Sandwich Complexes

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Threshold Ionization of Cobaltocene: The Metallocene Molecule Revealing Zero Kinetic Energy States**

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Dedicated to Professor Gleb Abakumov on the occasion of his 75th birthday

Since the discovery of ferrocene 60 years ago,[1] metallocenes have represented 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. In contrast, intense chemical interest has been focused on these compounds during the last decade because of their relevance to organic synthesis, catalysis, bioorganometallic chemistry, and materials science.[2] Redox parameters appear to play a key role in tuning the chemical reactivity of cyclopentadienyl metal complexes and properties of the metallocene-based materials.[3] Precise information on ionization energies (IEs) of these sandwich compounds is, therefore, of fundamental importance in predicting their chemical behavior.

High-resolution IEs can be obtained with zero kinetic energy (ZEKE) and mass-analyzed threshold ionization (MATI) techniques[4] based on the laser excitation of jet-cooled molecules to high Rydberg levels (ZEKE states) and subsequent ionization by an electric pulse. Recently, fascinating insight into the electronic structures of transition-metal bis(arene) derivatives has been provided by ZEKE and MATI studies.[5] However, no successful attempts to measure the ZEKE or MATI spectra of metallocenes have been reported so far. Multiphoton excitation of [Cp_2Fe] and [Cp_2Ni] (Cp = η^5-cyclopentadienyl) gave no MATI signals, probably because of the instability of the corresponding ZEKE states.[5b] Herein we report the first example of a metallocene MATI spectrum. In this work, we studied cobaltocene which, like ferrocene, represents one of the key sandwich compounds. This complex attracts the attention of theoretical chemists[6] because of its degenerate ground electronic state, $^2E_1''$ in the D_{5h} point group (the [Cp_2Co] 19-electron configuration is …$[3d(e_2')]^2\,[3d(a_1')]^2\,[3d(e_1'')]^1$). The neutral molecule should, therefore, appropriately lower its symmetry as a result of the Jahn–Teller (JT) effect. This makes it especially interesting to obtain a high-resolution photoionization spectrum of cobaltocene. Moreover, ionization of the [Cp_2Co] molecule yields the 18-electron cation which is an isoelectronic analogue of the highly symmetric (D_{5h}) ferrocene. The surprisingly well-resolved MATI spectrum of [Cp_2Co] measured in this work demonstrates that the powerful MATI and ZEKE techniques can be efficiently used to investigate fine electronic effects in metallocene molecules.

Indeed, when conditions for the one-photon excitation of the cobaltocene ZEKE states in a supersonic jet were found in our experiments, the MATI spectrum having a rich vibronic structure was recorded (Figure 1). In contrast to the classical UV photoelectron spectrum[7] (PES) showing a single broad $3d(e_1'')$ ionization band with the full width at half-maximum (FWHM) of about 0.3 eV, the MATI spectrum of jet-cooled [Cp_2Co] reveals extremely narrow peaks (FWHM is 0.0025 eV in the low-energy region). These peaks correspond to the vibrational levels of the ground-state [Cp_2Co]$^+$.

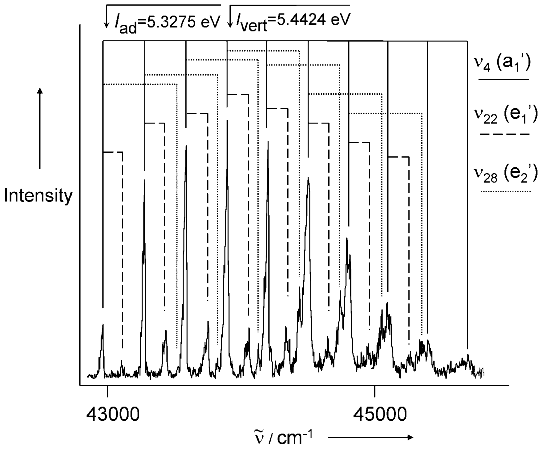

Figure 1. MATI spectrum of [Cp_2Co] and assignment of the key vibronic features.

The precise adiabatic and vertical IEs of cobaltocene can now be easily determined. The electron detachment from a sandwich molecule in the absence of an electric field is observed at the wavenumber corresponding to the edge of the blue wing of the MATI peak.[5f] The IEs found from the parameters of the lowest-energy and the strongest MATI signal are, respectively, $I_{ad.} = (5.3275 \pm 0.0006)$ eV and $I_{vert.} = (5.4424 \pm 0.0006)$ eV. The former value agrees well with $I_{ad.} = (5.24 \pm 0.08)$ eV, which was obtained on the basis of Fourier

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transform ion cyclotron resonance mass spectrometry[8] and the MATI $I_{\mathrm{vert.}}$ magnitude is in accord with that determined from the PES[7] (5.55 ± 0.1 eV). However, the ion cyclotron resonance and PES measurements[7,8] were carried out at elevated temperatures (ca. 350 K) whereas typical rotational and vibrational temperatures of large jet-cooled molecules in the MATI experiment are on the order of 10 and 100 K, respectively.[9] The high-resolution MATI spectrum obtained in this work provides, therefore, the most accurate and reliable values for the cobaltocene IEs.

Besides the adiabatic and vertical IEs of the neutral molecule, the vibrational frequencies of the gas-phase $[Cp_2Co]^+$ can be determined from the MATI experiment. To assign the MATI vibronic features, the $[Cp_2Co]^+$ vibrational frequencies were estimated by DFT calculations[10] at the BPW91/TZVP level of theory, which has demonstrated the best agreement with the experiment for the isoelectronic $[(\eta^6\text{-}C_6H_6)_2Cr]$ molecule.[11] The theoretical $I_{\mathrm{ad.}}$ value, found as a difference between the sums of the electronic and zero-point vibrational energies for the cation and neutral molecule (5.263 eV), agrees well with that obtained from the MATI spectrum. The calculated and experimental $[Cp_2Co]^+$ vibrational frequencies are very close (Table 1). The MATI spectrum (Figure 1) shows a long progression on the totally symmetric Co-Cp stretching mode ν_4 (the vibrational modes of $[Cp_2Co]^+$ are numbered according to the conventional scheme for metallocenes[6a]). The progression members are accompanied by the weaker peaks which correspond to the composite frequencies of the degenerate ν_{22} (e_1') and $\nu_{28}(e_2')$ modes excited together with the ν_4 vibration (Figure 1). Few weak features lying between the ν_{22} and ν_{28} peaks can be attributed to the CH out-of-plane bend $\nu_2(a_1')$. A complete interpretation of the cobaltocene MATI spectrum is given in the Supporting Information (Table S1).

Table 1: Calculated (BPW91/TZVP) and experimental (MATI) frequencies (cm^{-1}) of the $[Cp_2Co]^+$ vibrations responsible for the structure of the cobaltocene MATI spectrum.

Vibrational mode[a]	Vibration symmetry (D_{5h}/C_{2v})	$\nu_{\mathrm{calc.}}$	$\nu_{\mathrm{exptl.}}$
ν_2	a_1'/a_1	844	851
ν_4	a_1'/a_1	303	309
ν_{22}	e_1'/a_1+b_1	163	158
ν_{28}	e_2'/a_1+b_1	570	589

[a] See text for the vibration notations.

The totally symmetric metal–ligand stretching and CH bending modes are also revealed by the MATI and ZEKE spectra of the $[(\eta^6\text{-}C_6H_6)_2M]$ (M = Ti, V, Cr, Mo) complexes.[5d–f] In contrast to threshold ionization of the bis(benzene) derivatives studied, which involves a nonbonding d_{z^2} metal electron (M = Cr, Mo)[5d] or an electron from the bonding molecular orbital (MO) formed mainly by the metal d_{xy} and $d_{x^2-y^2}$ wavefunctions (M = Ti, V),[5f] the MATI spectrum of cobaltocene corresponds to ionization of the antibonding single-occupied MO derived from the metal $3d_{xz}$ and $3d_{yz}$ levels. Detachment of an electron from this MO strengthens the Co–Cp bond and decreases the Co–C average distance in the DFT-optimized geometry from 2.120 Å for neutral $[Cp_2Co]$ to 2.061 Å for the $[Cp_2Co]^+$ ion. The BPW91/TZVP ν_4 vibrational frequency increases correspondingly from 267 to 303 cm^{-1} upon ionization. The theoretical intensity distribution for the ν_4 progression in the $[Cp_2Co]$ MATI spectrum derived from Franck–Condon analysis[12] is in accord with the experimental data (Figure 2). This result confirms the suitability of the BPW91/TZVP DFT level of theory for the description of the cobaltocene potential energy surface shift upon ionization. The theoretical $0_0^0/4_0^1$ intensity ratio is 0.27. Therefore, if the origin were located below 5.3275 eV, the corresponding peak would be observed in the MATI spectrum since its intensity is well above the detection threshold. We found, however, no longer-wavelength MATI features so we assign the 5.3275 eV ionization as the origin.

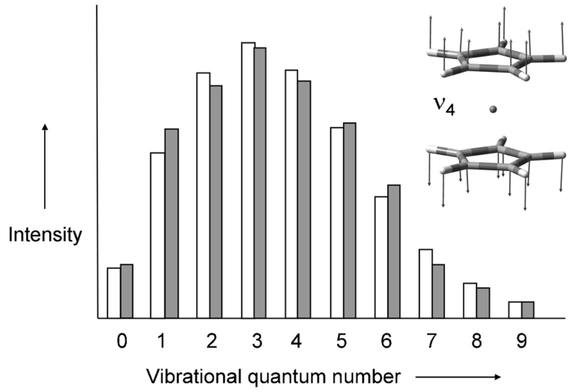

Figure 2. Theoretical (white) and experimental (gray) intensity distribution in the ν_4 progression of the $[Cp_2Co]$ MATI spectrum.

The appearance of the cationic $\nu_{28}(e_2')$ mode in the MATI spectrum is a result of the JT distortion of the neutral $[Cp_2Co]$ molecule. The 18-electron $[Cp_2Co]^+$ ion possesses a totally symmetric $^1A_1'$ (D_{5h}) ground electronic state excluding the JT activity. However, the vibronic interactions involving the e_2' modes in the neutral $[Cp_2Co]$ complex reduce symmetry from the D_{5h} to the C_{2v} point group.[6] As a result of this JT coupling, the degenerate $^2E_1''$ ground electronic state of cobaltocene splits into the $^2A_2$ and $^2B_2$ components. The e_2' (D_{5h}) modes transform into the a_1 and b_1 vibrations on the symmetry reduction, the former corresponding to the normal coordinate of the JT distortion and the latter allowing mixing of the $^2A_2$ and $^2B_2$ electronic states. The vibronic interactions lead, therefore, to a shift of the potential energy minimum along the a_1 components of the e_2' vibrations upon ionization of cobaltocene.

The DFT calculations[6c] predict the ring out-of-plane deformation ν_{28} to provide the main contribution to the JT stabilization energy and the largest distortion along the corresponding normal coordinate. That is why the ν_{28} mode (Figure 3) is expected to be revealed by the MATI spectrum of $[Cp_2Co]$. On the other hand, it is surprising to see that the MATI peaks corresponding to excitation of the $\nu_{22}(e_1')$ mode are even more intense than the ν_{28} vibronic components (Figure 1). The 22_0^1 ionization corresponds to the weak peak at 42104 cm^{-1} separated from the origin by 153 cm^{-1} (see Table S1 in the Supporting Information). An alternative

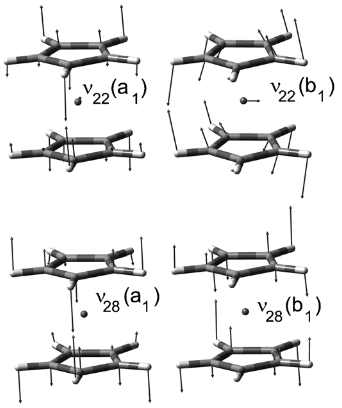

Figure 3. Relative atomic displacements (BPW91/TZVP) for the ν_{22} and ν_{28} modes in $[Cp_2Co]^+$. The vibration symmetry in the C_{2v} point group is indicated.

assignment of this feature to ionization of a lower-lying spin-orbit component of the $[Cp_2Co]$ ground state[13] can be ruled out because of its low relative intensity (Figure 1).

On the $D_{5h} \rightarrow C_{2v}$ symmetry reduction of the $[Cp_2Co]$ molecule, the $\nu_{22}(e_1')$ degenerate mode transforms into the a_1 and b_1 components (Figure 3). The equilibrium geometry shift along the totally symmetric ν_{22} component upon ionization of cobaltocene could be responsible for appearance of the corresponding peaks in our MATI spectrum. However, the DFT calculations[6c] demonstrate that the ν_{22} contribution to the JT distortion of $[Cp_2Co]$ is much less than that of ν_{28} (0.04 % versus 64.9 %, respectively). The ν_{22} peaks (Figure 1) cannot therefore arise from the totally symmetric component of this vibration. In contrast, the $\nu_{22}(b_1)$ mode allows mixing of the closely lying $^2A_2$ and $^2B_2$ cobaltocene electronic states. The strong pseudo JT (PJT) effect[14] corresponding to this interstate vibronic coupling leads to an additional shift of the $[Cp_2Co]$ potential energy minimum along the $\nu_{22}(b_1)$ coordinate. The MATI spectrum measured in this work reveals, therefore, that vibronic interactions in the cobaltocene molecule are more complicated than those described by the JT effect only. The molecular dynamics arising from the ν_{22} PJT activity is especially interesting since, in contrast to the ν_{28} mode, this vibration involves the metal atom (Figure 3).

In conclusion, we have demonstrated that MATI spectroscopy combined with DFT calculations can be applied productively as a powerful tool for studying the electronic structures of metallocenes. Cobaltocene represents the first cyclopentadienyl sandwich complex revealing ZEKE states. As a result of the extremely high resolution, the MATI technique provides precise values of adiabatic and vertical $[Cp_2Co]$ ionization energies as well as vibrational frequencies of the free $[Cp_2Co]^+$ ion. Both JT and PJT effects in the neutral cobaltocene molecule appear to be responsible for the rich vibronic structure observed in the MATI spectrum.

Experimental Section

All manipulations with cobaltocene were carried out under a nitrogen atmosphere. The MATI spectrometer as well as the details of the measurement procedure were described elsewhere.[5i,15] The sample of $[Cp_2Co]$ at 140°C, seeded in the Ar carrier gas at 1.4 bar, was expanded through a heated pulsed nozzle and the molecular beam was selected by two skimmers into the vacuum ionization chamber. The ions produced on irradiation of the jet-cooled molecular beam with nanosecond laser pulses were analyzed with a reflectron time-of-flight mass spectrometer. To record the one-photon photoionization and MATI spectra of cobaltocene, the peak corresponding to $^{12}C_{10}{}^{1}H_{10}{}^{59}Co^+$ (m/z 189.01) in the mass spectrum was selected when scanning the laser frequency.

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