THE IONIZATION ENERGY OF Be₂. AND SPECTROSCOPIC CHARACTERIZATION OF THE (1)³Σ⁺, (2)³Πₑ, AND (3)³Πₑ STATES

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Beryllium dimer is formed by pulsed laser ablation of Be metal in the presence of helium carrier gas, followed by free jet expansion into vacuum. Its low-lying electronic states are investigated by laser induced fluorescence (LIF) and resonance enhanced multiphoton ionization (REMPI) techniques. Differences between the 1+1 REMPI and LIF spectra of the $B^1Σ_u^+(v) ← X^1Σ_g^+(v = 0)$ bands observed in the ionization continuum are due to resonances with Rydberg series correlating with vibrations of the ion. Photoionization efficiency (PIE) measurements yield an accurate value of 7.418(5) eV for the ionization energy (IE), in good agreement with the results from multi-reference configuration interaction (MRCI) theory. By fitting the Rydberg progressions and making use of this IE, the Be²⁺ vibrational frequency and binding energy of 498(20) and 16076(40) cm⁻¹, respectively, are determined, again in agreement with MRCI calculations. Rotationally resolved spectra of the (2)³Πₑ ← (1)³Σ⁺ and (3)³Πₑ ← (1)³Σ⁺ Be₂ transitions provide further experimental benchmarks for ab initio calculations. PIE measurements also yield an accurate value for the (1)³Σ⁺ ← X¹Σ⁺ interval. Rotationally resolved spectra for the A¹Πₑ(v = 15 – 18) ← X¹Σ⁺(v = 0) transitions in Be₂ have also been observed allowing for a more precise determination of the A¹Πₑ potential energy surface. New MRCI calculations are described in order to refine the theoretical IE as well as to quantify the role of spin-orbit coupling in the (2)³Πₑ and (3)³Πₑ states.