PROBING SPIN-ORBIT COUPLING OF ORGANOCERIUM RADICALS FORMED IN Ce ATOM REACTIONS WITH ALKYLAMINES.

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Ce atom reactions with alkyamines are carried out in a pulsed-laser ablation molecular beam source and characterized by mass-analyzed threshold ionization (MATI) spectroscopy. The MATI spectra of CeNR (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, and $\mathrm{C_3H_7}$) formed by Ce reactions with $\mathrm{H_2NR}$ exhibit two band systems, separated by 78, 74, and 72 $\mathrm{cm^{-1}}$, respectively. In contrast, the MATI spectrum of $\mathrm{CeNC_2H_5}$ formed in the Ce + $\mathrm{HN(CH_3)_2}$ reaction show two band systems with a much larger separation, 130 $\mathrm{cm^{-1}}$. These separations are attributed to the spin-orbit (SO) splitting from the Ce $4f^1$ electron. The different splittings between CeNR from the reactions of primary amines and $\mathrm{CeNC_2H_5}$ from the reaction of secondary amine are due to their different structures. The CeNR complexes from the primary amines have acyclic structures with Ce double bonding to the N atom, whereas $\mathrm{CeNC_2H_5}$ from the dimethylamine has a cyclic structure with Ce bonding to the N atom and one of the C atoms. The considerably smaller SO splittings in the CeNR species suggests that N coordination has a stronger quenching effect on the SO coupling of the Ce 4f electron than the C coordination.