Pyrex tube. All but the face of the film was then coated with an electrically insulating resin (Microstop, Michigan Chrome and Chemical Co.). The electrode was then placed in a silica cell which was filled with 0.2 M sodium acetate. A platinized Pt foil with approximately five times the geometrical surface area of the oxide and oxyfluoride films was used as the counterelectrode. The electrodes were illuminated by either the full output of a 150-W xenon lamp or the output of a Model 7155 monochromator (Oriol Corp.). Absolute light intensity measurements were made using a Pyroelectric Radiometer (Model RK 3440, Laser Precision Corp.). The current vs. wavelength curves were corrected for intensity variations by normalizing the spectral output of the lamp-monochromator system to 440 nm and using the resulting values to correct the measured photocurrents. All measurements were made with the electrolyte in equilibrium with air.



**Figure 1.** Photocurrent vs. applied bias for several  $\text{WO}_{3-x}$  samples in 0.2 M  $\text{NaC}_2\text{H}_3\text{O}_2$  (pH 7.8).

Stability against reoxidation was determined by heating the films in a stream of flowing oxygen at a rate of 100 °C/h to 1000 °C and the weight change monitored with a Cahn Electrobalance.

Analysis for fluorine in the  $\text{WO}_{3-x}\text{F}_x$  samples was made by dissolving approximately 0.2 g of the samples in 9 M NaOH, adjusting the pH to 5.5 with a sodium acetate/acetic acid buffer, and measuring the fluoride ion concentration using a fluoride specific electrode (Model 94-09, Orion Research, Inc.). By the use of a specific electrode,  $\text{F}^-$  concentrations of 24  $\mu\text{g/L}$  could be determined with a reproducibility of  $\pm 2\%$ . From the weight of the samples analyzed, the value of  $x$  in the  $\text{WO}_{3-x}\text{F}_x$  samples can be reported with an accuracy equivalent to  $\pm 0.0002$ .

### Results and Discussion

**1. Crystallography.** There have been conflicting reports concerning the structure of pure  $\text{WO}_3$ .<sup>13–16</sup> It was found that  $\text{WO}_3$  prepared by completely oxidizing tungsten foil could best be indexed on a triclinic system similar to the one reported by Roth and Waring.<sup>16</sup> It transforms to a monoclinic phase upon the removal of small amounts of oxygen<sup>17</sup> or the addition of small amounts of hydrogen or sodium.<sup>18</sup>

Whereas the system  $\text{WO}_{3-x}$  ( $0 < x \leq 1$ ) is monoclinic throughout the entire range,<sup>17</sup> the system  $\text{WO}_{3-x}\text{F}_x$  ( $0 < x \leq 1$ ) undergoes the following transitions: triclinic  $\rightarrow$  monoclinic  $\rightarrow$  orthorhombic  $\rightarrow$  tetragonal  $\rightarrow$  cubic.<sup>19,20</sup> The structural properties of the  $\text{WO}_{3-x}\text{F}_x$  prepared in this study are summarized in Table I. It can be seen that the structure remains triclinic for very small ( $x = 0.0079$ ) amounts of substituted fluorine in the system  $\text{WO}_{3-x}\text{F}_x$ . When the amount of substituted fluorine is  $x = 0.0177$  the structure has undergone the transition to the monoclinic phase and when  $x = 0.0663$  the resulting phase is orthorhombic. These are consistent with results of previous investigators.

**2. Resistivity and Optical Properties.** The resistivity of the pure  $\text{WO}_3$  samples was between  $10^6$  and  $10^8 \Omega \text{ cm}$ . The resistivities of the  $\text{WO}_{3-x}$  samples ranged between  $1.2 \times 10^4$  and  $7 \times 10^{-1} \Omega \text{ cm}$  and the resistivities of the  $\text{WO}_{3-x}\text{F}_x$  samples ranged between 100 and 5  $\Omega \text{ cm}$ . Absorption measurements indicated that the band gap of  $\text{WO}_3$  and all  $\text{WO}_{3-x}\text{F}_x$  samples was  $2.65 \pm 0.10 \text{ eV}$ . This is consistent with previous investigations.<sup>8,9,21,22</sup>

**3. Photoelectrolytic Properties.** In Figure 1 are plotted the photocurrents vs. applied voltage (SCE reference) for several

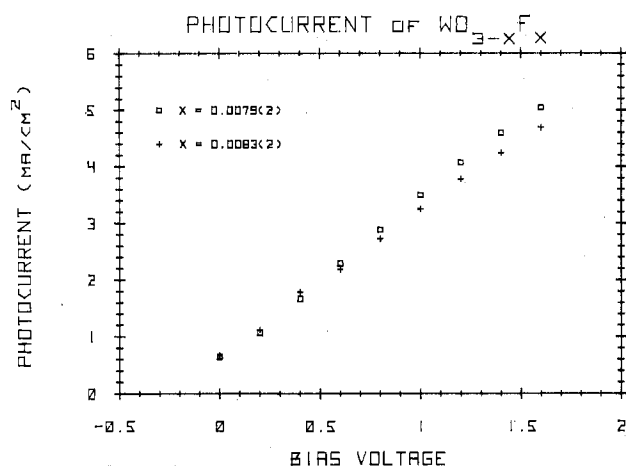


Figure 2. Photocurrent vs. applied bias for several  $\text{WO}_{3-x}\text{F}_x$  samples in 0.2 M  $\text{NaC}_2\text{H}_3\text{O}_2$  (pH 7.8).

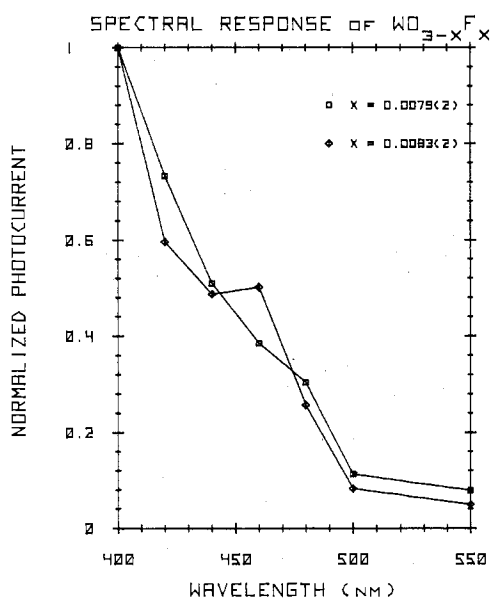


Figure 3. Normalized spectral response of  $\text{WO}_{3-x}\text{F}_x$  in 0.2 M  $\text{NaC}_2\text{H}_3\text{O}_2$ .  $E_g$  = optical band gap (2.7 eV).

$\text{WO}_{3-x}$  samples. Measurements were made with the electrolyte in equilibrium with air. As can be seen the largest photocurrent is reached for the  $\text{WO}_{3-x}$  sample having the lowest resistance, with the photocurrents of the remaining samples decreasing as the resistance increases. These results are consistent with the only effect being a change in the overall cell resistance.

The photocurrents for two triclinic samples of  $\text{WO}_{3-x}\text{F}_x$  are shown vs. applied bias in Figure 2, the measurements being made with the electrolyte in equilibrium with air. Although photocurrents were observed for all of the tungsten oxyfluorides studied, the monoclinic and orthorhombic compositions ( $x \geq 0.0177$ ) show more complex behavior.

The spectral responses of the  $\text{WO}_{3-x}\text{F}_x$  samples shown in Figure 3 were obtained with an applied bias of 0.5 V. The photocurrents plotted here were normalized for clarity by taking the ratio of the photocurrent at a given wavelength to the maximum photocurrent obtained (i.e., at 400 nm). The actual photocurrents at 400 nm are for  $x = 0.0079$   $I = 16.06 \mu\text{A}/\text{cm}^2$  and for  $x = 0.0083$   $I = 6.07 \mu\text{A}/\text{cm}^2$ . The colors of the materials varied from a light green for the  $x = 0.0079$  sample to darker green for the  $x = 0.0083$  sample.

**4. Stability.** Stability of the  $\text{WO}_{3-x}$  and  $\text{WO}_{3-x}\text{F}_x$  samples was investigated by three procedures: stability against re-oxidation, stability against hydrolysis or dissolution, and

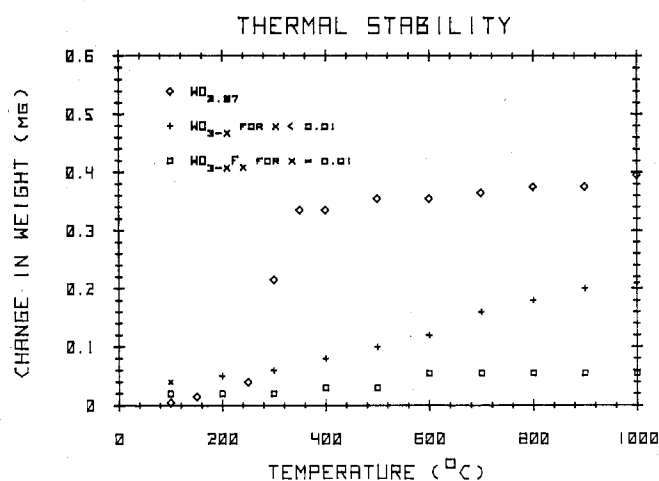


Figure 4. Stability against reoxidation for  $\text{WO}_{3-x}$  and  $\text{WO}_{3-x}\text{F}_x$  in flowing oxygen.

stability in a working cell arrangement.

Figure 4 shows the results of the reoxidation experiments. It can be seen that while  $\text{WO}_{3-x}$  readily reoxidizes at 250–300 °C, the  $\text{WO}_{3-x}\text{F}_x$  sample was stable to 600 °C, implying an increased stability to reoxidation.

It is also clear that the thermal gravimetric data shown in Figure 4 indicates that the composition of the oxyfluoride samples prepared in this study can be represented by the formula  $\text{WO}_{3-x}\text{F}_x$ . If the composition of the samples was of the stoichiometry  $\text{WO}_{3-x}\text{F}_y$ , then there would have been a gain in weight recorded equivalent to the value of  $x - y$ . It can be seen from Figure 4 that the sensitivity of this method is such that values of  $x$  (representing an oxygen deficiency) in the system  $\text{WO}_{3-x}$  can be determined where values of  $x$  are less than 0.01.

Hydrolysis and dissolution experiments were made by placing samples of  $\text{WO}_{3-x}$  and  $\text{WO}_{3-x}\text{F}_x$  in 0.2 M  $\text{H}_2\text{SO}_4$  and leaving these at 90 °C for 350 h. Neither sample showed any hydrolysis or dissolution.

Stability in a working cell, with the electrolyte in equilibrium with air, was determined by biasing the electrode at 0.5 V with respect to the platinum cathode, illuminating then with the full output of a 150-W xenon lamp and monitoring the changes in photocurrent with time. It was found that while the slightly reduced  $\text{WO}_{3-x}$  films gave stable photocurrents, the more reduced samples were less stable. The most reduced sample ( $x \sim 0.03$ ) was very unstable with the photocurrent decreasing by 30% over a period of 2 h. This is consistent with the results found by Hardee and Bard.<sup>10</sup> On the other hand, the triclinic samples of  $\text{WO}_{3-x}\text{F}_x$  gave stable photocurrents of 2  $\text{mA}/\text{cm}^2$  for periods up to 46 h ( $\sim 700$  °C). In addition, there was no significant weight loss and no visible change on the surface of the electrodes.

## Conclusions

The photoelectrolytic behavior of  $\text{WO}_{3-x}$  and  $\text{WO}_{3-x}\text{F}_x$  has been investigated. It was found that substituting fluorine for oxygen in  $\text{WO}_3$ , in small amounts, does not affect adversely the photoelectrolytic behavior of  $\text{WO}_3$  but increases the stability of the compound when used as an electrode for photoelectrolysis of water. A safe and easily controlled method of preparing  $\text{WO}_{3-x}\text{F}_x$  was described.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of C. A. Castro. The Office of Naval Research, Arlington, Va., supported the work of C. Derrington, and the National Science Foundation, Washington, D.C. (Grant No. 37104), supported the work of

W. S. Godek. The authors would also like to acknowledge the support of the Materials Research Laboratory Program at Brown University and the helpful advice of Dr. A. Nozik of Allied Chemical Corp. and Dr. Kirby Dwight of Brown University.

Registry No.  $\text{WO}_3$ , 1314-35-8;  $\text{KHF}_2$ , 7789-29-9.

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## Xenon-129 Pulse Fourier-Transform Nuclear Magnetic Resonance Spectroscopy

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Received October 21, 1977

High-resolution xenon-129 pulsed Fourier-transform NMR studies have been carried out on a variety of  $^{129}\text{Xe}$ -containing compounds. New chemical shift data for this heavy nucleus in a wide range of oxidation states are summarized. The chemical shift range for  $^{129}\text{Xe}$  in its compounds exceeds 4000 ppm which is consistent with large paramagnetic contributions to the shielding constant. In lieu of a comprehensive theory of heavy element chemical shifts, empirical correlations among  $^{129}\text{Xe}$  chemical shifts are described which provide a sensitive probe for assessing the degree of ionic character in the Xe-F bond.

### Introduction

Widespread interest in defining structures and properties of xenon fluorides and oxyfluorides, their cations, and related covalent species has resulted in several recent studies of their  $^{19}\text{F}$  NMR spectra.<sup>3-7</sup> Among the naturally occurring isotopes of xenon, nuclear magnetic resonance spectroscopy of the nuclide  $^{129}\text{Xe}$  ( $I = 1/2$ , 26.2%) can, in principle, yield valuable complementary structural information. At the same time  $^{129}\text{Xe}$  provides an ideal subject for a thorough investigation of a heavy nucleus since it can be obtained in a variety of compounds and in a wide range of oxidation states (+2, +4, +6, and +8).

A major difficulty in direct observation  $^{129}\text{Xe}$  NMR spectroscopy has been the relatively low gyromagnetic ratio  $\gamma$  of  $^{129}\text{Xe}$ , which yields a much smaller Boltzmann exponent,  $2\gamma p_0 H/kT$ , than that of fluorine. Xenon-129 resonance spectra are, therefore, weak and not easy to observe by conventional continuous-wave techniques. For this reason, early studies of the  $^{129}\text{Xe}$  resonance have been confined to double-resonance "tickling" experiments in which one observes the effect on the  $^{19}\text{F}$  spectrum of a small radio-frequency field swept through each line in the  $^{129}\text{Xe}$  spectrum. These early experiments have yielded chemical shift values for  $\text{XeOF}_4$ ,  $\text{XeF}_4$ , and  $\text{XeF}_2$ .<sup>8,9</sup> While the receptivity of natural-abundance  $^{129}\text{Xe}$  is only  $5.60 \times 10^{-3}$  compared to the proton, natural-abundance  $^{129}\text{Xe}$  possesses a receptivity that is 31.6 times that of natural-abundance  $^{13}\text{C}$ , a nuclide now routinely studied by Fourier-transform techniques. Thus, the present availability of commercial pulse Fourier-transform spectrometers allows ready access to  $^{129}\text{Xe}$  data which were previously unobtainable. Recent studies by direct observation F-T techniques have

yielded new  $^{129}\text{Xe}$  chemical shift data for  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{XeO}_3$ ,  $\text{Xe}(\text{OSeF}_5)_2$ ,  $\text{Xe}(\text{OTeF}_5)_2$ ,  $\text{FXeOSeF}_5$ ,  $\text{FXeOTeF}_5$ , and  $\text{F}_5\text{SeOXeOTeF}_5$ .<sup>10,11</sup> In the light of these developments it seemed timely to undertake an extensive study of all previously known and recently prepared xenon compounds. Preliminary results of our work have already been reported in a brief communication.<sup>12</sup>

The present state of understanding of chemical shifts of heavy nuclei is unclear. Our data, however, provide a substantial body of information on a single heavy nucleus, which can be used to probe the basis of these shifts. In lieu of a comprehensive theory of chemical shifts for heavy nuclei, our approach to the discussion of  $^{129}\text{Xe}$  chemical shifts has remained essentially an empirical one. Where possible, however, attempts have been made to single out those factors which might play a dominant role in determining the observed trends. Thus, we have chosen to emphasize the very great sensitivity of the  $^{129}\text{Xe}$  chemical shift to (1) formal oxidation state of xenon, (2) the ionic character of the Xe-F bond, and (3) solvent interactions. Structural elucidation of xenon species in solution by means of  $^{129}\text{Xe}$  NMR has not been given great emphasis, as this aspect has already been adequately dealt with in a large number of instances using  $^{19}\text{F}$  NMR spectroscopy. However, we have chosen to briefly discuss two examples in the light of the present  $^{129}\text{Xe}$  NMR results which exhibit novel structural features, namely, the proposed tetramer  $(\text{XeF}_6)_4$  and the recently reported xenon-nitrogen bonded compound  $\text{FXeN}(\text{SO}_2\text{F})_2$ .

### Discussion

**Structures of Xenon Fluorides, Oxyfluorides, and Their Cations in Solution.** Although the majority of the species