ELECTRONIC STATES OF Nd-BENZENE AND Nd-NAPHTHALENE: HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY AND AB INITIO CALCULATIONS

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Neodymium complexes with benzene and naphthalene were synthesized in a laser-ablation supersonic molecular beam source. High-resolution electron spectra of these complexes were obtained using pulsed-field ionization zero electron kinetic energy (ZEKE) photoelectron spectroscopy. B3LYP and MP2 methods, with effective core potential basis sets for Nd and 6-311+G(d,p) for C and H, were employed to predict low-lying electronic states and vibrational frequencies of the neutral and ionized complexes. The adiabatic ionization energies were measured to be 38081 (5) cm^{-1} for Nd-benzene and 37815 (5) cm^{-1} for Nd-naphthalene. The observed frequencies 288, 605 and 831 cm^{-1} in the Nd-benzene ZEKE spectrum were assigned to metal-ligand stretching, C-H out-of-plane bending and ring breathing modes, respectively. To confirm the C-H bending mode, the ZEKE spectrum of the deuterated species was recorded, and the C-D bending frequency was measured to be 502 cm^{-1}. For Nd-naphthalene, the vibrational modes measured in the ZEKE spectrum were attributed to inter-ring bending (80 cm^{-1}), ring twist (105 cm^{-1}), metal-ring stretch (271 cm^{-1}), metal-ring stretch (286 cm^{-1}) and inter-ring waving (394 cm^{-1}). By comparing the spectroscopic measurements and theoretical calculations, the ground electronic states of the neutral and ionized forms of these two complexes appear to be the septet and sextet, respectively. The accuracies of the calculated ionization energies and vibrational frequencies are discussed for these heavy lanthanide complexes.