

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 analysis^{1,2}, 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 between species.

In the present work, we compare the computed infrared (IR) spectra of isolated CH₄ and CF₄ molecules to those of their dimer counterparts. The ~40 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. Thus, beyond dispersion (electron motion), the strongly polarized C-F bonds in CF₄ enable mutual interaction via the transient dipoles and quadrupoles created by vibrational motion. In the splitting, the lowered vibrations show displacements that produce mutually attractive dipoles between the CF₄ fragments, whereas in the raised frequencies, they are repulsive. These dynamic dipole-dipole interactions may help explain why alkanes and perfluorinated alkanes phase separate.

To probe dispersion (electronic instantaneous polarization) effects, SAPT³ calculations were also run, finding that while dispersion is attractive throughout the vibrational motions, electrostatics are more significant contributors to the attractive interactions. Though based on nuclear, rather than electronic motions, this concept of dynamic coupling of transient dipoles is intuitively reminiscent of the traditional van der Waals concept, offering an easily understood explanation for the otherwise puzzling failure of two nonpolar compound classes 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) Tsuzuki, S.; Uchimaru, T. Magnitude of Attraction in CF₄-CH₄ Interactions: Are CF₄-CH₄ Interactions Weaker than Average of CF₄-CF₄ and CH₄-CH₄ Interactions? **2020**. <https://doi.org/10.1016/j.jfluchem.2020.109468>.
- (3) 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.