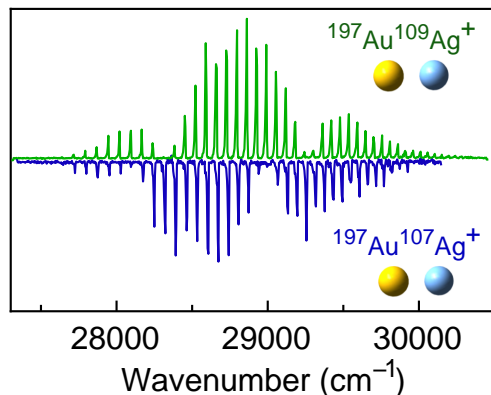


RESONANCE ENHANCED PHOTODISSOCIATION SPECTROSCOPY OF AuAg⁺ REVEALS ISOTOPIC DEPENDANCE ON PHOTODISSOCIATION

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Bimetallic materials comprised of gold and silver have useful optical and electronic properties, which are complicated by quantum mechanical, relativistic, and isotopic effects. To provide a bottom-up perspective on these larger systems, the smallest monocation comprised of gold and silver—diatomic AuAg⁺—is spectroscopically probed using resonance enhanced photodissociation (REPD). The ¹⁹⁷Au¹⁰⁷Ag⁺ and ¹⁹⁷Au¹⁰⁹Ag⁺ isotopologues are confined in a cryogenically cooled (ca. 5 K) quadrupole ion trap and are exposed to tunable light while detecting Au⁺ photofragment ions using a time-of-flight mass spectrometer. Electronic spectra in the UV exhibit a transition from the X²Σ_{1/2}⁺ ground state to an excited state that is yet to be assigned. Vibronic progressions for this transition extend over more than 30 quanta for both isotopologues, but with striking differences in band intensities (see Figure). This difference in photodissociation yield between the two isotopologues arises because the vibronic energies and associated wavefunctions depend on

the reduced mass, leading to a difference in the coupling of the excited state levels and the repulsive electronic state that leads to dissociation. The observed photodissociation intensities for ¹⁹⁷Au¹⁰⁷Ag⁺ and ¹⁹⁷Au¹⁰⁹Ag⁺ are successfully modelled by calculating respective vibronic energies and wavefunctions of their bound and dissociative electronic states.