IR PHOTODISSOCIATION SPECTROSCOPY OF M^+-$(C_2H_2)_n$ COMPLEXES: EVIDENCE FOR INTRACLUSTER REACTIONS

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Transition metal ion-acetylene complexes of the form M^+-$(C_2H_2)_n$ and M^+-$(C_2H_2)_n$RG (M=Ni, Co; RG=Ne, Ar) are produced by laser vaporization in a pulsed nozzle source. They are mass-selected and excited by an IR OPO laser in a reflectron time-of-flight mass spectrometer. Photodissociation occurs by the elimination of intact acetylene molecules in the pure complexes, while the mixed clusters fragment by the loss of the rare gas atom. Monitoring the fragment yield versus wavelength produces the IR photodissociation spectra for these complexes. Vibrational bands in the 2900-3500 cm^{-1} occur to the red of the C-H stretches in free acetylene, consistent with metal-π bonding. Experimental data are compared to the predictions of density functional theory and structures are proposed for the smaller complexes (n=1-3). Additional red-shifted bands observed in the larger complexes are attributed to π-bonded cyclobutadiene formed from an intracluster reaction of two acetylenes.