

MICROSOLVATION OF Ni²⁺ AND Co²⁺ BY ACETONITRILE AND WATER: PHOTODISSOCIATION DYNAMICS OF M²⁺(CH₃CN)_n(H₂O)_m

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The microsolvation of metal dications by acetonitrile and water study is important in understanding the interaction of solvents with the metal center and how the nature of the solvent, protic water and aprotic acetonitrile, affect binding and charge transfer dynamics. The clusters were produced by electrospray and characterized by photofragment spectroscopy in an ion trap dual time-of-flight mass spectrometer.

The homogeneous clusters with acetonitrile, n=4 and 3 dissociated by simple solvent loss and only n=2 showed electron transfer as a dissociation pathway. Mixed clusters with water and acetonitrile reveal more interesting dissociation dynamics. In larger mixed clusters (n=4 and 3), the water loss was favored over acetonitrile loss by a significant yield which is understandable because acetonitrile is a better solvent in the gas phase due to its higher dipole moment and polarizability. Proton transfer was observed as a minor channel for M²⁺(CH₃CN)₂(H₂O)₂ and M²⁺(CH₃CN)₂(H₂O) but was not seen in M²⁺(CH₃CN)₃(H₂O). In our lab, we previously observed proton loss as the major channel for M²⁺(H₂O)₄. Studies of deuterated clusters confirm that water acts as the proton donor. Considering the photodissociation yield it was clear that four coordinate clusters of cobalt dissociated more readily than nickel clusters whereas for the three coordinate clusters, dissociation was more efficient for nickel clusters over cobalt. For the two coordinate clusters, dissociation is via electron transfer but the yield is low for both metals. Our calculations of reaction energetics, dissociation barriers, and the positions of excited electronic states complemented the experimental work.