

MATI SPECTROSCOPY OF $\text{Ln}(\text{OH})_2$ ($\text{Ln} = \text{La}$ AND Ce) FORMED BY O-H BOND ACTIVATION OF WATER.

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Lanthanide ($\text{Ln} = \text{La}$ and Ce) atom reactions with water are carried out in a pulsed-laser ablation molecular beam source and characterized by mass-analyzed threshold ionization (MATI) spectroscopy and quantum chemical calculations. Both reactions yield $\text{Ln}(\text{OH})_2$ as the main product through a hydrogen atom elimination of each water molecule. The MATI spectra of $\text{Ln}(\text{OH})_2$ are dominated by the origin band and metal-ligand symmetric stretching and bending vibronic progressions. Adiabatic ionization energies measured from the spectra are $40135(5) \text{ cm}^{-1}$ for $\text{La}(\text{OH})_2$ and $40756(5) \text{ cm}^{-1}$ for the $\text{Ce}(\text{OH})_2$. The molecular symmetry of $\text{Ln}(\text{OH})_2$ is C_{2v} , and the observed transitions are $^1\text{A}_1 - ^2\text{A}_1$ for $\text{La}(\text{OH})_2$ and $^2\text{B}_1 - ^3\text{B}_1$ for $\text{Ce}(\text{OH})_2$. The ground valence electron configurations of $\text{La}(\text{OH})_2$ and $\text{Ce}(\text{OH})_2$ are $\text{La } 6s^1$ and $\text{Ce } 4f^1 6s^1$, respectively. Ionization of each species removes a Ln 6s-based electron, and the resultant ion also has C_{2v} symmetry. The spectrum of $\text{Ce}(\text{OH})_2$ has a broader linewidth than that of $\text{La}(\text{OH})_2$, which is attributed to the unresolved spin-orbit levels by comparing with relativistic quantum calculations at the level of spin-orbit multi-reference quasi-degenerated perturbation theory. The metal-mediated hydrogen elimination of water is predicted to be thermodynamically and kinetically favorable by the density functional theory calculations.