PHOTODISSOCIATION SPECTROSCOPY OF THE Ca^+-Ar_2 COMPLEX

J. E. REDDIC, J. VELASQUEZ, K. N. KIRSCHNER, M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602, USA.*

The weakly bound complex Ca^+-Ar_2 produced by laser ablation in a pulsed nozzle cluster is studied with mass-selected resonance enhanced photodissociation spectroscopy. A short doublet progression.(ω_e' = 82.07 cm^{-1}) to the blue of the $^2D \leftarrow ^2S$ atomic transition is assigned to the $D^2\Pi_r \leftarrow X^2\Sigma^+$ system. Spin-orbit splitting (A = 19.67 cm^{-1}) of the doublets suggests a linear geometry. A peak observed at 13956 cm^{-1} is assigned the $C^2\Sigma_r \leftarrow X^2\Sigma^+$ system. No systems are detected from the derived atomic transition $^2P \leftarrow ^2S$ in this complex. Additionally, complexes with more than two rare-gas ligands were probed and showed no sharp structure. MØller-Plesset second-order perturbation theory was used to determine the Ca^+-Ar_2 bond distances (r_e) of 3.064 $\AA$ and a dissociation energy (D_e) for atomization of 4.864 kcal/mol (Ca^+-$Ar_2 \rightarrow Ca^+ + 2Ar$). This calculation included the correlation of the valence and core electron using a generated basis set for calcium and the aug-ccVQZ basis set for the argon atoms, resulting in a total of 271 basis functions for the calculations.