EXPERIMENTAL AND THEORETICAL APPROACHES TO HIGH-RESOLUTION PHOTOIONIZATION SPECTROSCOPY OF METALLOCENES

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Metallocenes form one of the most important and intriguing classes of organometallics. They are relevant to various fields of practical use in synthetic chemistry, biomedicine, molecular electronics and materials science. Many unique properties of these metal complexes arise from their ability to produce stable or reactive molecular ions. The details of ionization processes in sandwich molecules are, therefore, crucial for understanding their reactivity. Unprecedented accuracy in determining ionization parameters of polyatomic molecules is provided by ZEKE and MATI spectroscopies. However, it is a great challenge to employ these methods for studying metallocenes and related compounds because they are air-sensitive, low-volatile and thermally unstable. Until recently, the only metallocene studied with the MATI technique was cobaltocene[1]. In this work, we report the first MATI spectra of its methylated derivatives, methylcobaltocene $(C_5H_4Me)(C_5H_5)Co$ and dimethylcobaltocene $(C_5H_4Me)_2Co$. The spectra show rich vibronic structures, the latter complex revealing MATI signals arising from individual rotational isomers. This is the first example of metallocene rotamers detected in the gas phase by photoionization spectroscopy. The MATI signals were modelled by DFT calculations that reproduced nicely the experimental vibronic structures. Similar DFT approaches were used to predict the MATI spectra of ferrocene corresponding to the detachment of an electron from the occupied metal d orbitals. Based on the wavefunctions produced by DFT, analysis of electron density transformations accompanying ionization of cobaltocene and its methylated derivatives was carried out. The results were compared with those obtained earlier for decamethylmanganocene[2].

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[1] doi:10.1002/anie.201205164, S.Y. Ketkov, H.L.Selzle, Threshold Ionization of Cobaltocene: The Metallocene molecule revealing zero kinetic energy states, Angew. Chem. Int. Ed. 51, 11527-11530 (2012).

[2] doi:10.3390/molecules27196226, S. Ketkov, S.-Y. Tzeng, E. Rychagova, W.-B. Tzeng, Ionization of Decamethylmanganocene: Insights from the DFT-Assisted Laser Spectroscopy, Molecules 27, 6226 (2022).

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