

Dynamic Intermolecular Interactions in the Alkane/Perfluoroalkane Dimers: Can transient dipoles offer an intuitive explanation of the unexpected phase separation?

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The hydrophobic effect is commonly summarized as “like dissolves like”. The usual explanation is that different forces hold polar vs nonpolar liquids together; molecules of hydrocarbons and other nonpolar compounds enjoy mutual attraction primarily via van der Waals (AKA dispersion) interactions, whereas electrostatics (dipole-dipole and hydrogen bonding) dominate among polar species such as water. Thus, “oil and water don’t mix”, aggregating instead into separate liquid layers. This phase separation is routinely exploited in the purification and isolation of reaction products.

One long known outlier of this trend is the phase separation between perfluorocarbons and hydrocarbons. Both are nonpolar and hydrophobic in nature, but when perfluorinated alkanes (PFAS) and alkanes are mixed, they form separate hydrocarbon and “fluorous phase” layers. Theoretical analysis¹, ascribes the PFAS’ mutual attraction to electron correlation and dispersive forces, specifically among the fluorine atoms. Why then do nonpolar perfluorocarbons, held together by dispersion, not mix with similarly nonpolar dispersion-bound hydrocarbons? The above theoretical treatment does not paint a complete physical picture, as it focuses on ground state equilibrium geometries and static interactions.

In the present work, we compare the computed infrared (IR) spectra of isolated per-fluoroalkane/alkane molecules, up to per-fluoropropane/propane, to those of their dimer counterparts. The ~30 cm⁻¹ splitting in the CF₄··CF₄ asymmetric stretching modes points to their strong coupling, suggesting a dynamic attractive interaction between the molecules. In contrast, the partners in the CH₄··CH₄ and CF₄··CH₄ dimers “feel” each other less, showing much lower splittings of 5 and 6 cm⁻¹ respectively. Similar splittings in the asymmetric stretching modes of the per-fluoroethane and per-fluoropropane dimers are observed in the calculated IR spectra. In the splitting, the lowered vibrations show displacements that produce mutually attractive multipoles between the per-fluoroalkane fragments, whereas in the raised frequencies, they are repulsive. The matching frequencies of the PFAS dimers help to optimize these multipolar couplings, whereas the hetero dimers see no such benefit.

To probe the electronic effects, SAPT² potential energy curves at rigid geometries find that for symmetric configurations, such as D_{3d}/C_{3v}, van der Waals energy dominates the interaction. However, “relaxed” potential curves show that the asymmetric equilibrium geometry of the CF₄ dimer is instead driven via Coulombic contributions to the interaction energy. This results in an attractive interaction between Monomer A’s positively polarized carbon atom and the negatively polarized fluorine atoms of Monomer B. SAPT calculations were also run at the normal mode geometries, finding that as the CF₄ dimer samples the vibrational degrees of freedom there arises attractive and repulsive electrostatic interactions. Thus, beyond dispersion, the strongly polarized C-F bonds in per-fluoroalkanes enable mutually attractive interactions via the transient dipoles and quadrupoles created by vibrational motion. Due to the strong dependence on electrostatics in the perfluoro-dimers, this may provide an explanation to the otherwise puzzling failure of PFAS and alkanes to mix.

(1) Pollice, R.; Chen, P. Origin of the Immiscibility of Alkanes and Perfluoroalkanes. *J Am Chem Soc* **2019**, *141* (8), 3489–3506. <https://doi.org/10.1021/JACS.8B10745>.

(2) Jeziorski, B.; Moszynski, R.; Szalewicz, K. Perturbation Theory Approach to Intermolecular Potential Energy Surfaces of van Der Waals Complexes. *Chem. Rev* **1994**, *94*, 1887–1930.