RYDBERG TRANSITIONS ORIGINATING AT METAL-LOCALIZED ORBITALS IN LARGE POLYATOMIC MOLECULES: A GAS-PHASE SPECTROSCOPIC STUDY OF TRANSITION- METAL SANDWICH COMPLEXES

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The transition-metal sandwich compounds with an occupied totally symmetric valence molecular orbital (MO) derived from the metal d_z2 appear to represent the first example of polyatomic molecules revealing in the photoabsorption spectra well-resolved Rydberg transitions from a metal-localized MO. The gas-phase UV absorption spectra of (η^6-Arene)$_2$M (M = V, Cr, Mo, W), (η^5-C_5H_5)$_2$M (M = V, Fe, Ru, Os), (η^6-Arene)(η^5-C_5H_5)Mn, (η^7-C_7H_7)(η^5-C_5H_5)M (M = V, Nb, Cr, Mo, W) show sharp bands arising from the transitions originating at the metal d_z2 orbital and terminating at Rydberg ns, np and nd levels. Due to the low d_z2 ionization energies, even higher Rydberg excitations in these compounds lie, as a rule, below 50000 cm^{-1} making it easy to investigate them using standard UV-visible spectrometers. Rydberg features disappear on going to the condensed media resulting in a dramatic difference between the gas-phase and solution-phase spectra of sandwich complexes. All Rydberg bands observed have been assigned on the basis of corresponding term values and effective quantum numbers. These parameters appear to change very little on going from one sandwich to another. For bisarene and mixed sandwiches, many-membered Rydberg np series converging on the d_z2 ionization limit have been revealed and the corresponding ionization potentials have been calculated with high accuracy using the Rydberg formula. Clear examples of molecular symmetry influence on the Rydberg structure, Rydberg/valence mixing and vibronic coupling in Rydberg states will be presented.