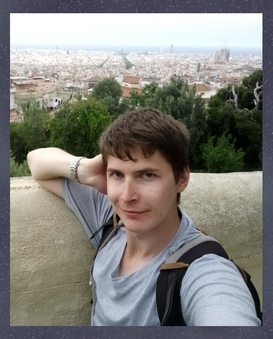


CHEMISTRY AND PHYSICS AT LOW TEMPERATURES ~~2020~~ ~~2021~~ 2022

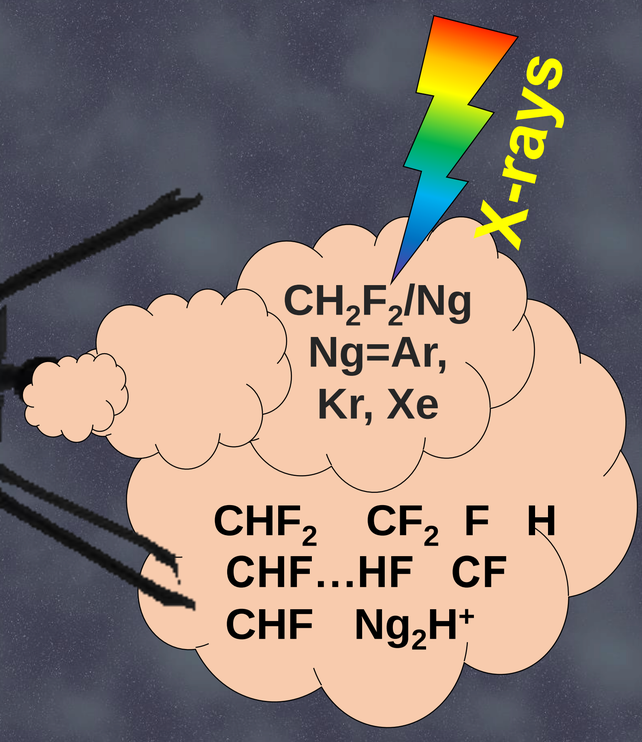
MATRIX ISOLATION STUDY OF DIFLUOROMETHANE RADIOLYSIS: FORMATION OF UNUSUAL INTERMEDIATES AND NOVEL NOBLE GAS COMPOUNDS

Ilya S. Sosulin, Vladimir I. Feldman

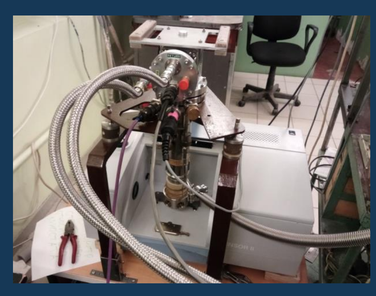
Department of Chemistry, Lomonosov Moscow State University, Moscow 119991 Russia

Introduction

Difluoromethane is widely used as an ecologically friendly alternative to conventional chlorofluorocarbons (CFCs). Being chemically and photochemically inert and insensitive to the near UV light, CH_2F_2 could come to the upper layers of the atmosphere, where it is subjected to VUV or ionizing radiation. The combined matrix isolation and quantum chemistry investigation of difluoromethane radiation-induced transformations is of particular interest for atmospheric chemistry. On the other hand, these studies may provide unique information on the structure and spectroscopic features of intermediates and noble gas compounds.



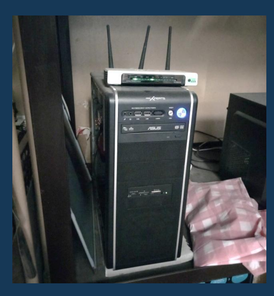
Experiment



Matrix isolation CH_2F_2/Ng (1/1000); CH_2F_2/N_2O/Ar (1/1/1000, 1/2/1000); Ng = Ar, Kr, Xe; Original close cycle helium cryostat:

- Deposition
- X-rays irradiation
- IR spectra
- Controlled annealing

Theory



Quantum chemical calculations CCSD(T), MP2; L2a_3, L3a_3 basis sets

- Structure
- Spectroscopic features (harmonic frequencies, IR intensities)

Difluoromethane radiolysis

«Ionic» channel

$Ng \rightsquigarrow Ng^{+\bullet} + e^-$

$Ng^{+\bullet} + e^- \rightsquigarrow Ng^{**}$

$CH_2F_2 + Ng^{+\bullet} \rightarrow CH_2F_2^{+\bullet} + Ng$

$CH_2F_2 + Ne^+ \rightarrow CHF_2^+; CF_2^+; CHF^+$

$CH_2F_2 + Ng^{**} \rightarrow CHF…HF$

$CH_2F_2^{+\bullet} \rightarrow {}^\bullet CHF_2 + H^+/Ng$

$CH_2F_2^{+\bullet} + e^- \rightarrow CH_2F_2^*$

$CHF_2 + Ng^{+\bullet} \rightarrow CF_2 + Ng_2H^+$

$X + e^- \rightarrow X^-$

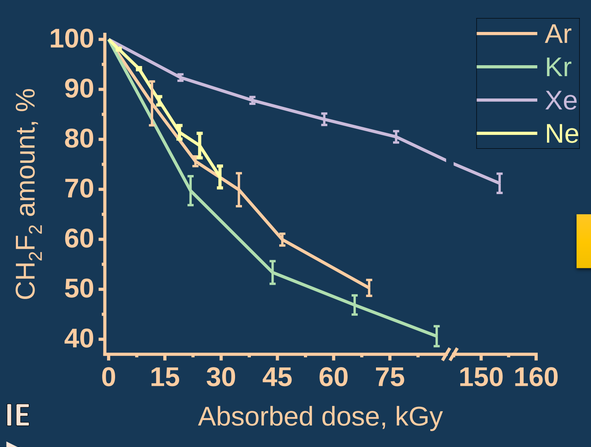
Ne, Ar, Kr

$IE(Ng) > IE(CH_2F_2)$

IE

Xe ~ 12 eV Kr ~ 14 eV Ar ~ 16 eV

CHF_3 ~ 13.3 eV



The decay of CH_2F_2 as a function of absorbed dose in X-irradiated Ne, Ar, Kr, and Xe matrices

«Neutral» channel

$Ng \rightarrow Ng^+ + e^- + Ng^*$

$Xe^+ + e\text{-} \rightarrow Xe^*$

$Ng^* + CH_2F_2 \rightarrow CH_2F_2^*$

$CH_2F_2^* \rightarrow CHF_2 + H$

$CH_2F_2^* \rightarrow CF_2 + H_2$

$CHF_2 + Ng^* \rightarrow CF_2 + H$

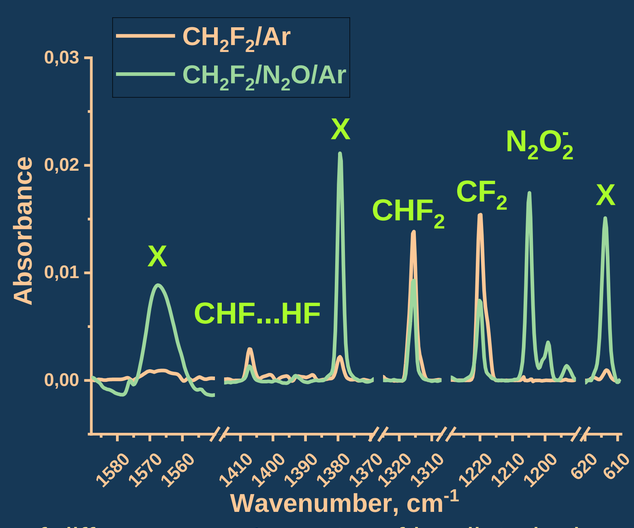
$CHF_2 + Ng^* \rightarrow CHF + F$

$CF_2 + Ng^* \rightarrow CF + F$

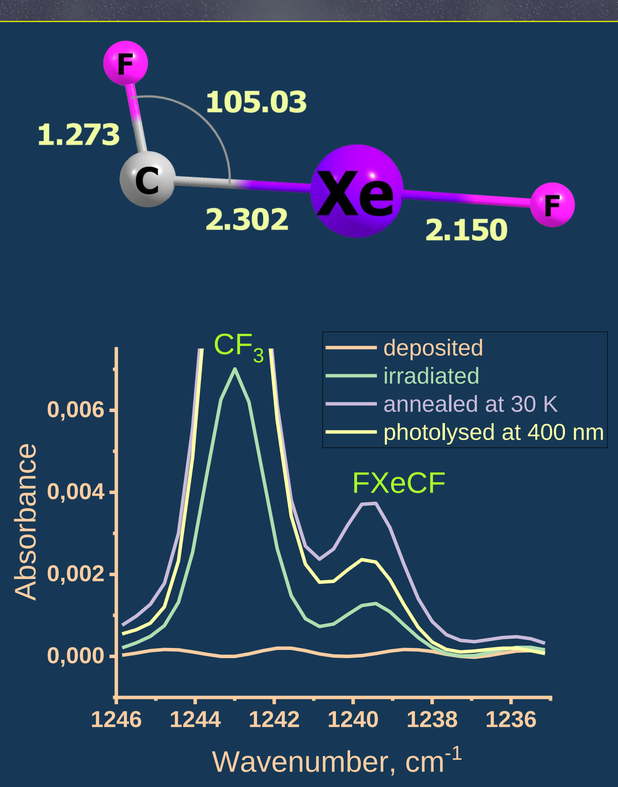
$F + CF_2 \rightarrow CF_3$

$Xe + F \rightarrow XeF$

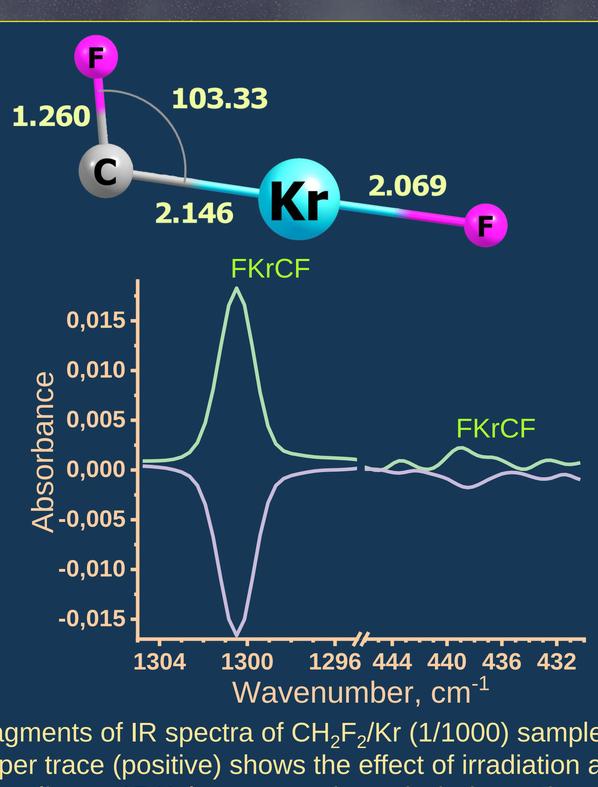
CF_2^+ identification



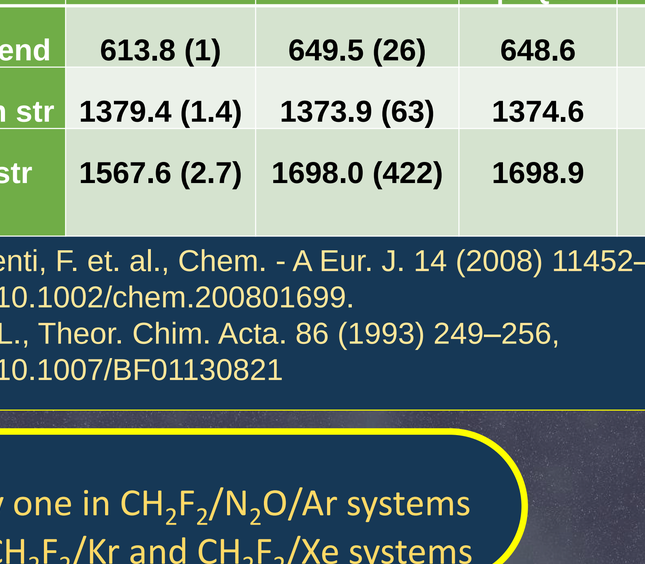
Fragments of difference FTIR spectra of irradiated minus deposited CH_2F_2/Ar (1/1000) and CH_2F_2/N_2O/Ar (1/1/1000) samples



Fragments of IR spectra of CH_2F_2/Xe (1/1000) sample



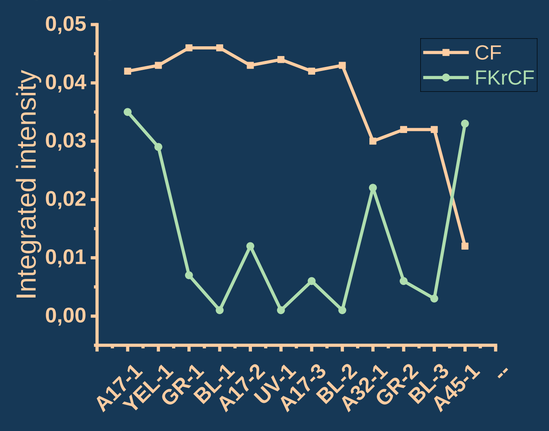
Fragments of IR spectra of CH_2F_2/Kr (1/1000) sample. Upper trace (positive) shows the effect of irradiation and annealing at 17 K, lower trace (negative) shows the effect of subsequent photolysis at 445 nm



Fragments of FTIR spectra of irradiated and photolyzed CH_2F_2/N_2O/Ar (1/2/1000) sample.

Calculated harmonic frequencies of FNgCF and corresponding experimental values; stabilization energies with respect to F + Ng + CF dissociation

	MP2/L2a_3		Experiment	
	FKrCF	FXeCF	Kr	Xe
F-Ng str	435.9 (312)	428.9 (264)	438,6	-
C-F str	1310.3 (531)	1266.4 (449)	1300.5	1239.6
E_{stab}	5.2	24.5		



Variations of the integrated intensity of FKrCF and CF bands annealing and photolysis of the irradiated sample

Calculated harmonic frequencies of CF_2^+ cation and corresponding experimental values

Mode	EXP	CCSD(T) L3a_3	CCSD(T) aug-cc-pVQZ[a]	MRSDCI DZP[b]
F-C-F bend	613.8 (1)	649.5 (26)	648.6	656
C-F sym str	1379.4 (1.4)	1373.9 (63)	1374.6	1259
C-F a str	1567.6 (2.7)	1698.0 (422)	1698.9	1599

[a] Innocenti, F. et. al., Chem. - A Eur. J. 14 (2008) 11452–11460, DOI: 10.1002/chem.200801699.

[b] Cai Z.L., Theor. Chim. Acta. 86 (1993) 249–256, DOI: 10.1007/BF01130821

Conclusions

- CF_2^+ was detected as a secondary radiolysis product in the CH_2F_2/Ar and as a primary one in CH_2F_2/N_2O/Ar systems
- FKrCF and FXeCF were first observed experimentally in the irradiated and annealed CH_2F_2/Kr and CH_2F_2/Xe systems

Sosulin, I.S., Feldman, V.I. Radiat. Phys. Chem. 189 (2021) 109672. https://doi.org/10.1016/J.RADPHYSCHEM.2021.109672.

Sosulin, I.S., Tyurin, D.A., Feldman, V.I. Chem. Phys. Lett. 744 (2020), 137211. http://dx.doi.org/10.1016/j.cplett.2020.137211

This work was supported financially by the Russian Foundation for Basic Research (Project No. 20-33-90179).