THE ROTATIONAL SPECTRA OF HAFNOCENE DIMETHYL AND ZIRCONOCENE DIMETHYL: A TWO-TOP INTERNAL ROTOR PROBLEM

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The rotational spectra of the hafnocene dimethyl and zirconocen dimethyl complexes have been obtained using a pulsed molecular beam Fourier transform microwave spectrometer. Hafnocene dimethyl and zirconocene dimethyl are bent metallocene complexes with two nearly equivalent methyl rotors directly coordinated to the metal center. The observed A rotational constant of these two complexes are nearly twice as large as the B and C rotational constants. Thus, hafnocene dimethyl and zirconocene dimethyl are near prolate asymmetric top molecules. We observed b-dipole type spectra with R and Q branch allowed transitions. Precise rotational constants have been determined for both hafnium and zirconium isotopomers and were used in the fitting program to determine the molecular structure of these complexes. Somewhat large quartic distortion constants in the order of 10-100 kHz were observed for these complexes, suggesting possible perturbations to the overall rotation energy by the internal rotation of methyl ligands. Broad lines and very narrow splittings were observed in some transitions and, in most cases, not well resolved. To gain further understanding about the effect of methyl rotors on the rotational energy spectrum, the internal rotational motions of two methyl ligands were analyzed using density functional theory calculations. Additional spectral simulations were carried out using an XIAM internal rotation program.