

Modeling parahydrogen clusters around molecular and ionic impurities: size effects and scaling laws

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Synopsis The interaction of parahydrogen molecules and different molecular or ionic dopants has been theoretically modeled using dedicated potential energy surfaces and path-integral molecular dynamics simulations. Size effects and special stabilities corresponding to 'magic numbers' are reported and compared with experimental measurements when available.

Parahydrogen clusters exhibit rich physics and chemistry, even at low temperature where the possible occurrence of supersolidity has been suggested and debated. In presence of a dopant, and much alike helium droplets, the interactions with the dopant compete with the weak forces between hydrogen molecules and can lead to enhanced localization.

In this contribution, we present a computational investigation of parahydrogen clusters coating two particular series of dopants consisting of neutral or cationic hydrocarbon molecules, either of the polycyclic aromatic hydrocarbon (PAH) [1] or fullerene [2] types.

Polarizable force fields have been constructed and parametrized against electronic structure calculations to represent the interaction between parahydrogen molecules, approximated as rotationless point particles, and the various atoms of the dopant molecule. The equilibrium properties at cryogenic temperatures (2 K or lower) were then determined as a function of the number of coating molecules using path-integral molecular dynamics (PIMD) simulations, neglecting possible exchange effects and bosonic statistics.

Combined with a careful determination of low-energy structures, our investigation reveals fundamental properties of these heterogeneous clusters, starting with the number of molecules required to solvate entirely the dopant and above which a second shell arises. However, non-monotonic size effects are also found, as usual in clusters physics, notably in the vicinity of shell completion.

At 2 K the parahydrogen molecules behave essentially as a (soft) solid but with significant vibrational delocalization especially away from the dopant. Around C_{60}^+ complete solvation is found to occur near 50 molecules, in good agreement with mass spectrometry measurements [3].

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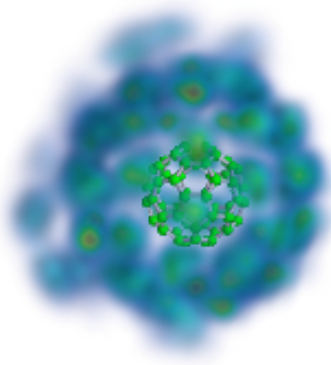


Figure 1. Density of 60 parahydrogen molecules around C_{60}^+ at 2 K

Repeating the PIMD simulations for a broad variety of dopants containing up to hundreds of atoms, the properties of the solvation shell are found to exhibit approximate scaling laws with the dopant size, with an additional but minor effects due to deuteration and, in the case of PAH dopants, both the carbon and hydrogen numbers.

Lastly, we will present our preliminary results on $(H_2)_nH^-$ clusters, which were recently produced and found to exhibit special stabilities interpreted as the result of icosahedral growth [4]. For these clusters, the united atom approximation does not hold and a full atomistic description appears necessary to account for polarization effects at shorter distances with the ion. Our PIMD calculations generally confirm the icosahedral interpretation but suggest that clusters containing more than about 40 molecules exhibit increasingly large delocalization and fluxionality, no single structure being especially stable.

References

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