Structural and Energetic Properties of Haloacetonitrile – GeF₄ Complexes

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ABSTRACT

The 1:1 and 2:1 complexes of FCH₂CN and ClCH₂CN with GeF₄ have been investigated by M06/aug-cc-pVTZ calculations, low-temperature, thin-film IR spectroscopy, and an x-ray structure has been obtained for (FCH₂CN)₂-GeF₄. Theoretical structures and binding energies for FCH₂CN-GeF₄ and ClCH₂CN-GeF₄ demonstrate that halogen substitution significantly weakens the Ge-N dative bonds. The Ge-N distances for the F- and Cl-complexes (2.447 and 2.407 Å, respectively) are about 0.2 Å longer than in CH₃CN-GeF₄, and the binding energies (6.5 and 6.9 kcal/mol) are 2 to 3 kcal/mol less. Furthermore, the Ge-N potential curves are flatter for the halogenated complexes, exhibit a greater response to dielectric media, and thus these systems are more prone to structural change in condensed-phases. For the 2:1 complexes, experimental and theoretical structure and frequency data are consistent with differences in the (calculated) gas-phase and solid-state structures. For (FCH₂CN)₂-GeF₄ the calculated gas-phase structure has Ge-N distances about 0.3 Å longer than those in the x-ray structure (2.366 Å vs. 2.059 Å (ave)). Also, low-temperature IR spectra of CH₃CN/GeF₄, FCH₂CN/GeF₄, and ClCH₂CN/GeF₄ thin films are consistent with the presence of 2:1 nitrile:GeF₄ complexes, and the splitting patterns of the GeF-stretching bands (~700 cm⁻¹) match predictions for the corresponding complexes, but are red-shifted relative to the gas-phase predictions, and reflect Ge-N bonds that are compressed in the solid-state, relative to predicted gas-phase structures.

Introduction

Interest in the structural and energetic properties of molecular complexes has persisted through the decades since the publication of several monographs devoted to the subject [1-4]. In particular, modern computational chemistry has been an effective tool for elucidating the factors that influence the bonding in these systems [5-8], though clear, *a priori* trends in the factors that effect strength have been elusive at times [5]. Because of such challenges, molecular complexes, often called “charge transfer complexes” in this context, often provide key energetic benchmarks for new computational methods [9, 10]. Experimental studies of these systems persist as well [11], and of particular note are those that illustrate the broad variability of the strengths of the donor-acceptor bonds in these systems [12], which can range from weak, non-bonding interactions to strong dative bonds within a single class of systems [12].

The focus of our work has been the extent to which bulk condensed-phase environments affect the structural properties of molecular complexes. The most direct illustration of these effects is provided by differences between gas-phase and solid-state structures, and to this day, nitrile - BF_3 complexes provide some of the most vivid examples of this behavior [12]. For example, the gas-phase B-N distance in $\text{CH}_3\text{CN}-\text{BF}_3$ is 2.01 Å, but this distance contracts to 1.63 Å in the solid-state; a change of nearly 0.4 Å. In turn, the N-B-F angle opens by nearly 10° [13]. For $\text{HCN}-\text{BF}_3$, the changes are more extreme; the gas-phase B-N distance contracts from 2.47 Å to 1.63 Å between the gas-phase and the solid-state and the N-B-F angle opens by 10° [14]. Comparable changes ($\Delta R(\text{B-N}) = \sim 0.7$ Å) have been predicted for $\text{FCH}_2\text{CN}-\text{BF}_3$ and $\text{ClCH}_2\text{CN}-\text{BF}_3$ (*i.e.*, they are based on theoretical gas-phase structures) [15]. Taken together, however, these results for complexes of weaker nitriles illustrate that condensed-phase sensitivity tends to increase when the gas-phase interaction is weaker,

so long as the stabilizing effects of the medium are enough to overcome any energetic disincentives to bonding.

Analogous effects have also been observed in bulk, condensed-phase environments, even inert, weakly interacting, noble gas matrices [16, 17]. For $\text{CH}_3\text{CN-BF}_3$, key structurally-sensitive vibrational modes (*e.g.*, the B-F asymmetric stretch) shift across a range of condensed-phase environments, and these shifts systematically parallel the charge stabilizing ability of these environments (*e.g.*, polarizability, dielectric constant) [16, 18]. Since the correlation between these shifts and a contraction of the B-N distance has been demonstrated [18, 19], these data convey the extent to which the B-N bond contracts in the more polarizable (or polar) media. Furthermore, the dynamic range of the shifts is even greater for $\text{FCH}_2\text{CN-BF}_3$ and $\text{ClCH}_2\text{CN-BF}_3$ [17], once again illustrating the greater potential for condensed-phase structural change in systems that are weaker in the gas-phase, so long as they are apt to react with some degree of solvent stabilization.

Computations have provide key insight into these effects, not only for establishing the connection between frequency shifts and structure, and but have also provided mechanistic insight via analyses of donor acceptor bond potentials [18, 20]. The common feature among medium-sensitive complexes, at least those that show extreme effects [21], appears to be a flat donor-acceptor potential, with a relatively long global minimum and a slight energy rise toward the inner wall. Because the complexes tend to be more polar at short donor-acceptor distances [20], the inner region of the potential is preferentially stabilized in the condensed-phase (as represented by a dielectric continuum in the computations), which causes the minimum to shift inwards.

At this point, we turn our attention to the nitrile complexes of GeF_4 . Previous work on the 1:1, N-donor – GeF_4 complexes includes both experimental [22] and theoretical [23-25] studies on the amine-containing systems as well as matrix-isolation-IR studies of the pyridine [26] and nitrile (HCN and CH_3CN) complexes [27]. Matrix-IR spectra of $\text{H}_3\text{N-GeF}_4$ are consistent with a trigonal-bipyramidal geometry about the Ge atom, with the NH_3 subunit bonded in an axial coordination site [22]. These observations are consistent with theoretical results [23, 24] that predict that the axial form is most stable, and furthermore, that $\text{H}_3\text{N-GeF}_4$ is a strong complex ($\Delta E = -32.7$ kcal/mol) with a short Ge-N distance ($2.16 \text{ \AA}$) [23]; only about $0.02 \text{ \AA}$ longer than the sum of the Ge and N covalent radii ($1.97 \text{ \AA}$) [28]. Just recently a computational study that examine a series of N-donor (and O-donor) complexes of MF_4 Lewis acids [25], including not only M=Ge , but also C, Si, Sn, and Pb, and the preference of axial coordination across the entire range of complexes was rationale on the basis of the “sigma hole” concept [29]; there is an energetic incentive to bond directly opposite the M-F bond, in a site where the electronegative fluorine manifests electron deficiency.

The 1:1 complexes of $\text{CH}_3\text{H}_2\text{N}$ and $(\text{CH}_3)_3\text{N}$ were also observed in matrix-IR experiments [22]. Across the series of amine/ NH_3 complexes, frequencies of the GeF_4 asymmetric stretching modes, which for $\text{H}_3\text{N-GeF}_4$ and $(\text{CH}_3)_3\text{N-GeF}_4$ were observed as two bands assigned respectively to the axial and equatorial Ge-F bonds, paralleled the expected strength of the complexes. Specifically, each band shifted to lower frequency with increasing base strength, which presumably results for increased electron donation to an anti-bonding orbital on the GeF_4 , which would soften of the Ge-F bonds [22]. In the matrix-IR investigation of $\text{C}_6\text{H}_5\text{N-GeF}_4$ [26], three bands were observed in the GeF_4 stretching region, which complicates a direct comparison to the amine- GeF_4 peaks, but the band shifts are consistent with a reasonably strong Ge-N dative bond. Three GeF_4 stretching peaks were also observed in the matrix-IR study of $\text{CH}_3\text{CN-GeF}_4$ and HCN-GeF_4 (at 679, 719, and 770

cm⁻¹ for the CH₃CN complex) [27], and the red-shifts of these bands are less than those for C₅H₅N–GeF₄, consistent with the lower basicity of the nitriles relative to pyridine.

Many earlier studies [30-34], including one that dates back over two centuries [30], found the Group IV halides tend to form 2:1 complexes with nitrogen donors, in which they assume octahedral coordination geometries about the Ge atom; ((CH₃)₃N)₂–GeF₄ is one such example, though the analogous 1:1 complex is also stable [31]. Recent theoretical results for NH₃/GeF₄ systems indicate that the 2:1 complex is more stable than its 1:1 analog at room temperature (from a free energy standpoint) [23]. Some time ago, solution-phase NMR studies [34] found that N-donor - TiF₄ and SnF₄, complexes assumed *cis* geometries in spite of steric considerations, which would place the larger substituents opposite one another in a trans configuration. Interestingly, (CH₃CN)₂GeF₄, is a convenient reagent for the preparation of various octahedral GeF₄L₂ complexes [35, 36], because it is reasonably stable and the CH₃CN ligands are fairly labile, while pure GeF₄ is less convenient because it is gas at room temperature.

In a recent paper [37], we reported a computational and low-temperature, thin-film IR study of a series of 1:1 and 2:1 complexes of CH₃CN with MX₄ acceptors (M= Si, Ge, Ti; X= F, Cl), and found that two of the six 1:1 systems, CH₃CN–SiF₄ and CH₃CN–GeF₄, exhibited some potential for condensed-phase structural changes. Though we predicted an extreme response for CH₃CN–SiF₄, no condensed-phase structural changes were detected experimentally. No sign of reactivity between CH₃CN and SiF₄ was observed, and furthermore, low-temperature IR spectra showed no shift in the degenerate Si-F stretching band of SiF₄ in CH₃CN/SiF₄ thin films. Computations predicted that CH₃CN–GeF₄ is a moderately strong complex, with a Ge-N distance of 2.19 Å and binding energy of 11.4 kcal/mol (MP2/6-311+G2df,p) [37]. The minimum-energy structure has the CH₃CN group

bonded in an axial site within a distorted trigonal bipyramidal coordination sphere about the GeF_4 , reminiscent of the $\text{H}_3\text{N-GeF}_4$ structure [23]. While we were unable to perform experiments on $\text{CH}_3\text{CN/GeF}_4$ systems at that time, computational scans of the Ge-N potential curve, both in the gas-phase and dielectric media predicted a $\sim 0.2 \text{ \AA}$ contraction of the Ge-N bond in dielectric media (between $\epsilon = 5$ and $\epsilon = 20$). Based in the effects noted above for nitrile- BF_3 systems, we expected that these effects would be amplified by adding halogens to the CH_3CN subunit that would weaken the Ge-N dative bond.

Accordingly, this manuscript will report an experimental and computational study of the structural and energetic properties of the 1:1 and 2:1 complexes formed from haloacetonitriles (FCH_2CN and ClCH_2CN) and GeF_4 . In addition to gas-phase structures and binding energies for the 1:1 systems, $\text{FCH}_2\text{CN-GeF}_4$ and $\text{ClCH}_2\text{CN-GeF}_4$, we will also present a thorough examination of the Ge-N potentials of these systems, both in the gas-phase and in dielectric media. Computed structures and binding energies will also be reported for the analogous 2:1 complexes, $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$ and $(\text{ClCH}_2\text{CN})_2\text{-GeF}_4$ (alternatively $\text{GeF}_4(\text{FCH}_2\text{CN})_2$ and $\text{GeF}_4(\text{ClCH}_2\text{CN})_2$). The direct, bulk-phase reactivity of nitriles and GeF_4 was also examined, not only for FCH_2CN and ClCH_2CN , but also for CH_3CN . A crystal structure was obtained for the product of the $\text{FCH}_2\text{CN/GeF}_4$ reaction; which was determined to be $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$, and the structural results do differ from the gas-phase predictions. Furthermore, IR spectra were obtained for nitrile/ GeF_4 thin films, including $\text{CH}_3\text{CN/GeF}_4$, $\text{FCH}_2\text{CN/GeF}_4$, and $\text{ClCH}_2\text{CN/GeF}_4$. These spectra are also consistent with the presence of 2:1 complexes in the films, and suggest significant differences in structure from their gas-phase counterparts, especially for the halogenated systems.

Materials and Methods

Computations

All computations were performed using Gaussian 09 (Revision B.01)[38]. We chose a preferred computational method for structure and frequency calculations via the same general process that we have employed in our previous work on analogous donor-acceptor systems [15, 20, 37, 39]. Because certain vibrational modes involving motion in the Lewis acid moiety tend to be quite sensitive to structure [16, 18, 19, 37], we have previously validated methods via (harmonic) frequency predictions for the free acceptor subunit. Presently, we assessed method performance via the RMS error relative to experimental GeF_4 frequencies [40], and in total nine implementations of DFT [41] were tested (X3LYP[42], B3PW91 [43], HSEh1PBE [43, 44], *m*PW1PW91 [45], TPSSH [46], B3LYP [43], ω -B97X-D [47], M06 [9], and M06-2X [9]) in addition to MP2 [43], all with the aug-cc-pVTZ basis set [48]. A complete listing of experimental and predicted frequencies with RMS errors is included as *Supplementary Content* (Table S2). Because M06 was found to have the lowest RMS error (4.6 cm^{-1}), by a significant margin, we chose to use M06/aug-cc-pVTZ to compute equilibrium structures and frequencies for the complexes and we report those results below. We also assessed the effect of anharmonicity on the M06 predictions, which has been shown to be significant recently for C-F frequencies [49], but the anharmonic corrections [50] altered the frequency predictions only slightly (by 0 to 11 cm^{-1}), and increased the RMS error increases to 10.7 cm^{-1} . Though this result may help justify the use of harmonic predictions, most likely reflects a fortuitous cancellation of model errors in this benefits this validation approach.

Due to the absence of any means by which to directly validate the equilibrium structural results, MP2 structures were also obtained as to provide a post-Hartree-Fock comparison to the DFT results, and we note here that the differences between the M06 and MP2 results were minor. Equilibrium

structures were initially calculated with convergence criteria set according to the “opt=tight” option, and maximum possible symmetry was invoked for each ideal starting structure. In some cases, symmetry was subsequently relaxed after obtaining the symmetric equilibrium structures, to ensure that the symmetry constraint was not leading us to erroneous results. Harmonic frequencies (M06/aug-cc-pVTZ) were obtained for each equilibrium structure that was considered, and the occurrence of imaginary frequencies further guided our choice for global minimum-energy geometry of each complex (see below). For the 2:1 systems, a few equilibrium geometries were obtained in bulk dielectric media via the Polarized Continuum Model [51] (PCM/M06/aug-cc-pVTZ), with ϵ -values of 5.0 or 10.0, and all other parameters set to default values. We also attempted to assess the effect of anharmonic corrections [50] on the frequencies of the complexes as well, but the demands of these computations exceeded our resource limits. Binding energies were calculated via the difference in M06 energy between the complex and the sum total of isolated fragments.

Potential energy curves were mapped along the Ge-N coordinate for FCH₂CN–GeF₄, ClCH₂CN–GeF₄, and CH₃CN–GeF₄, in a point-wise manner from 1.3 to 3.6 Å, in 0.1 Å steps, and all degrees of freedom aside from the fixed Ge-N distance were optimized at each point. In addition to the methods used for structure and frequency calculations (MP2 and M06, *above*), we also included ω -B97X-D/aug-cc-pVTZ because it was previously found to be optimal for mapping the Si-N potential for CH₃CN–SiF₄ [37]. We focused our discussion of the potential on the M06 curves, and based our solvation study on them as well, because the gas-phase M06 energies along the Ge-N coordinate were intermediate between MP2 and ω -B97X-D. The effects of bulk, dielectric media on the potentials for the halogenated complexes were examined using the Polarized Continuum Model [51] (PCM/M06/aug-cc-pVTZ), and these energies were plotted relative to the total electronic energy of the separated, gas-phase fragments (same reference as the gas-phase curves). Dielectric constants

ranged from 1.5 to 20.0, and all other parameters, including the cavity dimensions, were left at default settings. In some instances, the optimization routine failed to hold symmetry at a few points on the curves in dielectric media, but the final structures exhibited only trivial differences from *Cs* symmetry and did not manifest any discontinuities.

Materials

Liquid nitrile compounds; CH₃CN (99.5%, VWR), FCH₂CN (98%, Aldrich), ClCH₂CN (99%, Aldrich), were purified by several freeze-pump-thaw cycles when preparing gas-mixtures for thin-film IR experiments, but used without further purification in bulk-reactivity studies. Gases, including nitrogen (Praxair, 99.9999%, for IR gas mixtures; standard purity for bulk reactivity) and GeF₄ (99.95%, Aldrich/Advance Research Inc.) were used without further purification.

Bulk-phase Reactivity

Reactivity between the nitrile compounds and GeF₄ was assessed by direct reaction of GeF₄ vapor and liquid nitrile. In manner similar to that in the preceding study [37], these reactions were conducted in dry Schlenk tubes with a Teflon stopcock side arms. Each tube was fitted with a septum through which vapor was introduced using a small hypodermic needle. First, about 2 mL of CH₃CN, FCH₂CN, or ClCH₂CN was added to the tube, which was then purged with nitrogen gas to displace room air. When GeF₄ vapor was added, all samples reacted immediately to form white solids, and the flow of GeF₄ was continued until it appeared that all the nitrile had reacted. The FCH₂CN/GeF₄ product was distinctly crystalline, and deemed suitable for x-ray crystallographic analysis (*see below*), thus it was subsequently transferred to a small plastic vial for transport. The CH₃CN–GeF₄ and ClCH₂CN–GeF₄ samples were amorphous, and deemed unsuitable for x-ray analysis.

Crystallography

X-ray diffraction data for the FCH₂CN/GeF₄ product were collected at 100 K on a Bruker D8 Venture using MoK α -radiation ($\lambda=0.71073$ Å) radiation. Data were corrected for absorption using the SADABS [52] area detector absorption correction program. Calculations and refinement of structures were carried out using APEX2 [53], SHELXTL [53], and Olex2 [54] software. Using Olex2, the structure was solved with the SHELXTL structure solution program using Direct Methods and refined with the SHELXTL refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms in the investigated structure were found from the residual density maps and refined with isotropic thermal parameters.

Thin-film Infrared Spectra

Thin-film infrared spectra were recorded using a Nicolet Avatar 360 FTIR at 2.0 cm⁻¹ resolution, and 200 scans were averaged for each spectrum. We utilized a previously described [55] low-temperature, matrix-IR apparatus, based on a Cryomech ST15 optical cryostat, which uses a Scientific Instruments 9600-1 temperature controller. This system was recently updated and rebuilt, however, and is now evacuated with a corrosive series turbomolecular pump (Pfeiffer HiPace 300 C) that is backed by a corrosive series rotary vane mechanical pump (Pfeiffer DUO 2.5 C). In this new configuration, the cryostat is mounted on a movable trolley that allows translation of the cold head into and out of the FTIR beam (and other instruments in the future). A KBr sample window was used for all experiments.

Gas mixtures, CH₃CN/N₂, FCH₂CN/N₂, and ClCH₂CN/N₂ (1/100), were made in glass 2 L bulbs on a glass manifold (Chemglass) evacuated with a diffusion pump (Chemglass). The GeF₄/N₂ mixture

(1/100) was prepared in a 4 L stainless steel tank to avoid reactions between GeF_4 and the glass bulbs, which seemed to take place over time. Thin films were deposited by simultaneously flowing the nitrile and GeF_4 mixtures through separate lines, which merged in a custom-designed, dual-deposition flange [55]. The mixtures were deposited at temperatures ranging from 100-150 K, with flow rates that varied between 2 and 14 mmol/hour. Flows were controlled using Granville-Phillips 203 variable leak valves, and for each sample, the film was deposited in several intervals, each lasting 20 to 60 minutes. Spectra were recorded after each interval. Target concentration ratios in the film were either 1:1 or 2:1 (nitrile/ GeF_4), as it was expected that we might see two reaction products (*i.e.*, 1:1 and 2:1 complexes; nitrile: GeF_4). In some cases, we conducted a series of annealing experiments in which the temperature was increased from 100 to 180 K in 10 K steps, and spectra were recorded at each step. Unreacted nitrile and/or GeF_4 desorbed preferentially with increasing temperature, and provided further insight into film composition.

Results and Discussion

Equilibrium Structures and Binding Energies of the 1:1 Complexes

Four possible isomers of the $\text{FCH}_2\text{CN-GeF}_4$ and $\text{ClCH}_2\text{CN-GeF}_4$ complexes were considered in our search for the equilibrium gas-phase structures, including two axial conformers with the nitrile halogen either eclipsed or staggered with respect to the (approximately) equatorial F's on the GeF_4 , as well as and two equatorial configurations (all C_s symmetry). The axial-eclipsed isomers were found to be the lowest energy forms for both complexes, as would be expected based on recent result for analogous systems [25], and they exhibited all real frequencies (M06/aug-cc-pVTZ). Thus, we based the investigation of the Ge-N potential and the frequency analysis on these forms (see below), and accordingly, these structures are displayed in Figure 1. The axial-staggered forms were not only

higher in energy, albeit by only 0.005 and 0.017 kcal/mol for FCH₂CN–GeF₄ and ClCH₂CN–GeF₄ respectively, they also exhibited imaginary torsional frequencies. Both equatorial structures considered for each complex rearranged to the axial-eclipsed geometry during the optimizations.

The Ge-N bond lengths in the equilibrium, axial-eclipsed geometries of FCH₂CN–GeF₄ and ClCH₂CN–GeF₄ are 2.447 Å and 2.407 Å, respectively. These distances are longer than previously reported value for CH₃CN–GeF₄ (2.274 Å, X3LYP/aug-cc-pVTZ) [37] as well as that for the M06/aug-cc-pVTZ structure (2.266 Å, *present study*). Thus by any measure, halogen substitution does lead to significant lengthening of the Ge-N bond, by about 0.2 Å. For context, we note that the Ge-N distances in FCH₂CN–GeF₄, and ClCH₂CN–GeF₄ are about 0.5 Å longer than the sum of the covalent Ge-N radii (1.91 Å) [28], yet about 0.9 Å shorter than the sum of the van der Waals radii (3.36 Å) [56]. In addition, the N-Ge-F angles of 78.3° (FCH₂CN–GeF₄) and 78.8° (ClCH₂CN–GeF₄) reflect an intermediate degree of distortion in the GeF₄ subunit; the ideal tetrahedral and trigonal bipyramidal values are 70.5° and 90°, respectively. The F-Ge-F angles of 101.9° and 101.3° also reflect an intermediate degree of distortion; the ideal tetrahedral and trigonal bipyramidal values are 109.5° and 90.0°, respectively. Thus, by every structural measure, the donor - acceptor interactions in these systems are intermediate between fully bonding and non-bonding interactions.

The binding energies for FCH₂CN–GeF₄ and ClCH₂CN–GeF₄ are 6.5 kcal/mol and 6.9 kcal/mol respectively, via M06/aug-cc-pVTZ. The corresponding MP2/aug-cc-pVTZ values are 7.9 kcal/mol, and 8.5 kcal/mol. These results quantify the extent that halogen substitution weakens the Ge-N dative bond; the binding energy for CH₃CN–GeF₄ is 2 to 3 kcal/mol larger; 11.4 kcal/mol via MP2/6-311+G(2df,p) [37], and 9.2 kcal/mol via M06/aug-cc-pVTZ.

Ge-N Bond Potentials

Ge-N bond potentials via M06, MP2 and ω -B97X-D (all with the aug-cc-pVTZ basis set) for $\text{FCH}_2\text{CN-GeF}_4$ and $\text{ClCH}_2\text{CN-GeF}_4$ are shown in Figure 2, and a comparison the two M06 curves with that for $\text{CH}_3\text{CN-GeF}_4$ is shown in Figure 3. The M06 curves will be discussed in detail here, and for a consistent comparison between curves, we will compare not only the minimum energy points, but also the relative energies at distances ± 0.3 Å from these minima. The $\text{FCH}_2\text{CN-GeF}_4$ the energy rises by about 0.4 kcal/mol at $+0.3$ Å, toward the outside wall of the minimum (2.4 Å), and about by 1.8 kcal/mol at -0.3 Å, toward the inner wall. Similarly, on the $\text{ClCH}_2\text{CN-GeF}_4$ curve, the energy rises by about 0.4 kcal/mol at $+0.3$ Å (relative to a 2.4 Å minimum), and by about 1.6 kcal/mol at -0.3 Å. In contrast, the $\text{CH}_3\text{CN-GeF}_4$ curve is much less flat, and the energy rise is about twice that observed in the $\text{FCH}_2\text{CN-GeF}_4$ and $\text{ClCH}_2\text{CN-GeF}_4$ curves. Specifically, the energy rises 0.9 kcal/mol toward the outer wall ($+0.3$ Å relative to a 2.3 Å minimum), and 2.7 kcal/mol toward the inner wall (-0.3 Å). Ultimately, these comparisons more broadly illustrate the effect of

halogenation on the energetic properties of these systems; not only is the equilibrium bond distance longer and the potential well shallower for the fluoro- and chloro-complexes, the curves become significantly flatter, which makes these systems more prone to condensed-phase structural changes than $\text{CH}_3\text{CN-GeF}_4$ [8, 20, 37].

Figure 2. Ge-N potential curves for $\text{FCH}_2\text{CN-GeF}_4$ (left) and for $\text{ClCH}_2\text{CN-GeF}_4$ (right) via M06, ω -B97X-D, and MP2 with the aug-cc-pVTZ basis set.

Figure 3. A comparison of Ge-N bond potentials (M06/aug-cc-pVTZ) for CH₃CN–GeF₄, FCH₂CN–GeF₄, and ClCH₂CN–GeF₄.

Effects of Dielectric Media

In order to assess the sensitivity of these systems to condensed-phase environments, we calculated hybrid Ge-N bond potentials by summing the gas-phase electronic energy with the electrostatic component of the solvation free energy, in a range of dielectric media with ϵ values ranging from 1.5 to 20 (via PCM/M06/aug-cc-pVTZ). These curves are displayed in Figure 4, wherein the top trace in each figure is the gas-phase data (*i.e.*, M06/aug-cc-pVTZ, from Figure 2). For both FCH₂CN–GeF₄ and ClCH₂CN–GeF₄, the minima shift -0.3 Å inwards, from 2.4 Å to 2.1 Å, between the gas phase and $\epsilon=20$. Also, the wells become more pronounced; the potential walls become much steeper on either side of the minimum. Furthermore, we note that these changes in the curves set in at lower dielectric values, though to a lesser extent. For example, the minima for both complexes shift from 2.4 Å to 2.3 Å in the $\epsilon=1.5$ curves, and to 2.2 Å in the $\epsilon=3.0$ curve. In any event, results do indicate that the Ge-N bonds in FCH₂CN–GeF₄ and ClCH₂CN–GeF₄ would contract significantly in

condensed-phase media, and moreover, these predicted changes exceed those noted previously for $\text{CH}_3\text{CN-GeF}_4$ [37].

Properties of the 2:1 Complexes

We also investigated the analogous 2:1, nitrile: GeF_4 complexes, and the equilibrium structures and binding energies (M06/aug-cc-pVTZ) of $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$ and $(\text{ClCH}_2\text{CN})_2\text{-GeF}_4$ are displayed in Figure 5. (Often, the structural formulas for coordination compounds of this type would be written $\text{GeF}_4(\text{FCH}_2\text{CN})_2$ or $\text{GeF}_4(\text{ClCH}_2\text{CN})_2$ though we choose to list the nitrile donor ligand first as to be consistent with the formulas for the analogous 1:1 systems.) We initially considered both *cis* and *trans* forms of these complexes, and found that the *cis* forms were found to be lower in energy by about 4 kcal/mol in each case. This is consistent with prior studies on these systems [34, 37], and

this issue we be discussed in more detail below. Subsequently, we also considered nine possible conformers of each cis isomer based on various possible torsional angles of the XCH_2CN subunits, including those that resembled the solid state structure for $(\text{FCH}_2\text{CN})_2\text{--GeF}_4$ (*below*). The conformers shown in Figure 5 belong to the C_{2v} point group, and have the nitrile halogens in the plane of the Ge-N bonds and directed toward one another. For $(\text{ClCH}_2\text{CN})_2\text{--GeF}_4$ this form is both lowest in energy, by about 0.5 to 1.0 kcal/mol relative to most other conformations, and the torsional frequencies are real. There is, however, a nearly isoenergetic C_2 -symmetry structure, nearly equivalent to the C_{2v} form but with the nitrile halogens tilted slightly away from one-another, and it is only 0.01 kcal/mol higher in energy. The nitrile torsional frequencies for this C_2 structure are imaginary, however. For $(\text{FCH}_2\text{CN})_2\text{--GeF}_4$, this C_2 -symmetry form is lowest in energy (by a mere 0.02 kcal/mol relative to the C_{2v} structure), but again the nitrile torsional frequencies are imaginary. While the torsional frequencies for the C_{2v} form are real, in both cases, the energy differences between the C_2 and C_{2v} forms are near the precision limit of the computations. We also note that several trial conformations for both complexes were unstable and rearranged to structures near those of the C_{2v} forms during the optimization. Because of this, we chose to report the results for the C_{2v} form, both in Figure 5 and in the frequency section (*below*), but it is clear that the torsional potential is particularly flat with respect to a concerted twist toward the C_2 form.

The Ge-N distances for $(\text{FCH}_2\text{CN})_2\text{--GeF}_4$, and $(\text{ClCH}_2\text{CN})_2\text{--GeF}_4$ are 2.319 Å and 2.367 Å, respectively, almost 0.1 Å shorter than in the analogous 1:1 systems (*above*). However, the GeF_4 subunit is not fully distorted to an ideal octahedral geometry, in which all bond angles about the Ge would be 90° . For $(\text{FCH}_2\text{CN})_2\text{--GeF}_4$, the F-Ge-F angle (in the plane of the nitrile-Ge bonds) is 104.2° , and the N-Ge-F angles (in the same plane, and not noted in the figure) are 84.5° . For $(\text{ClCH}_2\text{CN})_2\text{--GeF}_4$, the corresponding values are 104.0° and 85.3° , respectively. The previously

reported values [37] for the Ge-N distances in $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ are 2.277 Å (X3LYP) and 2.177 Å (MP2), and again for the sake of consistent comparison, we computed an M06/aug-cc-pVTZ structure (C_{2v}), for which the Ge-N distances values for $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ are 2.241 Å. (In the present case, however, we find that the conformer with two C-H bonds pointing inwards, in the plane of the Ge-N bonds, is the structure for which the torsional frequencies are real.) Regardless, by any measure, halogenation of the nitriles results in Ge-N distances that are about 0.1 Å longer. Furthermore, the shortening of the Ge-N distances that occurs with the second nitrile moiety, about 0.1 Å for $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$ and $(\text{ClCH}_2\text{CN})_2\text{-GeF}_4$, is more extreme than for the CH_3CN complex, for which the Ge-N distances differ by only about 0.02 Å between the 1:1 and 2:1 complexes. Thus, the tendency for the bond to contract with addition of another nitrile ligand parallels the effect of solvation by a bulk medium (*see below*), and is clearly more significant in the weaker, halogenated systems.

While the preference of the *cis* isomers in these systems may seem at odds with simple steric arguments, this was observed long ago that MX_4L_2 complexes with N-donors (at least $\text{M}=\text{Ti}$ and Sn) [57], and we also noted this in our recent study of 2:1 $\text{CH}_3\text{CN}/\text{MX}_4$ complexes. For the $\text{M}=\text{Ti}$ systems, this a good illustration of a “cooperative effect”, in which the ligands can donor to different (3d) orbitals via the *cis* geometry, and there is a substantial energetic benefit [37]. With Group 14 metals such as Ge (or presumably Sn as well) the LUMO is primarily s character [37], and the nitrile-M interactions are classified as “anti-cooperative”; they donate to the same orbital [57], and there is less preference for the *cis* isomers. Nonetheless, the *cis* forms are still lower in energy, and this may stem from an electrostatic benefit to bonding opposite the electronegative F atoms, in accord with the sigma-hole concept [57]. In addition, we note here that the halogenated systems

seem to have a greater preference, which may indicate a stabilizing, attractive (dispersion) interaction between the nitrile groups.

The binding energies, relative to the three separated fragments, are 9.0 and 9.7 kcal/mol, for $\text{FCH}_2\text{CN-GeF}_4$ and $\text{ClCH}_2\text{CN-GeF}_4$, respectively. These data indicate that the bonding energy for the second nitrile group is 2.5 kcal/mol for the FCH_2CN complex, and 2.8 kcal/mol for the ClCH_2CN complex, which corresponds to about 60% of the binding energies for the 1:1 complexes. The weaker bond for the second ligand is consistent with an “anti-cooperative” interaction [37, 57] as discussed above. The M06/aug-cc-pVTZ binding energy for $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ is 12.8 kcal/mol, 3 to 4 kcal/mol larger in magnitude than in the halogenated systems, which again illustrates and quantifies the extent to which halogenation weakens the Ge-N dative bonds.

Figure 5. Calculated (M06/aug-cc-pVTZ) equilibrium structures and binding energies for the 2:1 complexes $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$ and $(\text{ClCH}_2\text{CN})_2\text{-GeF}_4$. The acute N-Ge-F angles, in the plane of the Ge-N bonds, are 84.5 and 85.3 degrees, respectively, and were omitted for clarity.

Bulk-phase Reactivity

When liquid samples of CH_3CN , FCH_2CN , and ClCH_2CN were exposed to GeF_4 vapor, white solids formed immediately, though little heat was evolved, *i.e.*, no extreme temperature changes were observed. The $\text{FCH}_2\text{CN}/\text{GeF}_4$ product was distinctly crystalline, and the crystals seemed to grow while the sample was stored for several days. Also, it seemed stable when it was exposed to ambient air when it was transferred from the reaction tube to a storage vial; there was no fuming or other clear sign of decomposition (at least over the course of a few weeks, in time these samples degraded). The $\text{CH}_3\text{CN}/\text{GeF}_4$ product was a milky white powder with no clear signs of crystallinity, and the $\text{ClCH}_2\text{CN}/\text{GeF}_4$ product was a white powder, also with no clear signs crystal formation, but both of these compounds were also stable when exposed to ambient air.

Solid State Structure of $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$

An x-ray crystal structure for the $\text{FCH}_2\text{CN}/\text{GeF}_4$ reaction product was obtained, which confirmed that its identity was the 2:1 complex $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$, and the structure is displayed in Figure 6. A complete set of supplementary crystallographic data for this structure is available, and can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (CCDC 1486404). This solid-state structure exhibits clear differences from its gas-phase counterpart, especially with respect to the Ge-N bond distances and the angles that reflect the extent of distortion within the GeF_4 subunit. While, the gas-phase Ge-N bond distances are 2.366 Å, these distances compress by about 0.3 Å to values of 2.065 Å and 2.052 Å in the solid state. Correspondingly, there is a greater degree of distortion in the GeF_4 as well; for the angle (approximately) in the plane of the Ge-N bonds (*same as noted above*), the F-Ge-F angles are 88.7° (average), and the F-Ge-F angle is 97.6°. The respective gas-phase values are 104.2° and 84.5°. However, while it is apparent that the interactions

in the solid state manifest shorter (and presumably stronger) Ge-N dative bonds, the coordination geometry about the Ge is still not fully octahedral.

Infrared Spectra and Frequency Analysis

Figures 7-9 show the experimental IR spectra collected for solid CH₃CN/GeF₄, FCH₂CN/GeF₄ and ClCH₂CN/GeF₄ films, together with simulated gas-phase spectra (M06/aug-cc-pVTZ) for the corresponding 1:1 and 2:1 complexes for each system. Complete sets of frequency predictions (M06/aug-cc-pVTZ) for all six gas-phase complexes, both 1:1 and 2:1 forms, are included as *Supplementary Content* (Tables S4-S6). The most prominent bands in these spectra are the GeF₄ asymmetric stretch ($\nu_{\text{GeF}}^{\text{A}}$, 600-800 cm⁻¹), for which the asymmetric designation here refers to the free GeF₄ molecule (T_d point group). In the complexes, which have varying degrees of lower symmetry, this band splits into components that can be either symmetric or anti-symmetric within the point group of the complex (see below), but we retain the parent $\nu_{\text{GeF}}^{\text{A}}$ label for part the discussion that

follows. The other prominent bands present in these spectra are the C-C stretch (ν_{CC} , $\sim 930\text{ cm}^{-1}$), as well as the carbon – halogen stretching bands, ν_{C-F} ($\sim 1040\text{ cm}^{-1}$, not visible in the figure) and the ν_{C-Cl} ($\sim 740\text{ cm}^{-1}$) for films containing FCH₂CN and ClCH₂CN, respectively. The observed Ge-F stretching peaks tended to be broad and asymmetrical, presumably due to the presence of five naturally occurring Ge isotopes; for which ⁷⁴Ge is the most abundant (36%) [58]. The predicted M06 frequencies are based on the ⁷⁴Ge isotopomers.

When we initially recorded the IR spectrum of a 1/1 CH₃CN/GeF₄ film at a relatively low temperature (100 K), two sets of ν_{GeF}^A peaks were observed, one corresponding to unreacted GeF₄ solid (at 788 cm^{-1}), and the other shifted to a lower frequency (687 cm^{-1} with a broad, unresolved shoulder at 724 cm^{-1}). However, as we annealed the sample to 150 K, the intensity 788 cm^{-1} peak diminished, while that of the 687 cm^{-1} peak remained constant, indicating a preferential desorption of the unreacted GeF₄. Based on this observation, we concluded that although the (initial) composition of the film was 1/1 (CH₃CN/GeF₄), unreacted GeF₄ was present, but no significant amount of unreacted CH₃CN could be detected. This is evidence that the ν_{GeF}^A band observed in the spectrum of the film corresponds to a 2:1 (CH₃CN:GeF₄) reaction product. Furthermore, in subsequent experiments with a CH₃CN:GeF₄ ratio of 2:1, the 687 cm^{-1} peak was still prominent, while the 788 cm^{-1} peak was virtually absent; which provided further evidence for a film composed of 2:1 complexes. The spectra displayed in Figure 7 were deposited at 150 K with an approximate 2:1 ratio of CH₃CN to GeF₄.

Figure 7. IR spectra of $\text{CH}_3\text{CN}/\text{GeF}_4$ thin films, together simulated gas-phase spectra (M06/aug-cc-pVTZ). From bottom to top: CH_3CN (100 K), GeF_4 (100 K), $\text{CH}_3\text{CN}/\text{GeF}_4$ (2:1, 150 K), $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ (M06, gas), $\text{CH}_3\text{CN-GeF}_4$ (M06, gas). The observed pattern for the ν_{GeF}^A bands best matches the $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ prediction, but is displaced by about 15 cm^{-1} .

The pattern of the experimental $\text{CH}_3\text{CN}/\text{GeF}_4$ spectrum in Figure 7 is also consistent with a film (at 150 K) that is composed 2:1 complexes, $(\text{CH}_3\text{CN})_2\text{-GeF}_4$. Though the experimental ν_{GeF}^A is much broader and more poorly resolved than the simulated spectrum, the observed pattern, including the expected intensities, matches the prediction quite well. There are actually four ν_{GeF}^A peaks in the simulated spectrum of $(\text{CH}_3\text{CN})_2\text{-GeF}_4$, which stem from symmetric (630 cm^{-1} and 695 cm^{-1} ; both A_1) and anti-symmetric (706 cm^{-1} , B_2 ; and 734 cm^{-1} , B_1) combinations of the two sets of symmetry-equivalent Ge-F bonds. These modes are essentially the symmetric and anti-symmetric combinations of the in-plane (with respect to the nitriles) and out-of-plane Ge-F bonds, and thus we designate

them (for all 2:1 systems) as follows: out-of-plane asymmetric stretch (OAS), in-plane, asymmetric stretch (IAS), in-plane symmetric stretch (ISS), and out-of-plane symmetric stretch (OSS), for the bands at 734, 706, 695, and 630 cm^{-1} respectively, in the present case.

However, though the inferred splitting and intensity pattern is a near match, the agreement is not exact; the observed ν_{GeF}^A bands are displaced to lower frequencies about 15 cm^{-1} . This shift between the calculated gas-phase frequencies and the observed solid-state bands is consistent with a slight structural difference between the gas-phase and solid-state complexes [37], but given the fairly small magnitude, and the fact that the individual bands in the experimental spectrum are not resolved, it is not clear as to what extent the difference stems from structural differences, and what stems from errors in the gas-phase predictions (an issue we explore in more detail below for $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$). Nonetheless, we did make a theoretical assessment of the overall medium sensitivity of this system by calculating structures in bulk dielectric media with $\epsilon = 5.0$ (chosen arbitrarily) using PCM/M06/aug-cc-pVTZ. The Ge-N bonds in the resulting structure were 2.010 Å, just over 0.1 Å shorter than the gas-phase result (2.242 Å), and the predicted Ge-F stretching bands were: 671, 661, 648, and 582 (for the OAS, ISS, IAS and OSS modes, respectively). The strong bands (671, 661, and 648) roughly coincide with broad feature in the experimental spectrum, and thus there is at least qualitative agreement, and some evidence that the solid-state structure of $(\text{CH}_3\text{CN})_2\text{-GeF}_4$ is significantly different from the (calculated) gas-phase geometry, but these data are much less conclusive than those for the halogenated systems (below).

While we observe no peaks that correspond to a 1:1 complex in the experimental spectrum, the ν_{GeF}^A bands for $\text{CH}_3\text{CN-GeF}_4$ were measured previously in argon matrices [27]. In turn, we are able to make some additional comparisons between these data and the M06 predictions for gas-phase

CH₃CN–GeF₄. The simulated spectrum of the 1:1 complex contains two prominent peaks. The equatorial Ge-F stretching bands are a nearly degenerate pair that occurs at 770 cm⁻¹. This is in perfect agreement with the argon-matrix spectrum, in which the equatorial Ge-F stretch is observed at 770 cm⁻¹ [27]. There is a slight difference between the predicted (729 cm⁻¹) and observed (719 cm⁻¹) [27] axial Ge-F stretching band, which could reflect a slight matrix effect on the structure, and we note that some medium sensitivity was predicted previously [37]. There is an additional band reported in the matrix spectrum, however, which does not correspond to any prominent band in the prediction, though we note here that the observed peak at 695 cm⁻¹ does very closely correspond to the prominent peak in the film and at least one of the predicted peaks for (CH₃CN)₂–GeF₄; thus it seems possible that this additional peak arises from the 2:1 complex.

For the most part, the spectra of the films with FCH₂CN or ClCH₂CN were quite similar to those involving CH₃CN, though for some reason the ν_{GeF}^A bands are split into more distinctive peaks, and in turn, the comparisons to the simulated spectra are more compelling. In addition, we observed the same temperature and composition dependence. Specifically, when the films were deposited at 100 K with a 1:1 nitrile/GeF₄ ratio, two ν_{GeF}^A bands were observed, including one nearly coincident with the ν_{GeF}^A band in the pure GeF₄ film. However, when a 2:1 nitrile/GeF₄ film was deposited, and/or the sample was annealed to 150 K, or deposited at 150 K, only one ν_{GeF}^A band was observed. This led us to believe that like the CH₃CN/GeF₄ sample, the FCH₂CN and ClCH₂CN-containing films were composed of 2:1 complexes.

Figure 8 displays the observed spectrum for the FCH₂CN/GeF₄ film (at 150 K), together with analogous reference spectra of FCH₂CN and GeF₄ films (100 K), and once again, simulated gas-

phase spectra (M06/aug-cc-pVTZ) for the 1:1 and 2:1 FCH₂CN:GeF₄ complexes. In these data, the predicted quartet pattern for the ν_{GeF}^A bands in the simulated spectrum of the 2:1 complex matches experimental spectrum quite well. The key differences between the are that the central peaks are only partially resolved in the experiential spectrum, and once again, the pattern is displaced to lower frequencies; in this case by about 60 cm⁻¹ for each for the four Ge-F stretching bands: 702, 667, 652, and 605 cm⁻¹ in the observed spectrum, and 763, 726, 711, and 660 cm⁻¹ in the predicted spectrum (for the OAS, IAS, ISS, and OSS modes, respectively).

The 60 cm⁻¹ red-shift for the Ge-F stretching band (*i.e.*, exp/solid vs. calc/gas), is presumably due to a difference in (calculated) gas-phase and solid-state structures, for which the Ge-N sictacnes are 2.37 Å and 2.06 Å (ave), respectively. However, it is not immediately clear to what extent this red shift stems directly from structural changes (either via a direct geometrical dependence or by an softening of the harmonic Ge-F force constants) versus errors in the harmonic gas-phase frequencies. Though the M06 method was chosen by validating against experimental, gas-phase frequencies for GeF₄, and the anharmonic corrections were reasonably insignificant, an increase in the extent of anharmonicity in the Ge-F force field that might accompany the formation of the Ge-N dative bonds could manifest some portion of the observed shifts. As noted above, anharmonic frequency predictions for the complexes exceeded our resource limit, but alternatively, we did make additional harmonic predictions for structures in bulk dielectric media with $\epsilon = 5.0$ and $\epsilon = 10.0$ (obtained via PCM/M06/aug-cc-pVTZ). The structures had Ge-N distances of 2.148 and 2.126 Å, respectively, only about 0.05 Å longer that the observed in the crystal structure. The predicted Ge-F frequencies were: 701 (OAS), 673 (ISS), 668 (IAS) and 595 cm⁻¹ (OSS) for the $\epsilon=5.0$ structure, and 692 (OAS), 667 (ISS), 656 (IAS) and 587 cm⁻¹ (OSS) for the $\epsilon=10.0$ structure. Both sets agree quite well with the observed solid-state spectrum (again, 702, 666, 649 and 603 cm⁻¹); most lie within 10 cm⁻¹, with 2

exceptions among the 8 peaks. These data demonstrate that these frequency shifts are a sensitive probe of structural change, and moreover that the majority of the red shift is a direct result of structural change, and not due to a neglect of anharmonicity or other model error. We do note however, that the PCM/M06 structures do have Ge-N distances that are just slightly longer than that observed for the solid state, and that an additional contraction for the Ge-N bonds would cause a greater red shift, so part of the quite favorable agreement we noted above between the PCM/M06 and measured solid state frequencies could be due to a cancelation of errors; the slightly longer bond length and a lesser degree of anharmonicity in the GeF force field in the complex (relative to free GeF₄). This is a minor consideration, however, given the magnitude of the red shifts.

Figure 8. IR spectra of FCH₂CN/GeF₄ thin films, together simulated gas-phase spectra (M06/aug-cc-pVTZ). From bottom to top: FCH₂CN (100 K), GeF₄ (100 K), FCH₂CN /GeF₄ (2:1, 150 K), (FCH₂CN)₂-GeF₄ (M06, gas), FCH₂CN-GeF₄ (M06, gas). The observed pattern for the ν_{GeF}^A bands matches the (FCH₂CN)₂-GeF₄ prediction, but is displaced by about 60 cm⁻¹.

Finally, figure 9 displays the observed spectrum for the ClCH₂CN/GeF₄ film (at 150 K), together with ClCH₂CN and GeF₄ reference spectra (100 K), as well as predicted gas-phase spectra (M06/aug-cc-pVTZ) for the 1:1 and 2:1 ClCH₂CN:GeF₄ complexes. Again, the observed pattern of the ν_{GeF}^A bands in the ClCH₂CN/GeF₄ film matches the predicted spectrum for the 2:1 complex, but again is shifted to the red, by 50 to 55 cm⁻¹ in this case. The comparison is obscured somewhat by the fact that the carbon-chlorine stretch ($\nu_{\text{C-Cl}}$) appears as a strong doublet in the 2:1 film trace (at 738 and 747 cm⁻¹), just to the high-frequency side of the quartet. Nonetheless, the observed components of the quartet occur at: 701, 665, 652 (shoulder), and 596 cm⁻¹ in the observed spectrum, and 754, 721, 706, and 650 cm⁻¹ in the predicted, gas-phase spectrum (again for the OAS, IAS, ISS, and OSS modes, respectively). Again we note that the splittings between components in each respective band, predicted vs. experimental, differ by only a few cm⁻¹, in spite of the sizable overall displacement. We also note that these gas-phase Ge-F frequencies of (ClCH₂CN)₂-GeF₄ are slightly red-shifted relative to the analogous values for (FCH₂CN)₂-GeF₄, which is consistent with the somewhat shorter Ge-N bonds in the former case. At this point, it seems reasonable that the 50-55 cm⁻¹ red shift of these bands reflects a structural difference in which the Ge-N bonds in the solid are compressed relative to those in the theoretical gas-phase structure. Furthermore, the fact that this shift rivals that for the FCH₂CN/GeF₄ system suggests a difference of comparable magnitude. Also for this complex, we explored the effect of dielectric media ($\epsilon = 5.0$ and 10.0) on the structure and frequencies via PCM/M06/aug-cc-pVTZ, and these structures exhibit Ge-N distances of 2.136 Å and 2.116 Å respectively, about 0.2 Å shorter than the gas-phase result. Again, the frequencies agree quite well with the measurements (within 10 cm⁻¹ with one exception among eight), the values are 696, 671, 663, and 598 cm⁻¹ for the $\epsilon=5.0$ structure, and 688, 665, 652, and 591 cm⁻¹ for the $\epsilon=10.0$ structure (again, for the OAS, ISS, IAS, and OSS modes, respectively). Thus, it is clear that there are

significant differences between the (calculated) gas-phase and solid-state structure for $(\text{ClCH}_2\text{CN})_2\text{-GeF}_4$ as well, though perhaps to slightly lesser extent than for $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$.

Conclusions

We have investigated the structural and energetic properties of the 1:1 and 2:1 complexes of FCH₂CN and ClCH₂CN with GeF₄, using quantum chemical computations, low-temperature IR spectroscopy, reactivity studies, and for one system, (FCH₂CN)₂-GeF₄, we obtained a solid-state, crystallographic structure. The Ge-N distances in the gas-phase equilibrium structures of FCH₂CN-GeF₄ and ClCH₂CN-GeF₄ are significantly longer than those for CH₃CN-GeF₄, by about 0.2 Å, and furthermore, the binding energies are much lower; 6.5 and 6.9 kcal/mol for the FCH₂CN and ClCH₂CN complexes, respectively, compared to 9.2 kcal/mol for CH₃CN-GeF₄ (M06/aug-cc-pVTZ). Thus, it is clear that halogen substitution on the nitrile moiety substantially weakens the Ge-N dative bonds in the 1:1 complexes. In addition, a computational examination of Ge-N potential curves reveal that the potentials of FCH₂CN-GeF₄ and ClCH₂CN-GeF₄ are much flatter than that for CH₃CN-GeF₄, which suggests a greater susceptibility to structural change in condensed-phase media. In turn, hybrid potential curves that account for the effects of a dielectric medium on the intermolecular potential do show a more significant response for the halogenated complexes, and thus indicate that weakening the Ge-N dative bond via halogenation does enable a more significant condensed-phase response. In bulk reactivity experiments, FCH₂CN, ClCH₂CN, and CH₃CN reacted quickly with GeF₄ to form relatively stable products, all white solids, and crystallographic analysis confirmed that the product of the FCH₂CN/GeF₄ reaction was the 2:1 complex, (FCH₂CN)₂-GeF₄. The structure was found to exhibit Ge-N bonds that were nearly 0.3 Å shorter than those in the calculated gas-phase structure; which in turn indicates that the 2:1 systems are also prone to condensed-phase structural change. In addition, calculated gas-phase structures of (FCH₂CN)₂-GeF₄, (ClCH₂CN)₂-GeF₄, and (CH₃CN)₂-GeF₄ indicate that adding the second nitrile to the complex results in a shortening of the GeN-bond(s); by about 0.1 Å for the halogenated complexes, but only 0.02 Å in (CH₃CN)₂-GeF₄. In a broad sense, a larger contraction upon on the addition of a second

nitrile ligand is another indication that the halogenated systems are more responsive to solvation effects. In addition, low-temperature IR spectra of nitrile/ GeF_4 films indicates that the relative composition of the films is 2/1 nitrile/ GeF_4 , and furthermore, that splitting patterns of the Ge-F stretching bands near 700 cm^{-1} closely match the predicted (M06/aug-cc-pVTZ) spectra of the 2:1 complexes. This further indicates that the films are composed of 2:1 complexes. However, the patterns are displaced to lower frequencies, and thus consistent with a contraction of the Ge-N dative bonds in the solid state, relative to the predicted gas-phase structures. This effect was confirmed for $(\text{FCH}_2\text{CN})_2\text{-GeF}_4$, and modeled via PCM/M06/aug-cc-pVTZ calculations for all three 2:1 complexes. Moreover, these red shifts are larger in magnitude for the halogenated systems, and further illustrate that the 2:1 systems also become more susceptible to condensed-phase structural change upon halogenation.

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