The condensed-phase dynamics of a solute are often considered as a simple extension of that molecule’s gas-phase behavior. Based on this approximation, knowledge of the molecule’s gas-phase potential energy surfaces would give, in principle, enough information to predict its behavior in the condensed phase. However, through mixed quantum/classical simulations of the sodium dimer (Na₂) and sodium dimer cation (Na₂⁺) molecules dissolved in liquid argon and liquid tetrahydrofuran (THF), we show that the solvent is capable of dramatically altering the dynamics, reactivity, and even chemical identity of a solute. By computing the full solute/solvent coupled potential energy surface on-the-fly, we find that even in liquid argon, a completely apolar solvent that weakly interacts with any solute, Pauli repulsion interactions between the solvent and solute compress the solute bonding electrons, creating relatively large solute instantaneous dipole moments. This entirely quantum mechanical effect can alter the spectral signatures of the solute and induce infrared activity in solutes that would be IR inactive in the gas phase. Furthermore, when local specific interactions between the solute and solvent are present, even if the interactions are energetically only about as strong as a hydrogen bond, the solvent can actually become part of the chemical identity of the solute. For Na₂ and Na₂⁺ in liquid THF, weak dative bonding interactions between the metal ion cores and the THF oxygen atoms result in multiple unique solvent coordination states, each with their own dynamics and spectroscopic signatures. Moreover, each of these coordination states must cross a free energy barrier of ~8 k_B T—undergoing a chemical reaction—to interconvert, so that the different coordination states are effectively different molecules whose identity is entirely determined by interactions with the solvent. Overall, our studies show that the way a solvent influences the dynamics and reactivity of condensed-phase solutes cannot simply be extrapolated from gas phase surfaces. Instead, the full complexity of the solute-solvent interactions must be considered.


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