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How do solvent structure and counterion distribution control quantum solvation in liquids?

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Molecular liquids differ from each other not only in their polarity or their ability to make or accept hydrogen bonds but also in their intrinsic packing. Here, we show that the way a solvent packs can have dramatic effects on the dynamics of electron transfer reactions. Using a combination of nonadiabatic mixed quantum/classical molecular dynamics simulations and ultrafast pump-probe spectroscopy, we show that the presence of intrinsic cavities in liquid THF makes charge transfer dynamics in this solvent different from that in other solvent such as water. For example, we find that photoexcitation can cause solvated electrons in THF to transfer from one cavity to another, providing a mechanism for light-induced electron relocalization. We also find that the way a solvent distributes counterions around a reacting solute can dramatically alter not only the rate but even the products of charge transfer reaction. For example, following excitation of the charge-transfer-to-solvent (CTTS) band of iodide in THF, we find that for soft counterions such as tetrabutylammonium, roughly 10% of the ejected electrons form a loose complex with the counterion within a few ps of excitation. For harder counterions such as sodium, however, we find that there can be photoinduced transfer of the CTTS electron from the of I^- anion to the Na^+. If the sodium cations are complexed into crown ethers, however, electron transfer to Na^+ is shut off. Finally, we also investigate electron solvation and the CTTS dynamics of I^- in THF/water mixtures. We find that CTTS excitation leads to ejection of the electron in an initially THF-rich environment characteristic of the I^- solvation structure, but that the electrons subsequently become hydrated on a tens to hundreds of ps time scale.