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Identification of Ion-Pair Structures in Solution by Vibrational Stark Effects JOHN HACK, University of Virginia, DAVID GRILLS, JOHN MILLER, Brookhaven National Laboratory, TOMOYASU MANI, University of Connecticut — Ion pairing is fundamental to a wide range of sciences and technologies including batteries and organic photovoltaics. Ions in solution are known to inhabit multiple possible states, including free ions (FI), contact ion pairs (CIP), and solvent-separated ion pairs (SSIP). However, it is difficult to distinguish between these states in solutions of organic radicals and nonmetal electrolytes. In this work we report evidence for the formation of SSIPs in low-polarity solvents and distinct measurements of CIP, SSIP, and FI, by using the nitrile infrared (IR) band of a nitrile-substituted fluorene radical anion. Use of time-resolved IR detection following pulse radiolysis allowed us to unambiguously assign the peak of the FI. In the presence of nonmetal electrolytes, two distinct red-shifted peaks were observed and assigned to the CIP and SSIP. The assignments are interpreted in the framework of the vibrational Stark effect (VSE) and are supported by the solvent dependence of ion-pair populations, the observation of a cryptand-separated sodium ion pair that mimics the formation of SSIPs, and electronic structure calculations. Additionally, we show that a blue-shift of the nitrile IR band due to the VSE can be induced in a nitrile-substituted fluorene radical anion by covalently tethering it to a metal-chelating ligand that forms an intramolecular ion pair upon reduction and complexation with sodium ion. These results combined show that we can identify ion-pair structures by using the VSE, including the existence of SSIPs in a low-polarity solvent.

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