Ionization Spectroscopy

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Direct Detection of Individual Bis(arene) Rotational Isomers in the Gas Phase by Mass-Analyzed Threshold Ionization Spectroscopy**

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Similar to metallocenes, transition-metal bis(arene) complexes play a key role in organometallic chemistry. Basic ideas on the electronic structures of metal π complexes arise from computational and experimental studies of these prototypical systems.[1] Metal arene derivatives are also an area of intense chemical interest because of their relevance for organic synthesis,[2] catalytic processes,[3] and preparation of metal-containing polymers.[4] Recently, fascinating insight into the bonding situation of bis(benzene) complexes has been provided by laser spectroscopic techniques.[5] Unique, precise information concerning ionization energies (IEs), excited-state properties, and vibrational frequencies of free (η^6-$C_6H_6)_2Cr$ molecules was obtained by resonance-enhanced multiphoton ionization (REMPI),[5a] zero electron kinetic energy (ZEKE),[5b] and mass-analyzed threshold ionization (MATI)[5c–e] methods. Substitution of hydrogen atoms in the benzene rings with various functional groups changes strongly the reactivity of sandwich systems, the properties of substituted molecules being dependent not only on the nature of the substituent but also on the conformational behavior. Here, we report first results indicating that MATI spectroscopy, which provides high-resolution IEs of neutral molecules and vibrational frequencies of gas-phase cations, may represent a powerful technique for studying substituent effects in bis(arene) compounds and the properties of distinct rotational sandwich isomers.

Methylated derivatives of bis(η^6-benzene)chromium bearing methyl (Me) groups in one and two benzene rings are useful model systems for understanding the conformational behavior determined by weak steric interactions in sandwich molecules. Bis(η^6-toluene)chromium (**1**) represents a simple example of a disubstituted complex showing conformational dynamics. DFT calculations[6] predict four stable rotational isomers of **1** with eclipsed benzene rings and relative Me-group orientation dihedral angle ϕ equal to 0, 60, 120, and 180° (Figure 1). We label these conformations **1_0**, **1_60**, **1_120**, and **1_180**, respectively. For the $\mathbf{1}^+$ ions in crystals, the ϕ values close to 0, 60, 160, and 180° were determined by X-ray diffraction analysis,[7] the $\mathbf{1}^+$ conformational behavior being dependent on the interactions with the counterions. However, no experimental evidence of distinct, neutral conformers of **1** has previously been obtained. Moreover, no structural isomers of other bis(arene) complexes have been observed in the gas phase so far. Gas-phase rotational isomers have been recently found[8] for a few ferrocene derivatives with microwave spectroscopy in a supersonic jet.

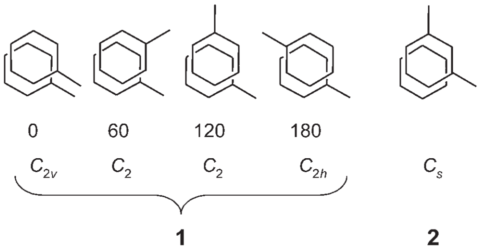

Figure 1. Stable geometries of compounds **1** and **2**. The dihedral angles between the C_{ring}–C_{Me} bond directions (ϕ) for the conformers of **1** and the symmetry point groups are given.

The photoionization and MATI spectra of jet-cooled **1** measured for the first time in this work reveal clearly the presence of the structural isomers in the gas phase. The photoionization curve shows two steps in the increase of the ion signal. Correspondingly, two intense MATI peaks at (42723 ± 5) and (42786 ± 5) cm^{-1} are observed (Figure 2).

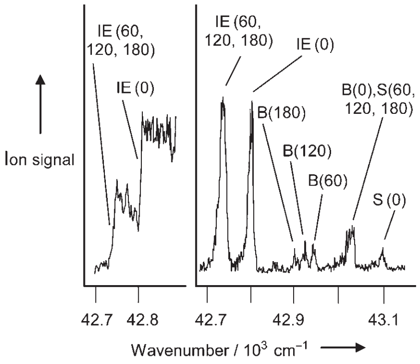

Figure 2. One-photon ionization (left) and one-photon MATI (right) spectra of jet-cooled **1**. The signals arising from the distinct rotational isomers are indicated by the IE or vibration notation and the ϕ value (see text).

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The "classical" gas-phase UV photoelectron[9] and absorption spectroscopies[10] at elevated temperatures provide much less accurate IE values for **1** ((42800 ± 100) and (42680 ± 60) cm^{-1}, respectively), and the isomers are indistinguishable.

To assign the MATI peaks, the IEs of the four conformers of **1** were estimated by DFT calculations[11] at the BPW91/TZVP level of theory, which gave the best agreement with experiment for the IE and vibrational frequencies of [(η^6-C_6H_6)$_2$Cr].[12] The calculated IEs are 42572, 42526, 42504, and 42499 cm^{-1} for **1_0**, **1_60**, **1_120**, and **1_180**, respectively.[13] The IEs of the **1_60**, **1_120**, and **1_180** isomers with weak steric interactions between the Me groups are very similar, the average value being 42510 cm^{-1}. The calculated IE of **1_0**, in which a short H(Me)···H(Me) interligand contact (2.58 Å) and a 3° tilt of the carbocycle planes in the optimized BPW91/TZVP structure are indicative of a repulsion between the Me substituents, is 62 cm^{-1} higher than the averaged IE of the other conformers. The IE difference is practically equal to the observed MATI peak separation (63 cm^{-1}). This finding suggests that the **1_60**, **1_120**, and **1_180** species contribute to the peak at 42723 cm^{-1}, whereas the 42786 cm^{-1} feature arises from the **1_0** conformer. Indeed, the long-wavelength peak is noticeably broader (Figure 2). Assuming similar ionization cross sections for the **1** structural isomers, one should expect that the corresponding MATI peak areas correspond to the relative abundance of the conformers. A further confirmation of our assignment comes from analysis of the spectra of (η^6-*m*-xylene)(η^6-benzene)chromium (**2**), which was synthesized by co-condensation of a mixture of benzene and *m*-xylene vapors with chromium atoms at liquid-nitrogen temperature.

Compound **2** bears two Me groups like complex **1**, but the mutual orientation of the substituents in **2** is fixed and there are no rotational isomers. This makes **2** a convenient model system for comparison with **1**. The most symmetric stable configuration of **2** with eclipsed benzene rings corresponds to the C_s point group (Figure 1). The shortest H(Me)···H(Me) distance in **2** (4.93 Å from our BPW91/TZVP calculation)[11] suggests that there is no steric interaction between the two substituents. One can expect, therefore, that the IE of **2** will be close to those of the **1_60**, **1_120**, and **1_180** species. The calculated IE of **2** is 42524 cm^{-1}, which is in excellent agreement with this prediction. In contrast to **1**, the photoionization curve of **2** reveals only one step and the MATI spectrum of **2** shows only one intense peak at (42726 ± 5) cm^{-1}, which corresponds to the IE (Figure 3). This MATI peak position coincides, within experimental error, with that of the long-wavelength peak in the MATI spectrum of **1**. Therefore, the IE values of **2** found from the MATI study and DFT calculations support strongly the assignment for **1** given above.

Besides high-resolution IE values, MATI spectra can provide precise information on cationic vibrational frequencies.[5c–e,14] Analysis of vibrational structures in the MATI spectra of **1** and **2** appears to give unambiguous evidence of the signals arising from distinct rotational isomers of the toluene complex. To interpret the vibrational features, we calculated the BPW91/TZVP frequencies of the 1^+ and 2^+ ion vibrations. The peak positions in the MATI spectra of **1** and **2** and the computed vibrational wavenumbers, $\tilde{\nu}_{\text{vibr.}}^{\text{calcd}}$, are given in Table 1. The spectrum of **2** (Figure 3) reveals weak peaks at (42908 ± 5) and (43009 ± 5) cm^{-1} arising from the vibrational states of the 2^+ cation. The peak at 43009 cm^{-1} is separated by 283 cm^{-1} from the IE. This shift corresponds to the frequency of a totally symmetric mode S, which involves the metal–ligand stretch and C_{ring}–C_{Me} out-of-plane bend ($\tilde{\nu}_{\text{vibr.}}^{\text{calcd}} = 278$ cm^{-1}). The corresponding peak is also revealed by the MATI spectra of [(η^6-C_6H_6)$_2$Cr].[5c–e] The feature at 42908 cm^{-1} (the separation from the IE is 182 cm^{-1}) is associated with a totally symmetric vibration B, which represents the ring tilt with the C_{ring}–C_{Me} out-of-plane bend and the Me group torsion ($\tilde{\nu}_{\text{vibr.}}^{\text{calcd}} = 180$ cm^{-1}).

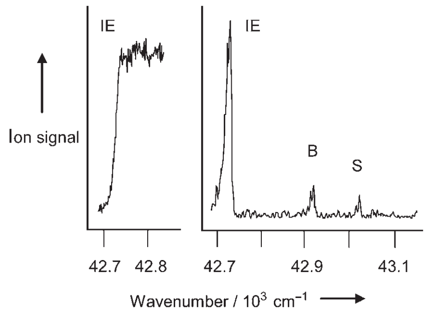

Figure 3. One-photon ionization (left) and one-photon MATI (right) spectra of jet-cooled **2**. The signal assignment is given using the vibration notation (see text).

Table 1: Positions $\tilde{\nu}$ [cm^{-1}] of the peaks in the MATI spectra of **1** and **2** (the individual rotational isomers of **1** are given), separations from the ionization threshold $\Delta\tilde{\nu}$ [cm^{-1}], calculated (BPW91/TZVP) vibrational wavenumbers $\tilde{\nu}_{\text{vibr.}}^{\text{calcd.}}$ [cm^{-1}] of the 1^+ and 2^+ ions, and the MATI peak assignment.

Compound	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}_{\text{vibr.}}^{\text{calcd}}$	Assignment[a]
1_0	42786	0		IE
	43014	228	217	B
	43081	295	289	S
1_60	42723	0		IE
	42923	200	201	B
	43014	291	277	S
1_120	42723	0		IE
	42907	184	172	B
	43014	291	270	S
1_180	42723	0		IE
	42882	159	155	B
	43014	291	272	S
2	42726	0		IE
	42908	182	180	B
	43009	283	278	S

[a] See text for the vibration notations.

On going from **2** to **1** the vibrational MATI structure becomes much more complicated (Figure 2). Five weak peaks are observed in the spectrum of the toluene complex. Their positions and separations from the IE are given in Table 1. The shortest-wavelength peak ((43081 ± 5) cm^{-1}), which lies 295 cm^{-1} above the IE of **1_0**, arises solely from the first S vibrational level of the $\mathbf{1\_0}^+$ ion ($\tilde{\nu}_{\text{vibr.}}^{\text{calcd}} = 289$ cm^{-1}). The stronger and broader feature at (43014 ± 10) cm^{-1} contains contributions from the B mode of **1_0**$^+$ and from the S vibration of the other three conformers. The largest difference between the calculated S wavenumbers of **1_60**$^+$, **1_120**$^+$, and **1_180**$^+$ is only 7 cm^{-1} (Table 1), so the corresponding MATI peaks overlap. However, the frequencies of the B mode in the **1**$^+$ rotational isomers lie in a much wider range (Table 1). This results in the appearance of three resolved MATI signals corresponding to the vibrational B level of **1_60**$^+$, **1_120**$^+$, and **1_180**$^+$ (Figure 2).

Comparison of the peak separations from the IE with the computed B frequencies leads to an unambiguous interpretation of the vibrational structure, each signal being assigned to an individual conformer of **1** (Table 1, Figure 2). The MATI spectrum of **1** reveals, therefore, all four stable rotational isomers of the toluene complex, while in the microwave spectrum of 1,1′-dimethylferrocene[8] only two structural isomers ($\phi = 0$ and 72°) were found. Interestingly, the change in ϕ value for the **1_0**$^+$–**1_60**$^+$–**1_120**$^+$–**1_180**$^+$ row is accompanied by a simultaneous decrease in the B-mode frequency. The experimental and calculated B frequencies of **1_120**$^+$ are very close to those of **2**$^+$ (Table 1), in which the angle between the C_{ring}–C_{Me} directions is the same.

In summary, the spectra of **1** and **2** demonstrate that MATI spectroscopy supported by DFT calculations can serve as a powerful tool for studying substituted bis(arene) complexes. High-resolution IEs of the **1** and **2** neutral molecules and low-energy vibrational frequencies of the gas-phase **1**$^+$ and **2**$^+$ ions were obtained. The signals arising from the four distinct gas-phase rotational isomers of **1** were revealed on the basis of comparison with the MATI spectrum of **2** and the computed molecular parameters. The repulsion between the Me groups in the eclipsed synperiplanar isomer of **1** ($\phi = 0°$) increases the ionization potential by 63 cm^{-1}. The low-energy vibrational frequencies of the free cations appear to depend on the mutual orientation of the substituents. The results presented herein for two methylated derivatives of bis(η^6-benzene)chromium show that MATI spectroscopy can be applied productively to future studies of the electronic structures and conformational behavior of more complicated bis(arene) systems.

Experimental Section

All manipulations with organometallics were carried out in a vacuum or under a nitrogen atmosphere. The photoionization and MATI spectra were measured with the spectrometer and techniques described in detail elsewhere.[15] The samples of the bis(arene) complexes at 140 °C, seeded in the Ar carrier gas at 1.4 bar, were expanded through a heated pulsed nozzle and were selected by two skimmers into the vacuum ionization chamber. Typical rotational and vibrational temperatures of large jet-cooled molecules are of the order of 10 and 100 K, respectively.[16] The ions produced on irradiation of the molecular beam with nanosecond laser pulses were analyzed with a reflectron time-of-flight mass spectrometer. To record the MATI spectra of **1** and **2**, the peak corresponding to $^{12}C_{14}{}^{1}H_{16}{}^{52}Cr^+$ (m/z 236.07) in the mass spectra of the samples was selected when scanning the laser frequency.

Complexes **1** and **2** were prepared by co-condensation of the corresponding organic ligands (Aldrich, 99 %) with chromium atoms at liquid-nitrogen temperature in the apparatus described previously.[17] The purity of the compounds was checked by mass spectrometric and NMR analyses. Details of the synthesis and characterization of **2** are given in the Supporting Information.

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