Structural and Energetic Properties of $FCH_2CN–GeF_4$ and $ClCH_2CN–GeF_4$ via Low-Temperature IR Spectroscopy and Computations

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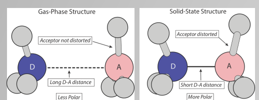
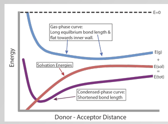
Introduction

We are interested in condensed-phase effects on structural properties of donor-acceptor complexes. One direct illustration of this is gas-solid structure differences, illustrated below at the left. A mechanism for bulk-condensed phase effects is depicted at the right.

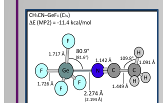


Gas-solid structure differences: In some complexes the donor-acceptor bond contracts upon crystallization, and the Lewis acid is more distorted.

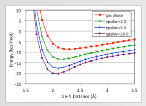


Generalization of bulk condensed-phase effects: The key is a long bond length in the gas phase with a very slight energy rise towards the shorter donor-acceptor distances. Addition of solvation energies can shift bond length inward.

The present study deals with nitrile-GeF_4 complexes. It was noted in a previous study[1] that $CH_3CN–GeF_4$ showed some potential for condensed-phase structural effects. We hypothesize that adding electronegative halogens to the nitrile will weaken the complex and enhance them.



CH_3CN-GeF_4: The Ge-N distance is slightly long and the binding energy is intermediate (left). The gas-phase potential is flat, minima shift inward in the condensed phase (right). Adding halogens to weaken the bond will lengthen the gas-phase Ge-N distance and raise the energy to flatten the potential curve.



Computational Methods

- We validated our methods by comparing computed vs. experimental frequencies for GeF_4. M06 gave best agreement (with aug-cc-pVTZ).

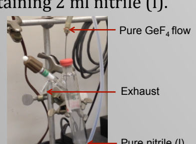
GeF_4	X3LYP	**M06**	ωB97X-D	MP2	B3PW91	HSEh1PBE	mPW1pw91	TPSSH	B3LYP
Sym Str (800)	778	797	781	810	783	791	793	776	774
Deg deform (260)	266	266	272	275	268	269	270	263	266
Deg Stretch (740)	713	734	720	740	719	726	728	710	710
Deg deform (200)	198	198	202	209	199	200	200	194	198
RMSD (NIST)	17.7	**4.6**	15.1	10.1	14.1	9.5	8.6	19.6	20.1

- We used both M06 and MP2 & the aug-cc-pVTZ basis set (G09 vB.01).
- Equilibrium structures, binding energies, frequencies, and potential energy curves (gas phase and solution).

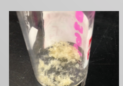
Experimental Methods

Bulk-phase Reactivity

- GeF_4 (g) into dry Schlenk tube containing 2 ml nitrile (l).

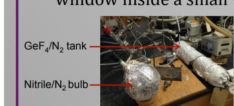


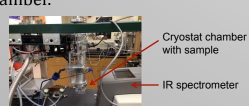
- $FCH_2CN + GeF_4$ gave a crystalline product and we obtained a solid-state structure.



Thin-film IR

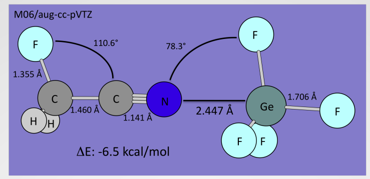
- We obtained IR spectra of nitrile/GeF_4 films at 100-150 K.
- Prepared by flowing dilute gas mixtures (~1%) onto cold KBr window inside a small vacuum chamber.



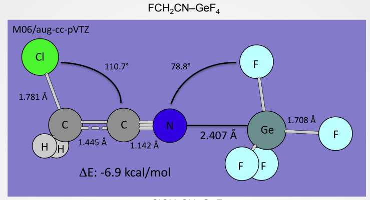


Equilibrium Structures/Binding Energies

- Four possible structures were considered: axial-eclipsed (C_{3v}), axial-staggered (C_{3v}), and two equatorial forms (C_s). <u>Axial-eclipsed</u> was lowest in energy and was the only structure with no imaginary frequencies.
- Detailed structure parameters:



$FCH_2CN–GeF_4$

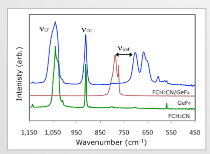


$ClCH_2CN–GeF_4$

IR Spectroscopy

Experimental Spectra

- Thin film spectra of FCH_2CN, GeF_4, and FCH_2CN/GeF_4 at 150 K.

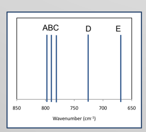


- The key feature of the spectra is the shift of the Ge-F asymmetric stretch (ν_{GeF}) in the presence of FCH_2CN.
- At lower temperatures, we observe unreacted GeF_4, even with balanced composition (1/1 FCH_2CN/GeF_4). This is evidence of a 2:1 complex in the spectrum: $(FCH_2CN)_2–GeF_4$.
- Similar spectra are observed with $ClCH_2CN$ and CH_3CN in the sample.

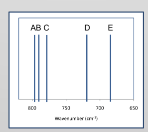
Frequency Shifts

- There is a systematic shift for the GeF_4 asymmetric stretching peak across all computational and experimental data. These are depicted below.

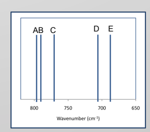
A. GeF_4 (g) Prediction → B. GeF_4 (s) Unreacted Observed → C. Nitrile–GeF_4 Calculated → D. (Nitrile)$_2$–GeF_4 Calculated → E. Nitrile/GeF_4 (s) Observed



FCH_2CN/GeF_4



$ClCH_2CN/GeF_4$



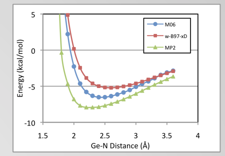
CH_3CN/GeF_4

- Calculated 2:1 frequencies agree much better with the solid-state spectra, this is evidence that the 2:1 complex exists in the solid sample.
- There is still a shift between gas-phase predictions and measured spectra, and this is consistent with a gas-solid structure difference.

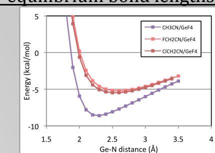
Ge-N Bond Potential Energy Curves

Gas-Phase Curves

- Three methods: M06, MP2, and ωB97X-D (used previously)[1].
- Halogenation effects: The curves with an electronegative atom are <u>much flatter and have longer equilibrium bond lengths.</u>



$FCH_2CN–GeF_4$

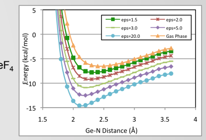


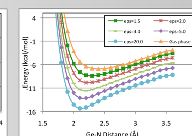
All 3 complexes using ωb97X-D

Condensed-Phase Media

- The condensed-phase curves change shape with increasing dielectric constant (eps). This reflects charge-stabilizing ability.
- The minimum energy point shifts ~2.5 Å (gas) to ~2.1 Å (ε=20).

$FCH_2CN–GeF_4$



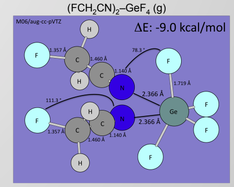


$ClCH_2CN–GeF_4$

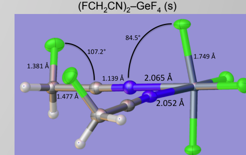
2:1 Complexes

- The product of the $GeF_4 + FCH_2CN$ reaction was found to be a 2:1 complex: $(FCH_2CN)_2–GeF_4$.
- Gas-solid structure difference: The Ge-N bond lengths are 0.3 Å shorter in the solid and the N-Ge-F bond angles increase by 6°.

$(FCH_2CN)_2–GeF_4$ (g)



$(FCH_2CN)_2–GeF_4$ (s)



- For gas-phase $(ClCH_2CN)_2–GeF_4$ the Ge-N distances are 2.319 Å and ΔE= -9.7 kcal/mol.

Conclusions

- Halogen substitution enhances condensed-phase effects.
- Stable products are 2:1 complexes for nitrile + GeF_4 reaction.
- Gas-phase and solid-state differences are evident in $FCH_2CN–GeF_4$.

Reference & Acknowledgements

Reference

1. Helminiak, H.; Knauf, R.; Danforth, S.; Phillips, J.A. *JPC A* **2014**, *118*, 4266-4277.

Acknowledgements

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