

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

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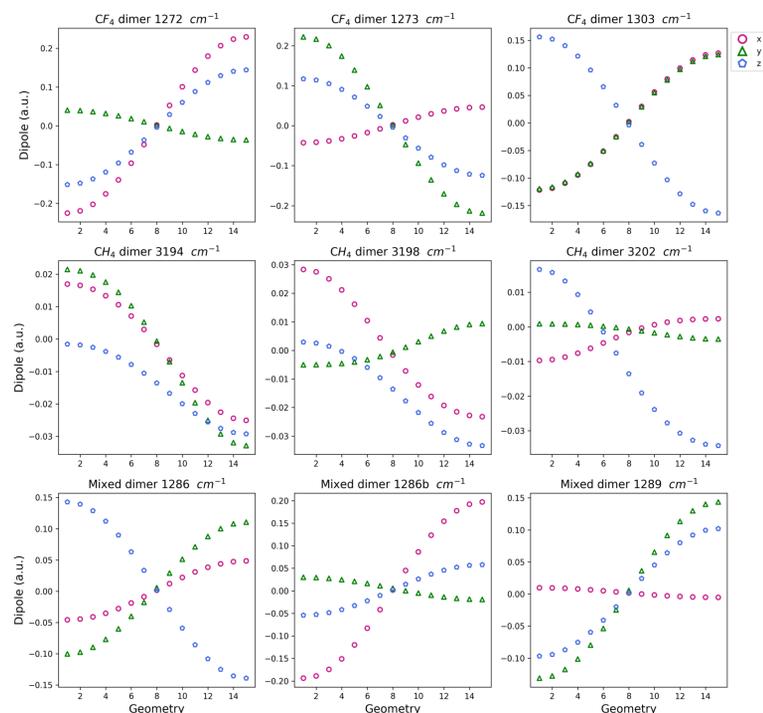
Introduction

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.

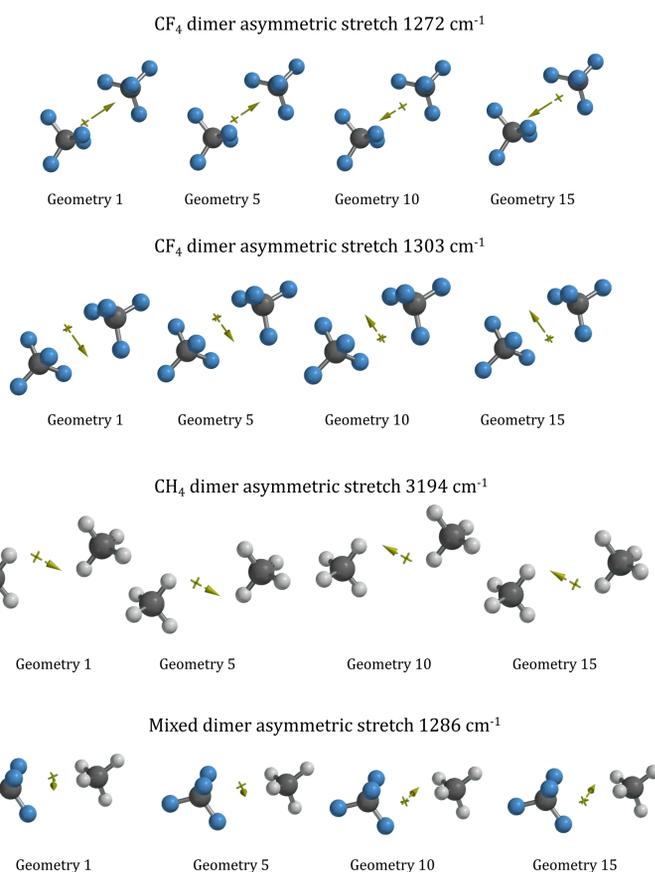
One long known outlier of this trend is the phase separation between perfluorocarbons and hydrocarbons. Both are nonpolar and hydrophobic in nature, but when perfluorinated alkanes (PFAs) and alkanes are mixed, they form separate hydrocarbon and “fluorous phase” layers. Theoretical analysis^{1,2} ascribes 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 ~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 8 and 3 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.

CCSD(T) C-X Stretching Normal Mode Dipoles



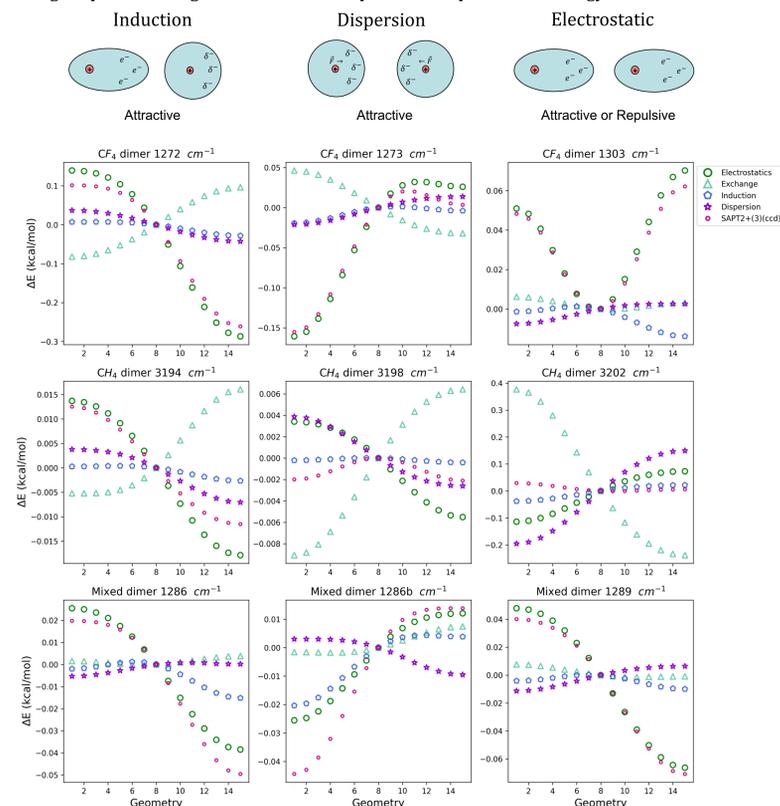
Evolving Transient Dipoles



The orientation of the evolving dipole of the pair in the asymmetric stretching modes of the CF₄ dimer is mutually attractive for the low energy splitting, the dipoles are additive parallel to the axis between the carbons, reinforcing the dimer dipole in an attractive manner. Conversely, the high energy splitting is additive perpendicular to the C-C axis, resulting in an unattractive interaction. This pattern is not seen in the splitting of vibrational modes for the asymmetric stretches of the CH₄ and mixed dimers.

Symmetry Adapted Perturbation Theory (SAPT)

To probe dispersion (electronic instantaneous polarization) effects, SAPT³ calculations were performed at the SAPT2+3(CCD)^{4,6} level with an aug-cc-pVTZ basis set. SAPT is a perturbative expansion of the interaction energy which decomposes terms in the perturbation into physically meaningful quantities; e.g. electrostatic vs dispersive components of energy.



While dispersion is the primary attractive force statically, throughout the vibrational motions of the CF₄ dimer, changes to the SAPT energy from the ground state are dictated by electrostatics; the interactions along the displacement coordinate of the 1272 cm⁻¹ mode are on average attractive, while 1303 cm⁻¹ is repulsive throughout the normal mode. In contrast, the change in total energy of the CH₄ dimer is dictated by exchange or induction. The energy differences in the CF₄ ... CH₄ follows a similar pattern as CF₄ ... CF₄, however the average lowering in energy is an order magnitude less.

	ΔE (kcal/mol)	ΔH(kcal/mol)	ΔG(kcal/mol)
CF ₄ ... CF ₄	-1.39	-1.73	8.78
CH ₄ ... CH ₄	-1.02	-0.85	6.51
CF ₄ ... CH ₄	-0.50	-0.35	4.80

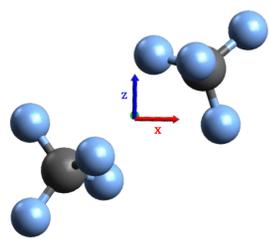
The interaction energy, enthalpy, and Gibbs free energy provide further evidence of the importance of vibrations. The calculated enthalpy values include thermal and vibrational contributions; Accounting for vibrations in the CF₄ dimer makes the association enthalpy more favorable (-1.39 → -1.73), whereas for the CH₄ and the mixed dimers, the vibrations make the interaction less favorable (-0.50 → -0.35 & -1.02 → -0.85). Evidently, the Gibbs free energy cost is higher for the CF₄ dimer; they are held more tightly, thus lose more degrees of freedom.

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.

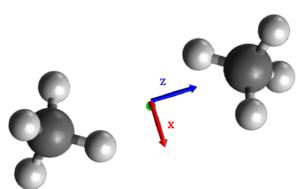
Geometry Optimization and Normal Mode Analysis

The geometry optimization and calculation of the IR spectrum for each dimer and the corresponding monomers were run at the MP2 level with an aug-cc-pVTZ basis. The IR frequencies of focus are the asymmetric stretching modes of the tetrahedral dimer, as these show the significant splitting in the CF₄ dimer. The frequencies are partitioned into 15 geometries corresponding to steps along the harmonic normal mode of the stretch, with the middle configuration as the ground state equilibrium geometry. With the given geometries, a multipole analysis was done via single point energy calculations at the coupled cluster CCSD(T) level. As MP2 scales O(N⁵) and CCSD(T) scales O(N⁷), the basis set used for the multiple calculations of CF₄-CF₄ and CF₄-CH₄ was aug-cc-pVDZ, and cc-pVTZ for CH₄-CH₄.

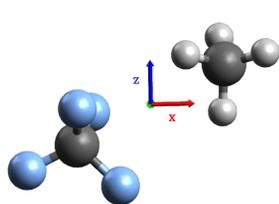
CF₄ dimer equilibrium geometry



CH₄ dimer equilibrium geometry



Mixed dimer equilibrium geometry



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Acknowledgments

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