IR SPECTROSCOPY Of M^+(ACETONE) COMPLEXES (M = Mg, Al, Ca): CATION-CARBONYL BINDING INTERACTIONS

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M^+(acetone) ion-molecule complexes (M = Mg, Al, Ca) are produced in a pulsed molecular beam by laser vaporization and studied with infrared photodissociation spectroscopy in the carbonyl stretch region. All of the spectra exhibit carbonyl stretches that are shifted significantly to lower frequencies than the free-molecule value, consistent with metal cation binding on the oxygen of the carbonyl. Density functional theory is employed to elucidate the shifts and patterns in these spectra. Doublet features are measured for the carbonyl region of Mg^+ and Ca^+ complexes, and these are assigned to Fermi resonances between the symmetric carbonyl stretch and the overtone of the symmetric carbon stretch. The carbonyl stretch red shift is greater for Al^+ than it is for the Mg^+ and Ca^+ complexes. This is attributed to the smaller size of the closed-shell Al^+, which enhances its ability to polarize the carbonyl electrons. Density functional theory correctly predicts the direction of the carbonyl stretch shift and the relative trend for the three metals.