

High resolution laser threshold ionization spectroscopy of jet-cooled metallocenes and related organometallics

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Since the discovery of ferrocene over 60 years ago metallocenes and other sandwich complexes have been attracting chemists as one of the most intriguing classes of organometallics. Numerous theoretical and experimental investigations of electronic structures of these prototypical systems form a basis for understanding the nature and fundamental properties of the metal-ligand delocalized chemical bonds. On the other hand, intense chemical interest has been focused on these compounds during last years because of their relevance to organic synthesis, catalysis, bioorganometallic chemistry and material science. New possibilities for studying electronic structures of sandwich systems appeared as methods of high resolution laser ionization spectroscopy have been developed. However, employment of resonance enhanced multiphoton ionization (REMPI), zero kinetic energy (ZEKE) and mass-analyzed threshold ionization (MATI) techniques to study sandwich compounds has been restricted for a long time because of extremely fast photodissociation of excited-state metal complexes. As a result, the REMPI spectra of metallocenes obtained earlier with nanosecond laser pulses consisted solely of the peaks corresponding to the states of bare metal atoms [1]. Only during the last decade we found conditions for multi-photon nanosecond ionization of sandwich molecules [2-4]. The REMPI and MATI spectra of $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$ and its substituted derivatives appeared to give unique information on the excited-state properties, ionization energies and vibrational frequencies of free sandwich molecules [5, 6]. In this presentation we summarize new results concerning the investigation of metallocene, bisarene and mixed sandwich systems with the MATI method supported by DFT calculations. The computed electronic energies and vibrational frequencies serve as a basis to interpret the spectroscopic results and to predict properties of metal complexes. On the other hand, supersonic cooling of organometallic molecules and employment of monochromatic laser radiation make it possible to achieve unique accuracy in the experimental determination of ionization energies and vibrational frequencies. As a result, new precise data on the spectroscopic parameters and electronic structures of metal sandwich derivatives are obtained. For instance, the MATI investigation of cobaltocene [7] demonstrates the first example of the delayed pulsed-field ionization of a stable metallocene molecule while the study of jet-cooled $(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)\text{Cr}$ reveals ZEKE states of a cycloheptatrienyl complex for the first time. The MATI spectrum of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ is indicative of a pseudo Jahn-Teller activity in the neutral molecule. The $(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)\text{Cr}$ MATI structure shows that the inter-ring distance remains practically unchanged on ionization, in contrast to that of isomeric $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$.

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