INFRARED RESONANCE ENHANCED PHOTODISSOCIATION SPECTROSCOPY OF $Al^+(CO_2)_n$ AND $Al^+(CO_2)_nAr$ CLUSTERS

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Weakly bound complexes, $Al^+(CO_2)_n$ and $Al^+(CO_2)_nAr$, are produced by laser vaporization in a pulsed supersonic expansion. The clusters are mass-selected and studied by laser photodissociation spectroscopy in a reflectron time-of-flight mass spectrometer. The excitation laser is an OPO/OPA system that produces tunable infrared light near the asymmetric stretch (ν_3) of CO_2. Dissociation is more efficient on resonance, thus monitoring the fragmentation channel as a function of wavelength produces the IR absorption spectrum of the complex of interest. $Al^+(CO_2)_n$ clusters fragment by the loss of CO_2, while $Al^+(CO_2)_nAr$ clusters fragment by the loss of argon. The spectra show a blue-shift of the asymmetric CO_2 stretch which decreases as the size of the cluster increases. $Al^+(CO_2)_nAr$ transitions appear at the same frequencies as the pure CO_2 complexes but with significantly narrower linewidths. The observed infrared bands are compared to theory and specific structures are proposed for the smaller clusters, while solvent effects are observed in the larger clusters. Photodissociation caused by exciting the combination band provides information on the symmetric stretch which is otherwise IR inactive.