

THRESHOLD IONIZATION SPECTROSCOPY AND SPIN-ORBIT COUPLING OF LnNH (Ln = La and Ce) FORMED BY Ln REACTIONS WITH AMMONIA

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Ln (Ln = La and Ce) atom reactions with ammonia are carried out in a pulsed laser vaporization supersonic molecular beam source, and metal-containing species are observed with time-of-flight mass spectrometry and characterized by mass-analyzed threshold ionization (MATI) spectroscopy. The MATI spectrum of LaNH exhibits a single vibronic band system with a strong origin band and two weak vibronic progressions, whereas the spectrum of CeNH shows two band systems separated by 80 cm^{-1} , with each being similar to the LaNH spectrum. By comparing with theoretical calculations, both LaNH and CeNH are identified as linear molecules with symmetry, and the two vibronic progressions are attributed to excitations of Ln-N stretching and LnNH bending modes in the ions. The additional band system observed for CeNH is due to spin-orbit splitting from interactions of a pair of nearly degenerate triplets and a pair of nearly degenerate singlets. The ground valence electron configurations of LaNH and CeNH are La $6s^1$ and Ce $4f^1 6s^1$, and ionization of each species removes the Ln $6s^1$ electron. The remaining two electrons that are associated with the isolated Ln atoms or ions are spin paired in a molecular orbital that is a bonding combination between a Ln 5d orbital and a N π^* antibonding orbital.