Condensed-Phase Effects on the Structural Properties of Nitrile—SiF4 Complexes: A Low-Temperature IR and Computational Study

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Our research involves the identification of molecular complexes that change structure when the chemical environment is altered, e.g., gas-phase to solid-state. This project stems from a previous study on $CH_3CN–SiF_4$, in which condensed-phase structural changes were predicted but not observed [1]. In the present case, we are dealing with four specific complexes: $CH_3CH_2CN–SiF_4$, $C_6H_5–SiF_4$, $(CH_3)_3CCN–SiF_4$ and pyridine-SiF_4. We expect the larger carbon groups to enhance the bonding interaction and lead to more significant structural change in the condensed phase. Using M06, MP2, ωB97XD, and the 6-311G+(2df,2pd) basis set, we computed equilibrium geometries, binding energies, frequencies, N-Si potential curves, in the gas phase and in bulk dielectric media (PCM/M06/6-311G+(2df,2pd)). In our search for the most stable structure we considered both axial and equatorial coordination (two conformers for each). Structures and binding energies were very similar to that of $CH_3CN–SiF_4$. Nitrile complexes were found to be weak (ΔE~4-5 kcal/mol) with long N-Si bonds (~2.8 Å) and the pyridine complex was stronger (ΔE= -12.3 kcal/mol) with a shorter N-Si bond (2.1 Å). Gas phase potentials show a long bond length in the gas phase and a very slight energy rise towards shorter donor-acceptor distances. For $C_6H_5–SiF_4$, the shape of the PE curve changes dramatically with increasing dielectric constant, and the minimum energy point shifts from 2.8 Å at ε=2 to 2.0 Å at ε=10. Future work will involve Infrared Spectroscopy of nitrile/SiF_4 thin-films, in an attempt to observe condensed-phase effects.

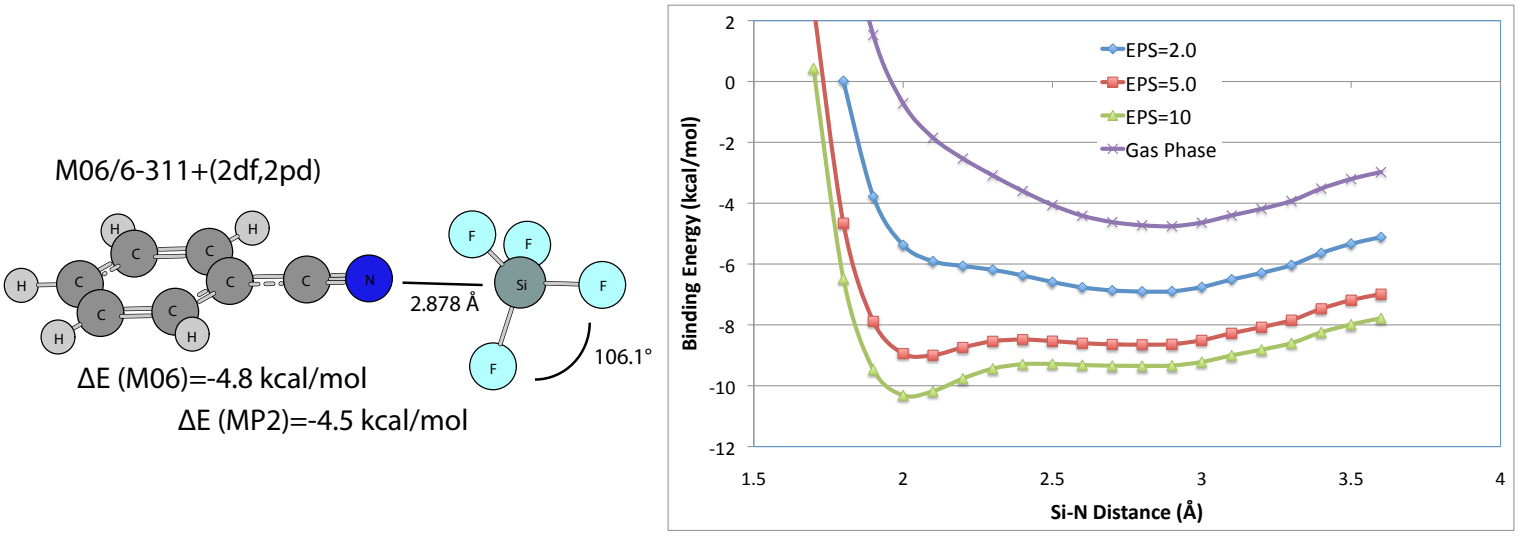

Figure 1. Equilibrium geometry of $C_6H_5–SiF_4$ (left) via M06, with binding energies for M06 and MP2. Also shown are potential energy curves for the gas phase as well as in bulk dielectric media using M06 (right).

1. Helminiak, H. M.; Knauf, R. R.; Danforth, S. J.; Phillips, J. A. *J. Phys. Chem. A* **2014**, *118 (24)*, 4266–4277.