PHOTODISSOCIATION SPECTROSCOPY OF THE Ca⁺-Ar₂ COMPLEX

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The weakly bound complex Ca⁺-Ar₂ produced by laser ablation in a pulsed nozzle cluster is studied with mass-selected resonance enhanced photodissociation spectroscopy. A short doublet progression (ω' = 82.07 cm⁻¹) to the blue of the ²D ← ²S atomic transition is assigned to the D²Πᵣ ← X²Σ⁺ 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 C²Σᵣ ← X²Σ⁺ system. No systems are detected from the derived atomic transition ²P ← ²S in this complex. Additionally, complexes with more than two rare-gas ligands were probed and showed no sharp structure. Möller-Plesset second-order perturbation theory was used to determine the Ca⁺-Ar₂ bond distances (rₑ) of 3.064 Å and a dissociation energy (Dₑ) for atomization of 4.864 kcal/mol (Ca⁺-Ar₂ → 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.