One-photon mass-analyzed threshold ionization spectroscopy of (cycloheptatrienyl)(cyclopentadienyl)chromium

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Transition metal sandwich complexes represent one of the most important classes of organometallics. The presence of two carbocyclic ligands in a sandwich molecule provides a unique type of a structural isomerism arising from the ring size variation. For example, for ferrocene, there are two unsymmetrical sandwich isomers, cyclobutadiene iron benzene complex $(\eta\text{-}C_6H_6)(\eta\text{-}C_4H_4)Fe$ and cycloheptatrienyl-cyclopropenyl derivative $(\eta\text{-}C_7H_7)(\eta\text{-}C_3H_3)Fe$. These mixed-carbocycle complexes are, however, unstable and they have not been synthesized so far. Only theoretical studies on their structures and properties were reported. On contrary, for the "isoelectronic" $(\eta\text{-}C_6H_6)_2M$ (M=Cr, Mo, W) sandwiches, the stable unsymmetrical cycloheptatrienyl-cyclopentadienyl isomers have been known for many years [1]. New possibilities to get precise experimental information on their electronic structures appear with the development of modern laser spectroscopy techniques adapted for studying organometallic systems. The zero kinetic energy (ZEKE) and mass-analyzed threshold ionization (MATI) spectroscopy provide unprecedented resolution in measuring ionization energies of neutrals and vibrational frequencies of gas-phase polyatomic ions. In this presentation we report the first one-photon MATI spectrum of a complex bearing the cycloheptatrienyl ligand, $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$, and compare the high-resolution ionization potential of the mixed sandwich and the MATI vibrational structure with those obtained earlier for bis(benzene)chromium [2-5] and other sandwich systems [6-8]. DFT calculations were used to explain differences in the spectroscopic parameters obtained for the two isomers. The ionization energy of $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$ appears to be (1153 ± 5) cm^{-1} or (0.1430 ± 0.0006) eV higher than that of $(\eta\text{-}C_6H_6)_2Cr$. This value coincides with the change of the B3PW91/TZVP energy (E+ZPE) difference between the mixed and symmetric sandwich on going from the neutrals to ions (3.3 kcal/mol or 0.143 eV). The vibrational structure of the $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$ MATI spectrum, in contrast to $(\eta\text{-}C_6H_6)_2Cr$ and other sandwich systems investigated, reveals no progression on the symmetric metal-ligand stretching mode. This is a consequence of a very small change of the equilibrium interligand distance in the $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$ molecule on ionization. The calculated $C5_{centroid}$ - $C7_{centroid}$ distance decreases by 0.008 Å on going from $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$ to $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr^+$, unlike the inter-ring distance in $(\eta\text{-}C_6H_6)_2Cr$ which increases by 0.039 Å. On the other hand, the MATI spectrum of $(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$ shows a vibrational component corresponding to the asymmetric metal-ring stretch which is forbidden for bisbenzene complexes and metallocenes.

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[1] M.L.H. Green, D.K.P. Ng, *Chem. Rev.* **1995**, *95*, 439 and the references cited therein.
[2] S. Yu. Ketkov, H. L. Selzle, E. W. Schlag, *Mol. Phys.* **2004**, *102*, 1749.
[3] K.-W. Choi, S. K. Kim, D.-S. Ahn and S. Lee, *J. Phys. Chem. A* **2004**, *108*, 11292.
[4] S.Yu. Ketkov, H.L. Selzle, E.W. Schlag, *Organometallics* **2006**, *25*, 1712.
[5] K.-W. Choi, S. Choi, S.J. Baek, S.K. Kim, *J. Chem. Phys.* **2007**, *126*, 034308.
[6] B.R. Sohnlein, Y. Lei, D.-S. Yang, *J. Chem. Phys.* **2007**, *127*, 114302.
[7] B.R. Sohnlein, D.-S. Yang, *J. Chem. Phys.* **2006**, *124*, 134305.
[8] D.–S. Yang, *J. Phys. Chem. Lett*. **2011**, *2*, 25.
[9] S. Yu. Ketkov, H. L. Selzle, *Angew. Chem. Int. Ed.* **2012**, *51*, 11527.