

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE Technical Papers		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER m2c8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				8. PERFORMING ORGANIZATION REPORT	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <div style="text-align: right; font-size: 2em; font-family: cursive;">1121 045</div>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			A
					19b. TELEPHONE NUMBER (include area code) (661) 275-5015

62

separate items are enclosed

CR

PR-TP-1998-

MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-099
Christe (Raytheon) Boatz, Sheehy "Theory and Synthesis of New High Energy Density Materials"
HEDM Conference Presentation (Statement A)

...ness of distribution

THEORY AND SYNTHESIS OF NEW HIGH ENERGY DENSITY MATERIALS

Karl O. Christe, William W. Wilson, Greg W. Drake, Jeff A. Sheehy, Jerry A. Boatz, Berthold Hoge, Ross I. Wagner, and Xiongzi Zhang
Raytheon STX and Propulsion Sciences and Advanced Concepts, Air Force Research Laboratory, Edwards Air Force Base, CA 93524-760, and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, CA 90089

Efforts are described to combine the NF_4^+ cation with highly energetic anions, such as NO_2^- , NO_3^- , and $\text{N}(\text{NO}_2)_2^-$. In the case of NO_3^- , the NO_3^- anion was fluorinated already at very low temperatures by NF_4^+ to give fluorine nitrate in high yield. In the case of NO_2^- , the reaction with NF_4^+ yielded an unknown unstable decomposition product in low yield, but the reaction was very difficult to control and consistently exploded. In the case of $\text{N}(\text{NO}_2)_2^-$, again no stable salt was formed, and a thermally unstable decomposition product, probably $\text{FN}(\text{NO}_2)_2$, was observed by ^{19}F NMR spectroscopy.

In search for new difluoroaminating agents, attempts were made to prepare $\text{SO}_2(\text{NF}_2)_2$ from N_2F_4 and either SO_2 or SO_2Cl_2 using thermal or photochemical methods. Only the previously known compounds, FSO_2NF_2 and ClSO_2NF_2 , were obtained.

The possibility of stabilizing ozone by protonation in superacid solution was investigated. It was found that ozone does not form a stable O_3H^+ cation at temperatures as low as -78°C .

The synthesis and reactions of oxidative oxygenators, which might lead to the novel oxidizer ClF_5O , were explored. It was found that HOF does not oxygenate ClF_3 , ClF_3O , BrF_5 or IF_5 .

Attempts to repeat a previously reported synthesis of H_2OF^+ salts from XeF^+ and water, which had been claimed to be capable of oxygenating ClF_3 to ClF_3O , revealed that the previous claims are incorrect. No evidence for the existence of H_2OF^+ salts was found. Instead a novel oxygen bridged water adduct of XeF^+ is formed in these systems. When reacted with ClF_3 , this adduct forms ClO_2^+ salts and not ClF_2O^+ salts, as previously claimed.

The $\text{ClF}_4^+\text{SbF}_6^-$ and $\text{O}_2^+\text{SbF}_6^-$ salts were prepared and their crystal structure were determined.

In the area of high coordination number compounds, our studies of the pentagonal planar IF_5^{2-} anion and the pentagonal bipyramidal SbF_7^{2-} and BiF_7^{2-} anions were completed and written up in manuscript form.

Extensive use of electronic structure calculations was made in these studies to determine the geometries, stabilities, vibrational and NMR spectra of these molecules.

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

20021121 045

THEORY AND SYNTHESIS OF NEW
HIGH ENERGY DENSITY MATERIALS

K.O. CHRISTE, W.W. WILSON, J.A. SHEEHY, J.A. BOATZ,
G.W. DRAKE, B. HOGE, R.I. WAGNER, X. ZHANG

RAYTHEON STX AND PROPULSION SCIENCES,
AIR FORCE RESEARCH LABORATORY, EDWARDS AFB
LOKER HYDROCARBON RESEARCH INSTITUTE, USC

COLLABORATIONS WITH:

G. OLAH USC

S. PRAKASH USC

G. RASUL USC

D. DIXON PNWL

G. SCHROBILGEN McMASTER

M. GERKEN McMASTER

R. BARTLETT UFG

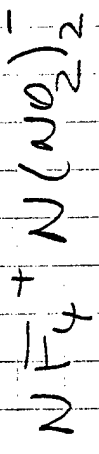
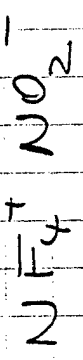
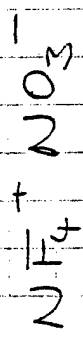
A. KORKIN UFG

NF_4^+ CHEMISTRY

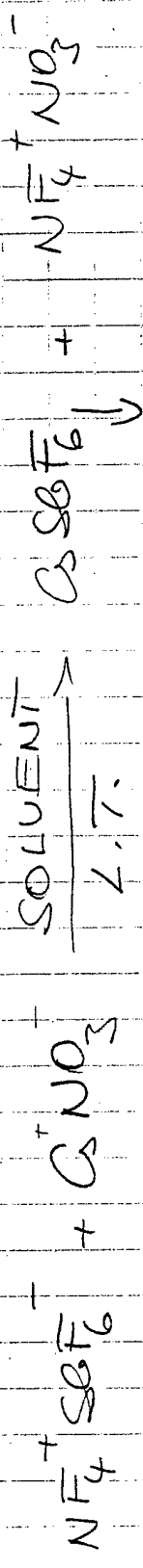
- NF_4^+ CATION FIRST PREPARED IN 1965 BY US AT STAUFFER AS $\text{NF}_4^+\text{AsF}_6^-$ SALT
- HIGHLY ENERGETIC CATION WHICH IS STABLE UP TO 250°C
- $\text{NF}_4^+\text{BF}_4^-$ HAS BEEN USED FOR DEVELOPMENT OF SOLID PROPELLANT NF_3/F_2 GAS GENERATORS FOR CHEMICAL HF/DF LASERS
- FOR ROCKET PROPULSION OR EXPLOSIVES APPLICATIONS, AN ENERGETIC COUNTERION IS REQUIRED
- THE ONLY ENERGETIC NF_4^+ SALT PREPARED SO FAR: $\text{NF}_4^+\text{CeO}_4^-$ (CHRISTE, WILSON, INORG. CHEM. 1980) BUT IS THERMALLY UNSTABLE

NF₄⁺ CHEMISTRY

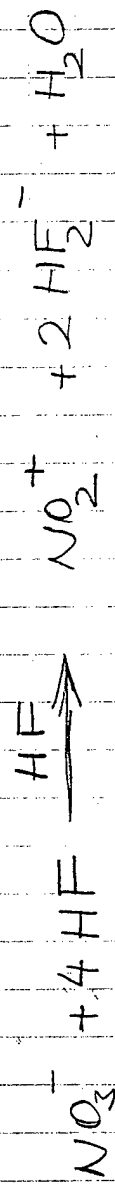
ENERGETIC NF₄⁺ SALTS OF INTEREST



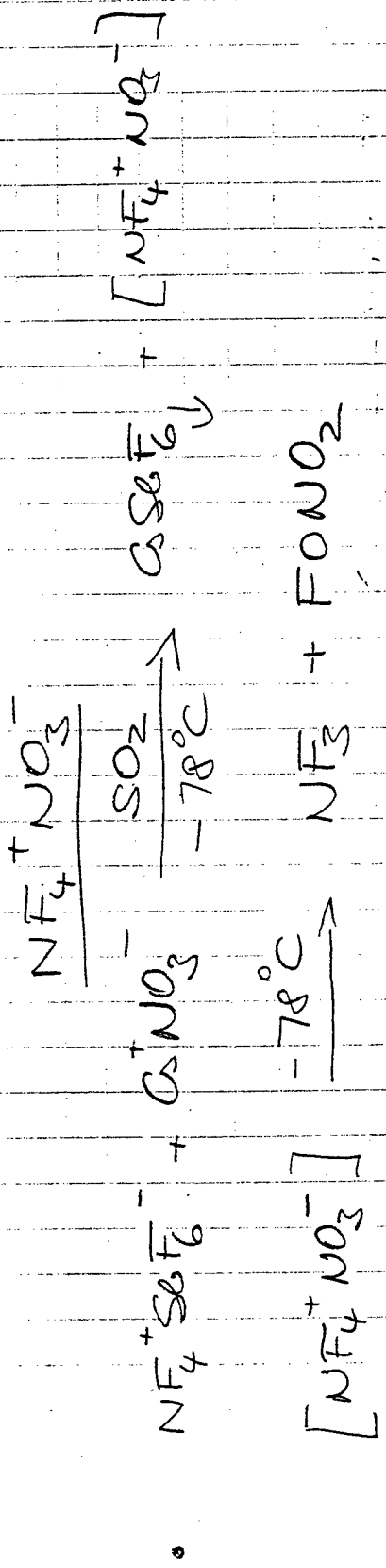
SYNTHESIS BY METATHESIS



PROBLEM: HF SOLVENT REACTS WITH NO₃⁻



ANSWER: USE SO₂ OR CH₃CN AS SOLVENTS



- NF_4NO_3 IS THERMALLY VERY UNSTABLE

- NEW SYNTHESIS OF FONO_2 IN QUANTITATIVE YIELD

NF₄⁺ / NO₂⁻ SYSTEM

REACTION OF NF₄⁺ SO₆²⁻ + K⁺ NO₂⁻ IN CH₃COOH SOLUTION

IS VIOLENT

OBSERVED A NEW, UNSTABLE COMPOUND WITH STRONG IR BANDS AT

1871 cm⁻¹

TERMINAL N=O STRETCH

1185 cm⁻¹

N-O STRETCH OR Asym F-O-N

832 cm⁻¹

O-F STRETCH OR Sym F-O-N

MOST LIKELY COMPOUND: "FONO", HOWEVER:

PREVIOUS MATRIX ISOLATION STUDY BY

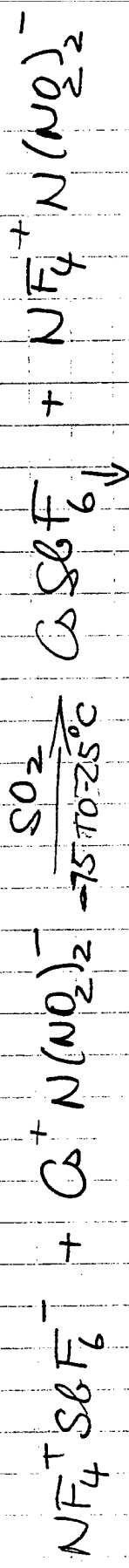
SHARDZEWSKI (1974) PROPOSED 1716, 1199, 702

cm⁻¹ FOR FONO

AB INITIO CALCULATIONS (SHEEHY, LEE, DIXON, SORENSON) DO NOT FIT WELL FOR EITHER DATA SET (PROBLEM CASE!)

$\text{NF}_4^+ / \text{N}(\text{NO}_2)_2^-$ SYSTEM

- LOW-TEMPERATURE ^{19}F NMR STUDY OF

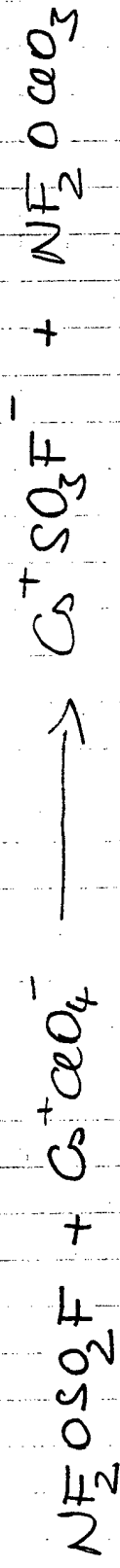


- SHOWED $\text{NF}_4^+ \text{N}(\text{NO}_2)_2^-$ TO BE STABLE BELOW -50°C
- ABOVE -50°C , NF_3 EVOLUTION AND FORMATION OF A THERMALLY UNSTABLE COMPOUND WITH $S = 53.3$
- AB INITIO CALCULATIONS FOR $\text{FN}(\text{NO}_2)_2$ GIVE $S = 53.9$ (IGLO II, B3LYP/6-31G*)

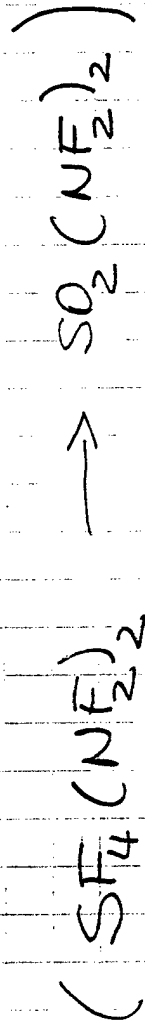
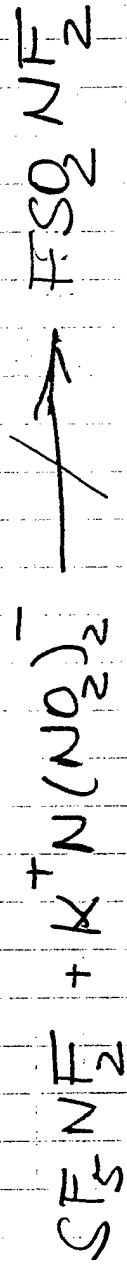
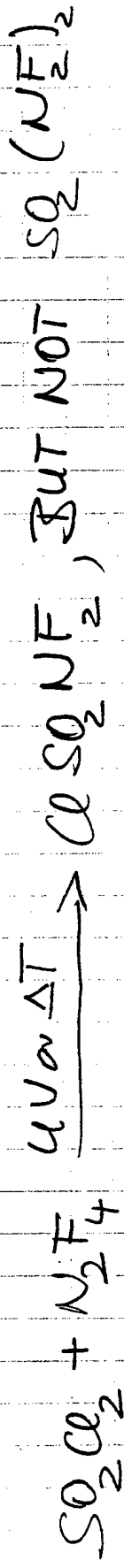
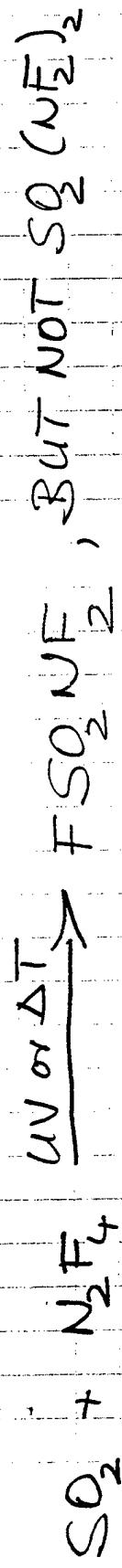
- FT-IR STUDY OF GASEOUS DECOMPOSITION PRODUCTS FROM $\text{NF}_4^+ \text{SbF}_6^- + \text{K}^+ \text{N}(\text{NO}_2)_2^-$ REACTION IN HF AT -78°C SHOW NEW BANDS AT 1711, 1324, 1301, 878, 803, 458 cm^{-1} IN ACCORD WITH EXPECTATIONS FOR $\text{FN}(\text{NO}_2)_2$
- MORE COMPLETE CHARACTERIZATION AND THEORETICAL CALCULATIONS ARE IN PROGRESS

WORK IN PROGRESS ON NOVEL NF_2 HEDM COMPOUNDS

• NF_2OCoO_3

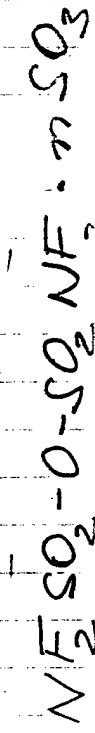


• $\text{SO}_2(\text{NF}_2)_2$ ("BAUM REAGENT")



• BAUM REAGENT IS NOT $\text{SO}_2(\text{NF}_2)_2$,

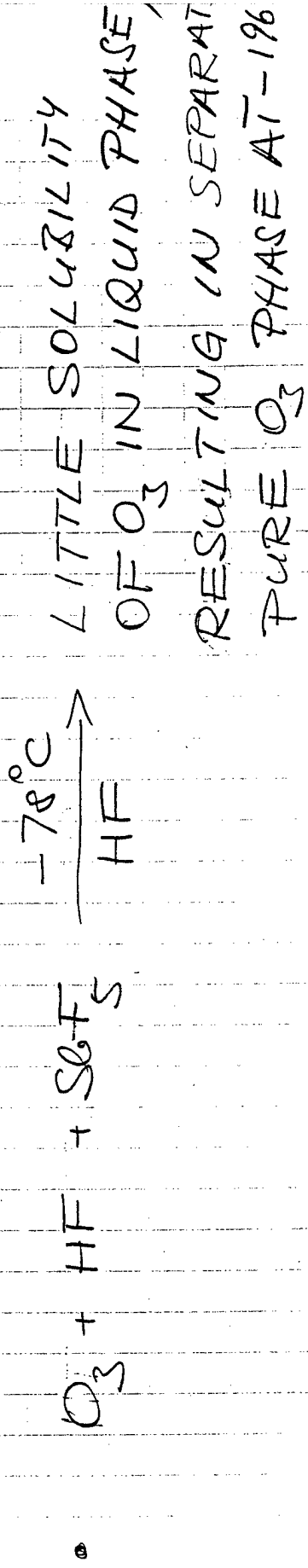
VIBRATIONAL SPECTRA AND PHYSICAL PROPERTIES SUGGEST



(8)

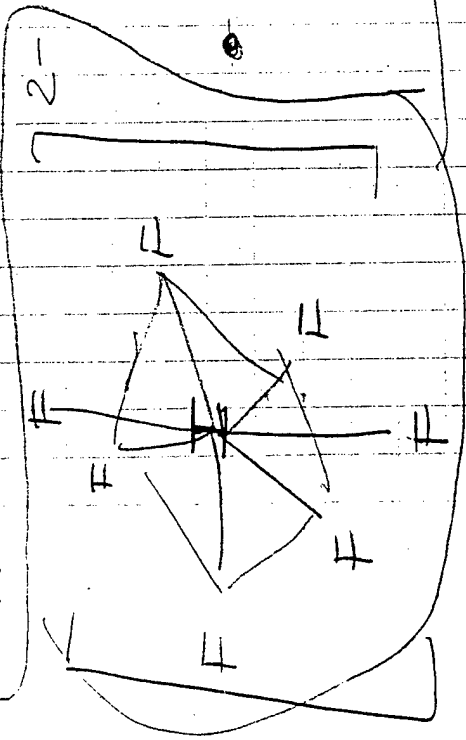
STABILIZATION OF OZONE

- O_3 IS 34.1 kcal/mol ENDOTHERMIC
- I ν OF O_3/H_2 IS 39 sec HIGHER THAN O_2/H_2
- O_3H^+ HAS BEEN OBSERVED BY ION CYCLOTRON RESONANCE SPECTROSCOPY (CACACE, 1994)
- SHOCK SENSITIVE O_3 MIGHT BE STABILIZED BY PROTONATION



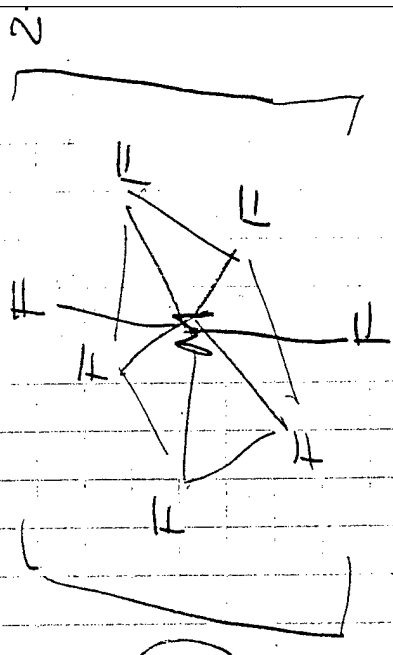
CHEMISTRY AT THE LIMITS OF COORDINATION

9) • WORK ON PENTAGONAL PLANAR IF_5^{2-} WAS COMPLETED AND PUBLISHED IN JACS (MAY 98)



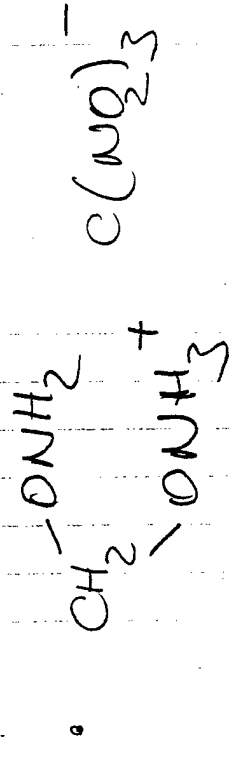
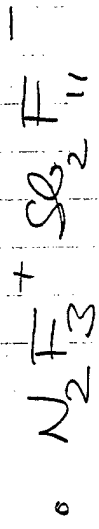
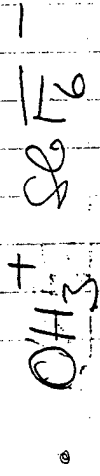
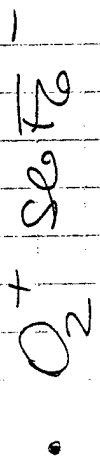
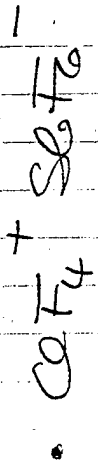
• XeF_5^- AND IF_5^{2-} ARE THE ONLY KNOWN PENTAGONAL PLANAR SPECIES

• WORK ON SbF_7^{2-} AND BiF_7^{2-} WAS ALSO COMPLETED AND IS IN PRESS (JACS)



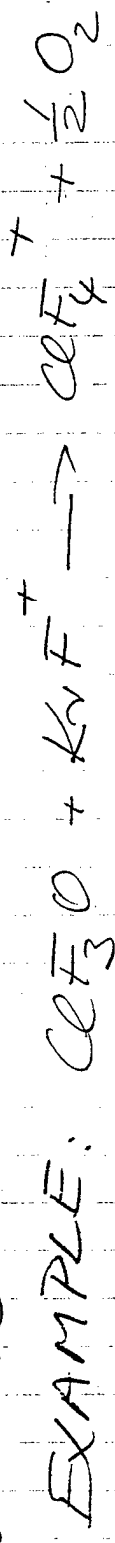
• ALTHOUGH SbF_6^- AND BiF_6^- HAD BEEN KNOWN FOR A VERY LONG TIME, SbF_7^{2-} AND BiF_7^{2-} HAD BEEN UNKNOWN

CRYSTAL STRUCTURE DETERMINATIONS.

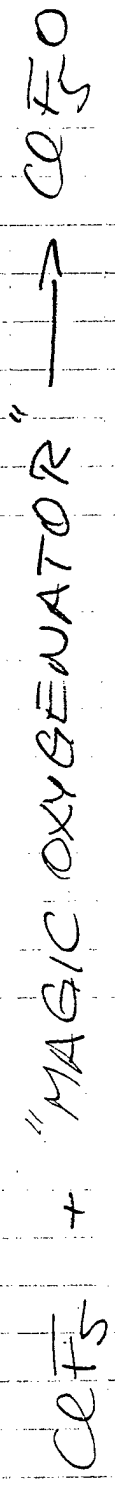


CeF₃O

- CeF₃O would be highest performing, earth-storable oxidizer with an I_{sp} being 10 sec higher than that of CeF₃O
- THEORETICAL CALCULATIONS SHOW THAT IT IS VIBRATIONALLY STABLE
- ALL PREVIOUS ATTEMPTS TO OXIDATIVELY FLUORINATE CeF₃O OR CeF₄O⁻ FAILED DUE TO OXIDATIVE ATTACK ON OXYGEN

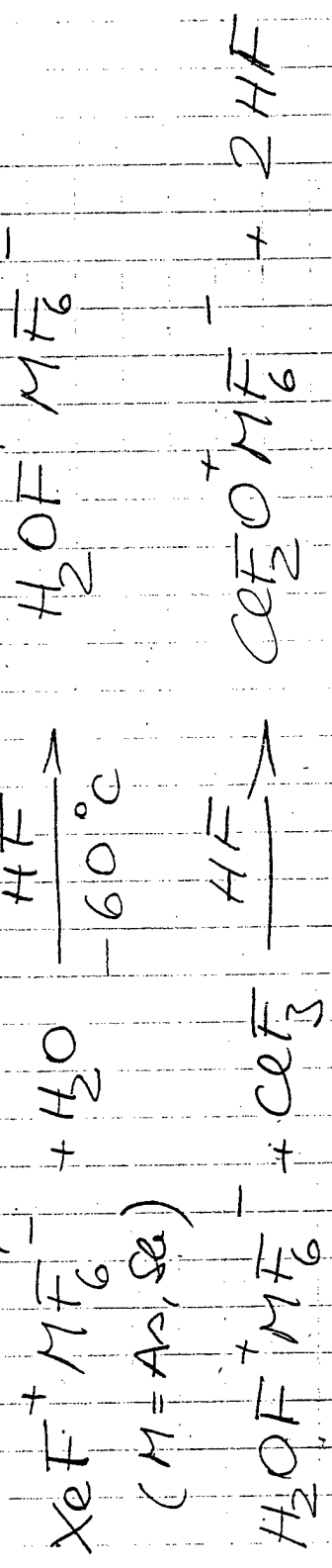


- ALTERNATE POTENTIAL ROUTE TO CeF₃O OXIDATIVE OXYGENATION OF CeF₃



"MAGIC OXYGENATOR"

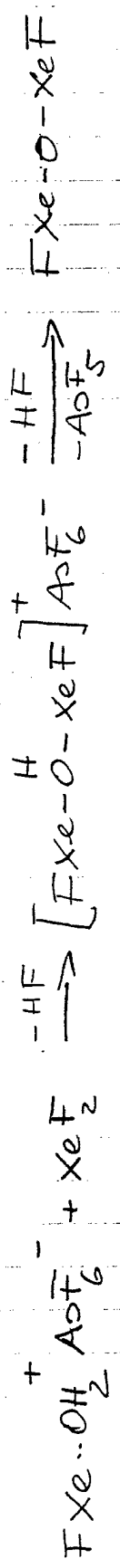
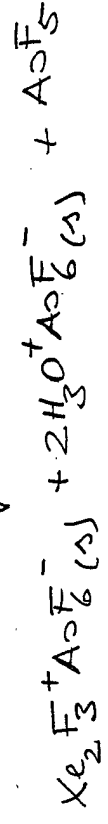
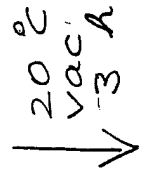
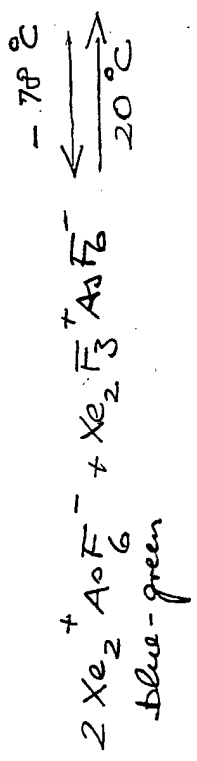
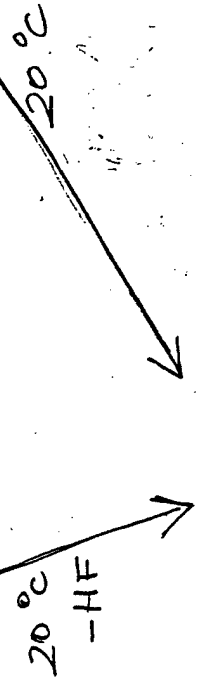
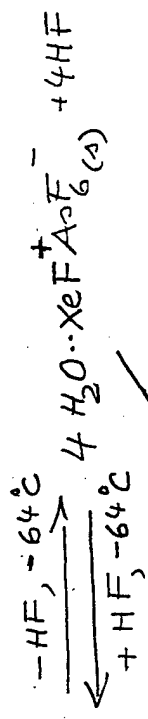
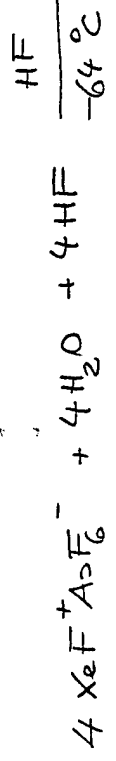
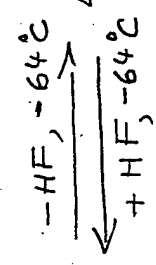
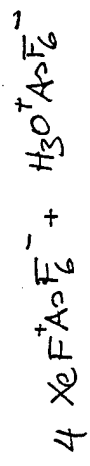
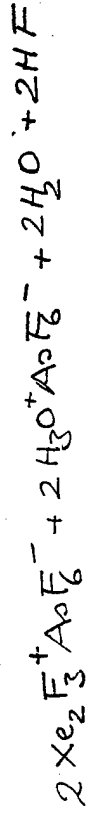
MINKWITZ, NOWICKI (ANGEW. CHEMIE, 1990)



OUR RESULTS

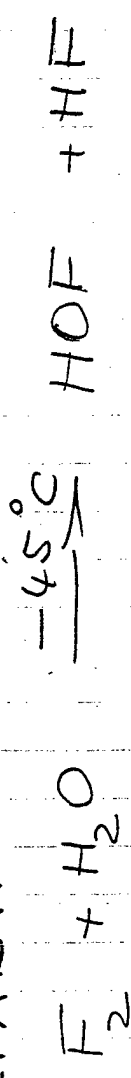
- XeF⁺/H₂O SYSTEM IS EXTREMELY COMPLEX, BUT DOES NOT GIVE H₂OF⁺ SALTS
- XeF⁺/H₂O REACTION PRODUCT DOES NOT OXYGENATE CeF₃, BUT HYDROLYSES IT TO CeO₂⁺
- WORK IN PROGRESS TO FULLY CHARACTERIZE THIS SYSTEM BY:
 - VIBRATIONAL AND MULTINUCLEAR NMR SPECTROSCOPY
 - SINGLE CRYSTAL X-RAY DIFFRACTION
 - COMPUTATIONAL CHEMISTRY

XeF⁺AsF₆⁻ / H₂O SYSTEM

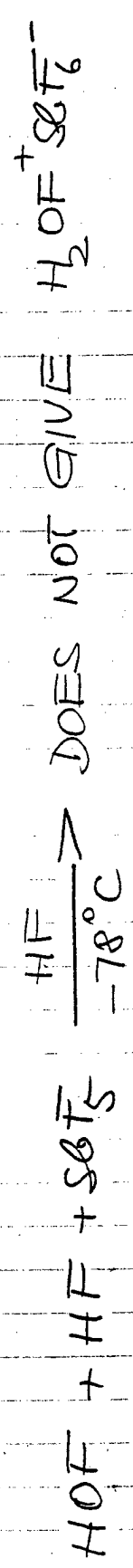


HOF REACTIONS

• PREPARATION



• PROTONATION



• REACTION CHEMISTRY

- REACTIONS OF HOF WITH CF_3 , CF_3O , CF_3 , CF_5 , BrF_5 OR IF_5
- WERE STUDIED IN GAS PHASE BY FT IR SPECTROSCOPY
- NO EVIDENCE FOR OXIDATIVE OXYGENATIONS

PUBLICATIONS DURING LAST YEAR

- 1) NAKED FLUORIDE ION SOURCES (JACS)
- 2) TETRAFLUOROPHOSPHATE ANION, PO_4^{3-} (JACS)
- 3) DISORDER AND POLYMORPHISM IN $N(CH_3)_4 I_4$ (INORG. CHEM)
- 4) PREPARATION, NMR, RAMAN AND DFT/FOLO/BIAO-MP2 STUDY OF MONO-, DI-, AND TRI-PROTONATED THIOUREA (JACS)
- 5) ^{17}O AND ^{13}C NMR / AB INITIO STUDY OF OXONIUM AND CARBOXYONIUM IONS (JACS)
- 6) DIRECT SYNTHESIS OF $N(CH_3)_4^+$ SALTS OF COMPLEX FLUORO ANIONS (J. FLUOR. CHEM.)
- 7) NOVEL HEDM MATERIALS. SYNTHESIS AND CHARACTERIZATION OF $C(N_3)^+$ SALTS OF $N(N_3)_2^-$, ceO_4^- AND B_7^- (JACS)
- 8) TRIMETHYL PEROXONIUM ION, $CH_3OO(CH_3)_2^+$ (JACS)
- 9) THEORETICAL STUDY OF NO_4^+ (J. PHYS. CHEM)
- 10) PENTAGONAL PLANAR AX5 SPECIES, IF_5^{2-} (JACS)
- 11) PREPARATION AND VIBRATIONAL SPECTRA OF $N(CH_3)_4^+$, IF_2^- AND ELECTRONIC STRUCTURE CALCULATIONS OF IF_2^- , BrF_2^- , ClF_2^- , XeF_4 AND K_2F (J. FLUOR. CHEM)

SUMMARY

THE ENERGETIC

(ANIONS) - YIELDS

- THE COMBINATION OF NF_4^+ WITH NO_3^- , NO_2^- AND $N(NO_2)_2$ THERMALLY UNSTABLE MATERIALS WHICH DECOMPOSE TO FO_2 AND INTERESTING NEW COMPOUNDS, TENTATIVELY IDENTIFIED AS FO_2 AND $FN(NO_2)_2$
- IN SEARCH FOR NOVEL NF_3 SUBSTITUTED OXIDIZERS AND DIFLUOROAMINATING REAGENTS, THE SYNTHESSES OF N_2O_2 AND $SO_2(NF_2)_2$ WERE PURSUED
- OZONE CANNOT BE STABILIZED THROUGH PROTONATION
- IN PURSUIT OF OF_2O , A NEW LIQUID EARTH-STORABLE OXIDIZER, THE PREVIOUSLY REPORTED H_2O^+ CATION AND ITS ALLEGED OXYDATIVE OXYGENATING POWER COULD NOT BE CONFIRMED. THE REPORTED H_2O^+ SALTS ARE ACTUALLY $[Fe(OH)]^+$ ADDUCTS.
- THE CRYSTAL STRUCTURES OF NUMEROUS HEDM COMPOUNDS WERE DETERMINED
- WORK WAS COMPLETED ON THE PENTAGONAL PLANAR IF_5^{2-} AND PENTAGONAL BIPYRAMIDAL SbF_5^{2-} AND BiF_5^{2-} ANIONS
- THIS PROGRAM CONTINUES TO BE A SHOWCASE FOR THE SYNERGISM BETWEEN THEORY AND SYNTHESIS AND HAS PRODUCED 11 PUBLICATIONS DURING THE PAST YEAR