MASS-ANALYZED THRESHOLD IONIZATION OF $M_2O_2$ ( M = Ce and Pr)

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$M_2O_2$ ( M = Ce and Pr) is produced in a pulsed laser-vaporization metal-cluster source and studied by mass-analyzed threshold ionization (MATI) spectroscopy. From the MATI spectra, the adiabatic ionization energy is determined to be 37300(5) $cm^{-1}$ for $Ce_2O_2$, and 37885 (5) $cm^{-1}$ for $Pr_2O_2$. Like group 3 transition metal $M_2O_2$ (M=Sc, Y, and La) clusters we reported previously, these lanthanide clusters have a $D_{2h}$ planer structure and the vibrational modes observed are from the in-plane motions. However, the ground and other low-energy electronic states of the lanthanide oxides have a much higher electron spin multiplicity due to the existence of 4f electrons in the Ce and Pr atoms. The 4f electron of Ce atom has significantly lower energies than the 5d or 6s electrons and remain uncoupled in $Ce_2O_2$. On the other hand, the energy differences between the 4f and 5d/6s electrons of Pr atom are relatively small, and a 4f $\rightarrow$ 5d electron promotion is required in the formation of $Pr_2O_2$. The electronic transitions responsible for the observed MATI spectra are tentatively determined to be $^4B_{1u} \leftarrow {}^5A_g$ for $Ce_2O_2$ and $^6B_{1u} \leftarrow {}^7B_{2g}$ and $^6B_{1u} \leftarrow {}^5B_{1u}$ for $Pr_2O_2$.