High-Resolution Mass-Analyzed Threshold Ionization Study of Deuterated Derivatives of Bis(η^6-benzene)chromium

Sergey Yu. Ketkov,*,† Heinrich L. Selzle,‡ and Edward W. Schlag‡

G. A. Razuvaev Institute of Organometallic Chemistry RAS, 49 Tropinin Street, 603950 Nizhny Novgorod, Russian Federation, and Institut für Physikalische und Theoretische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85748 Garching, Germany

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Two-color multiphoton mass-analyzed threshold ionization (MATI) spectra of jet-cooled (η^6-C_6D_6)$_2$-Cr and (η^6-C_6D_5H)(η^6-C_6D_6)Cr have been obtained for the first time with excitation of the sandwich molecules via vibronic components of the $3d_{z^2} \rightarrow R4p_{x,y}$ Rydberg transition. The ionization energies determined with extremely high accuracy (±0.0004 eV) on the basis of the MATI experiment are 5.4558 and 5.4562 eV, respectively. The simultaneous measurement of the two MATI spectra in one experiment reveals clearly the increase in the ionization energy caused by substitution of one deuterium atom in (η^6-C_6D_6)$_2$Cr with hydrogen. The MATI experiment demonstrates a nonlinear dependence of the ionization potential on the number of deuterium atoms in the bis(η^6-benzene)chromium molecule. Deuteration appears to decrease both the ionization energy and the $R4p_{x,y}$ Rydberg term value. The decrease in the term value is a result of the Jahn−Teller instability of the $R4p_{x,y}$ Rydberg state. The ground-state cation vibrational frequencies of the totally symmetric valence metal−ligand stretch ν_{21} and CH umbrella vibration ν_{11as} determined from the MATI spectra are, respectively, 249 ± 3 and 594 ± 3 cm^{-1} for (η^6-C_6D_6)$_2$Cr$^+$ and 251 ± 3 and 595 ± 3 cm^{-1} for (η^6-C_6D_5H)(η^6-C_6D_6)Cr$^+$. These values correspond to the free gas-phase cations.

Introduction

In 2005, chemists celebrated a 50-year anniversary of discovery of bis(η^6-benzene)chromium (**1**). An intriguing history of this discovery has been published recently.[1] (η^6-C_6H_6)$_2$Cr represents a highly symmetric (the D_{6h} point group)[2] closed-shell sandwich molecule with the ground-state electronic configuration[3] ...$[3d_{xy,x^2-y^2}, Bz(e_{2g})]^4[3d_{z^2}]^2[3d_{xz,yz}, Bz(e_{1g})]^0$-$[Bz(e_{2u})]^0$, where 3d and Bz indicate the metal and ligand contributions to the molecular orbitals. Together with ferrocene, bis(η^6-benzene)chromium plays a fundamental role in organometallic chemistry.[4] Basic ideas concerning the nature of metal−ligand bonds in organometal π-complexes are deduced from theoretical and experimental studies of electronic structures of these prototypic systems. To verify the quality of quantum-chemical calculations and to study thoroughly molecular properties of sandwich systems, precise information on the ionization energies (IEs), energies of excited electronic states, and vibrational frequencies of free sandwich molecules would be necessary. Such information can be obtained from high-resolution multiphoton ionization (MPI) spectra measured in a supersonic jet. Resonance-enhanced multiphoton ionization[5,6] (REMPI), zero kinetic energy photoelectron[7] (ZEKE), and mass-analyzed threshold ionization[8,9] (MATI) spectroscopies based on excitation of jet-cooled molecules with nanosecond pulses of tunable lasers provide unprecedented resolution and accuracy of molecular parameter measurements. It would be very attractive, therefore, to employ these methods for studying **1** and related systems.

However, numerous earlier experiments on excitation of sandwich complexes with nanosecond pulses of tunable lasers via molecular valence-shell excited states[10−23] showed that multiphoton dissociation (MPD) preceding MPI of organometallic molecules occurred, giving bare metal ions in photoionization mass spectra. As a result of MPD, the REMPI spectra

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* To whom correspondence should be addressed. Tel: ++7 (831) 2627370. Fax: ++7 (831) 2627497. E-mail: sketkov@imoc.sinn.ru.

† G. A. Razuvaev Institute of Organometallic Chemistry RAS.

‡ Technischen Universitat Munchen.

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of sandwich compounds revealed peaks corresponding to the electronic transitions in the metal atoms. Only for chromocene has a low-resolution molecular REMPI spectrum containing one broad structureless band been obtained.[24]

On the other hand, recently we have demonstrated that ferrocene,[25,26] nickelocene,[27] and **1**[28] can be efficiently ionized with nanosecond laser pulses when the transition from the metal-localized $3d_{z^2}$ orbital to the lowest Rydberg $p_{x,y}$ level is used as the first step of the multiphoton excitation. The REMPI spectrum of **1**[28] revealed a structured Rydberg transition with well-resolved vibronic components. This made it possible to determine precisely molecular parameters of **1** and related compounds with multiphoton ZEKE and MATI techniques. These methods involve an excitation of a neutral molecule to high Rydberg states lying a few wavenumbers below the ionization threshold (ZEKE states) and a subsequent delayed ionization with an electric pulse.

The ZEKE and MATI spectroscopies provide an extremely high accuracy in determination of ionization energies of neutral molecules and vibrational frequencies of the corresponding free ions. Very recently we have reported results of the first two-color MATI study of jet-cooled **1**.[29,30] A very high resolution of the REMPI and MATI methods makes it possible to study fine effects arising from deuteration of the **1** molecule. In our previous work, an influence of the deuterium atoms on the vibronic structure of the $3d_{z^2} \rightarrow R4p_{x,y}$ Rydberg transition in the REMPI spectrum of **1** has been analyzed.[31] In the present paper, we report the results of the two-color MATI spectroscopic investigation of $(\eta^6\text{-}C_6D_6)_2Cr$ (**2**) and $(\eta^6\text{-}C_6D_5H)(\eta^6\text{-}C_6D_6)Cr$ (**3**) cooled in a supersonic jet.

Experimental Section

Deuterated compounds **2** and **3** were prepared by metal vapor synthesis.[32] Chromium atoms were co-condensed with C_6D_6 (99% D, Aldrich) at liquid-nitrogen temperature using the apparatus constructed in the Inorganic Chemistry Laboratory of the University of Oxford.[33] A mixture of **2** and **3** formed was taken for the spectroscopic measurements without separation. The sandwich complexes were purified by crystallization from toluene and subsequent vacuum sublimation.

The spectroscopic measurements were performed with a REMPI-MATI spectrometer described elsewhere.[34−36] To obtain the REMPI spectra, as the first step of the MATI experiment, the jet-cooled molecules **1**−**3** were excited with two tunable dye lasers (Quanta Ray PDL-1) pumped simultaneously by a Nd:YAG laser (Quanta Ray DCR1-A, pulse duration 8 ns). The frequency-doubled first laser L1 was scanned in the 26 600−27 400 cm^{-1} region corresponding to the $3d_{z^2} \rightarrow R4p_{x,y}$ transition in **2**.[37] Laser L2 fixed at 17 600 cm^{-1} ionized the Rydberg-state molecules. The laser frequencies corrected from air to vacuum were reproducible within ±1 cm^{-1}. The laser intensities were adjusted so that the ion yield produced through one-color absorptions was negligible compared to that produced through two-color absorptions.

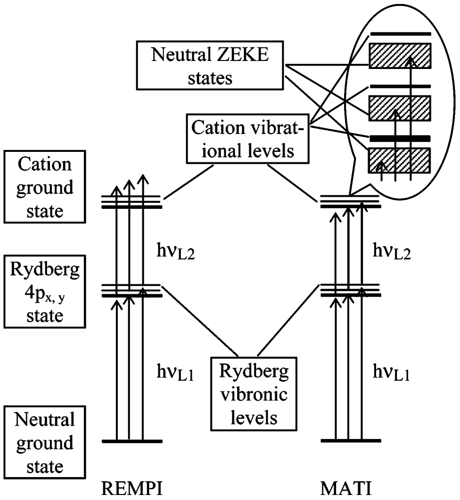

Figure 1. Excitation schemes of the **2** and **3** molecules in the REMPI (left) and MATI (right) experiment.

The ions formed in the ionization chamber were extracted into a reflectron time-of-flight mass spectrometer. The mass resolution was sufficient to separate the isotopomers for each type of sandwich cations. The REMPI and MATI spectra were recorded at m/z = 219.8−220.4 ($^{12}C_{12}{}^2H_{12}{}^{52}Cr^+$) for **2** and m/z = 218.8−219.4 ($^{12}C_{12}{}^1H^2H_{11}{}^{52}Cr^+$) for **3**.

For measuring the MATI spectra the L1 frequency was chosen to correspond to one of the $3d_{z^2} \rightarrow R4p_{x,y}$ vibronic components. Laser L2 was scanned in the 17 300−17 900 cm^{-1} region. The schemes of the **2** and **3** multiphoton excitations in the REMPI and MATI experiment are compared in Figure 1. To separate the ZEKE neutrals from the background ions, the molecular beam was exposed to a spoiling potential (0.4 V cm^{-1}) in the laser excitation region. A 75-ns electric pulse providing a zero potential can be applied to stabilize the ZEKE neutrals.[38] An electric pulse of 200 V cm^{-1} ionized the ZEKE neutrals, giving the MATI signals arising solely from the ZEKE states of **2** and **3**.

Results and Discussion

As we have shown earlier,[28] when exciting molecule **1** via the $R4p_{x,y}$ Rydberg state, the experimental conditions can be found for generation of solely intact molecular ions observed in the photoionization mass spectra. This made it possible to measure the **1** REMPI spectrum, revealing a vibronic structure of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition. Deuterated compounds **2** and **3** studied in this work also appear to produce efficiently the molecular ions on the one-color and two-color multiphoton nanosecond excitation through the $R4p_{x,y}$ level. The photoionization mass spectra of the deuterated complexes are given in Figure 2. The strongest peak (m/z = 220.1) corresponds to the $^{12}C_{12}{}^2H_{12}{}^{52}Cr^+$ species. It is seen that the molecular ion signal

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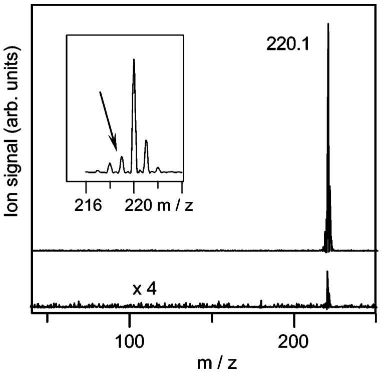

Figure 2. One-color (bottom) and two-color (top) photoionization mass spectra of jet-cooled deuterated bis(benzene)chromium **2** and **3** measured at $\nu_{L1} = 28\,690$ cm^{-1} (one-color) and $\nu_{L1} = 28\,690$ cm^{-1}, $\nu_{L2} = 17\,570$ cm^{-1} (two-color). The inset shows the isotopic structure of the molecular ion signal in the two-color mass spectrum. The arrow indicates the peak corresponding to complex **3**.

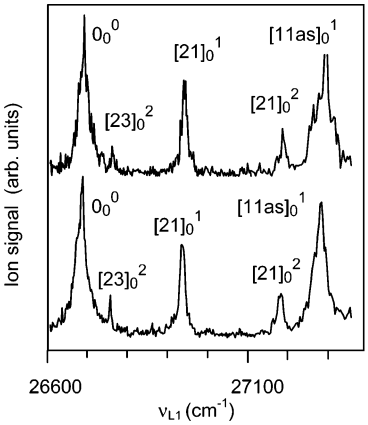

Figure 3. Two-color REMPI spectrum of **2** (bottom) and **3** (top) measured at $\nu_{L2} = 17\,570$ cm^{-1}. See text for the vibration notation.

Table 1. Frequencies ν (cm^{-1}) and Separations from the Origin $\Delta\nu$ (cm^{-1}) for the $3d_{z^2} \rightarrow R4p_{x,y}$ Vibronic Components Observed in the REMPI Spectra of 1[28] and 2 and 3 (this work)[a]

	1		2		3	
transition[b]	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
0_0^0	26 754	0	26 695	0	26 700	0
$[23]_0^2$	26 833	79	26 764	69	26 769	69
$[21]_0^1$	27 017	263	26 943	248	26 948	248
$[21]_0^2$	27 282	528	27 188	493	27 192	492
$[11as]_0^1$	27 544	790	27 286	591	27 301	601

[a] The uncertainties in the REMPI peak maximum determination are ±3 cm^{-1}. [b] Description of the normal vibrations is given in the text.

increases strongly when an intense pulse of the second dye laser ionizes the Rydberg-state molecules.

The isotopic structure of the molecular ion signals for the mixture of **2** and **3** (inset in Figure 2) reveals weaker signals corresponding to the species containing the ^{13}C, ^{50}Cr, and ^{53}Cr isotopes. On going from **1**[28] to the deuterated compounds, an additional peak appears at $m/z = 219.1$ (the $^{12}C_{12}{}^{1}H^{2}H_{11}{}^{52}Cr^{+}$ ion). It is possible, therefore, to measure the REMPI and MATI spectra of **2** and **3** simultaneously in one experiment.

As in the spectrum of **1**,[28] in the REMPI spectra of **2** and **3** (Figure 3) the peaks corresponding to the vibronic components of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition are observed. The REMPI peak positions and the separations from the 0_0^0 transition are given in Table 1 for **1**−**3**. The vibronic components observed can be assigned unambiguously on the basis of the vibration frequencies known for sandwich systems **1** and **2** both from calculations[39,40] and from the experimental solid-state Raman spectra.[41−43]

Similar to the gas-phase electronic absorption spectra of **1** and **2**,[36] the $3d_{z^2} \rightarrow R4p_{x,y}$ transition in the REMPI spectra of **1**,[28] **2**, and **3** (Figure 3) shows a progression on the symmetric metal−benzene stretching mode ν_{21} and a component corresponding to the excitation of the CH out-of-plane bending mode (umbrella vibration) ν_{11as} in the Rydberg state (we use here the notation system[41,44] for the normal vibrations in molecule **1** , which is based on Wilson numbering[45] the benzene ring modes). However, in contrast to the absorption spectra,[37] where the peaks overlap strongly, making it difficult to determine the Rydberg-state vibrational frequencies, the REMPI vibronic components (Figure 3) are completely resolved. A new vibronic component separated from the origin by 79 cm^{-1} in the REMPI spectrum of **1**[28] and by 69 cm^{-1} in the spectra of the deuterated analogues ($\nu = 26\,764$ and 26 769 cm^{-1} for **2** and **3**, respectively) can be revealed. The excitation of two quanta of the low-frequency a_{1u} torsion mode ν_{23} in the $R4p_{x,y}$ Rydberg state of **1** or **2** produces an optically allowed E_{1u} vibronic level. An assignment of the component under consideration as the $[23]_0^2$ transition leads to the Rydberg-state ν_{23} frequency of 40 cm^{-1} for **1** and 35 cm^{-1} for the deuterated complexes. These values agree very well with those derived from the DFT calculation[39] (46 and 42 cm^{-1} for **1** and **2**, respectively) as well as with the ring torsion frequency of isoelectronic ferrocene (44 cm^{-1}).[46]

Photoionization yield for the Rydberg-state **1**−**3** molecules obtained when scanning laser L2 in the absence of the spoiling potential shows a sharp increase on approaching the ionization threshold. For example, the ion signal of **1**$^{+}$ increases in the 17 330−17 345 cm^{-1} region ($\nu_{L1} = 26\,745$ cm^{-1}), giving IE[29,30] as 44 075−44 090 cm^{-1}. It is worth noting that the 15 cm^{-1} range of the “step” on the two-color photoionization curve is much narrower than that observed with the one-photon ionization of jet-cooled **1** (∼100 cm^{-1}).[22] This demonstrates the advantage of the state-selected multiphoton spectroscopy employed in the present work.

The IE value of a molecule can be determined more accurately when one goes from a simple photoionization curve to a ZEKE or MATI spectrum obtained with use of pulsed ionization in the presence of the spoiling field.[7−9] The ionization threshold lies at the energy corresponding to a narrow region of signal decrease observed in such a spectrum. The MATI spectra of **2** and **3** ($\nu_{L1} = 26\,692$ cm^{-1}) obtained without the stabilization potential show a narrow peak (fwhm 5 cm^{-1}) with the maximum at 17 308 and 17 311 cm^{-1}, respectively (Figure 4). This peak arises from the ionization of the ZEKE states lying just below the IE. The MATI signal decrease is observed for **2** in the 17 308−17 310 cm^{-1} region, leading to the IE value of 44 000−44 002 cm^{-1}.

Under our experimental conditions, the spoiling electric field decreases[7] the IE by 3 cm^{-1}. The corrected IE from this ZEKE-MATI experiment is, therefore, 44 003−44 005 cm^{-1}. Taking into consideration some uncertainty in the laser wavenumber determination (±1 cm^{-1} before the frequency doubling), the

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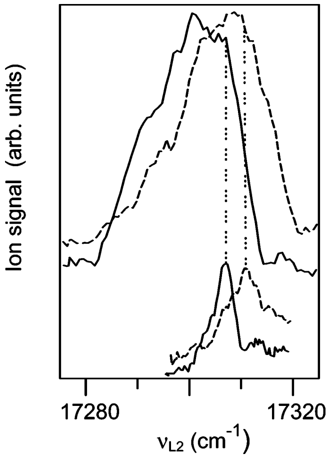

Figure 4. MATI spectra of **2** (full line) and **3** (dashed line) for stabilized (top) and nonstabilized (bottom) ZEKE states with the L1 wavenumber corresponding to the 0_0^0 component of the R4p$_{x,y}$ transition, $\nu_{L1} = 26692$ cm^{-1}.

Table 2. Ionization Energies (IE) (eV), R4p$_{x,y}$ Rydberg Term Values *T* (cm^{-1}), and Vibrational Frequencies (cm^{-1}) in the Neutral Rydberg-State Molecules ν_t(R) and Ground-State Cations ν_t(c) Found for 1−3 from the REMPI and Multiphoton MATI Spectra in Comparison with Those Obtained with Other Spectroscopic Techniques

parameter	**1**	**2**	**3**
IE[a]	5.4661 ± 0.0004	5.4558 ± 0.0004	5.4562 ± 0.0004
IE[b]	5.40−5.47		
IE[c]	5.463 ± 0.006		
IE[d]	5.4681 ± 0.0006		
IE[e]	5.4665 ± 0.0002		
IE[f]	5.459 ± 0.004	5.446 ± 0.004	
IE[g]	5.4661 ± 0.0006		
T[a]	17333 ± 3	17308 ± 3	17306 ± 3
T[f]	17370 ± 30	17370 ± 30	
ν_{23}(R)[a]	40 ± 3	35 ± 3	35 ± 3
ν_{21}(R)[a]	263 ± 3	248 ± 3	248 ± 3
ν_{21}(R)[f]	260 ± 60	220 ± 60	
ν_{11as}(R)[a]	790 ± 3	591 ± 3	601 ± 3
ν_{11as}(R)[f]	770 ± 60	600 ± 60	
ν_{21}(c)[a]	262 ± 3	249 ± 3	251 ± 3
ν_{21}(c)[g]	262 ± 6		
ν_{21}(c)[h]	279 ± 5		
ν_{11as}(c)[a]	788 ± 3	594 ± 3	595 ± 3
ν_{11as}(c)[h]	790 ± 5		

[a] Multiphoton REMPI and MATI spectra in a supersonic jet (refs 28−31 and this work). [b] Classic UV photoelectron spectroscopy (refs 3, 48); the uncertainty varies from ±0.005 to 0.02 eV. [c] One-photon photoionization curve in a supersonic jet (ref 22). [d] One-photon ZEKE spectrum in a supersonic jet with the laser frequency not corrected from air to vacuum (ref 23). [e] Multiphoton photodissociation/photoionization spectrum in a supersonic jet (ref 23). [f] One-photon gas-phase electronic absorption spectrum at 120 °C (ref 37). [g] One-photon MATI spectrum in a supersonic jet (ref 47). [h] Solid-state Raman spectrum of bis(η^6-benzene)chromium iodide (ref 42).

IE value of 44 004 ± 3 cm^{-1} or 5.4558 ± 0.0004 eV can be accepted for compound **2**. By analogy, the ionization energy of **3** is obtained in this work as 44 007 ± 3 cm^{-1} or 5.4562 ± 0.0004 eV.

The IE values measured for **1**−**3** with various spectroscopic techniques are compared in Table 2. It is seen that the ionization energy of **1** (5.4661 ± 0.0004 eV) resulting from the multiphoton MATI spectrum[29,30] is in excellent agreement with that obtained with other laser techniques using jet-cooled molecular beams.[23,47] Moreover, the one-photon MATI spectroscopic study of **1**[47] carried out a few months later than our two-color experiment[29,30] has produced exactly the same IE (5.4661 ± 0.0006 eV). If the laser frequencies in the one-photon ZEKE experiment[23] were corrected from air to vacuum, the value of 5.4681 eV (Table 2) would decrease to 5.4665 eV, becoming very close to the MATI[29,30,47] and MPD/MPI[23] results. The values obtained with the traditional UV photoelectron spectroscopy[3,48] (5.40−5.47 eV) are much less accurate, although the most recent photoelectron result[48] (5.473 ± 0.005 eV) agrees very well with the MATI data.

The difference between IEs of **3** and **2** is very small. However, the shift of the ionization energy on going from **2** to **3** is clearly seen in the spectra measured simultaneously in the high-resolution MATI experiment (Figure 4). For these MATI spectra, the uncertainty in the difference between the ionization energies of **3** and **2** is determined by the width of the laser line (0.5 cm^{-1}). This example demonstrates an extremely high sensitivity of the MATI spectra to changes in the structure of the sandwich molecule. The decrease in IE of **1** on deuteration (Table 2) arises from higher zero-point energy (ZPE) of the cation **1**$^+$ as compared to that of the neutral molecule.[37] Comparison of the ionization energies of **1**−**3** (Table 2) shows that the difference between the IE of **1** and **2** (0.0104 eV) is much larger than that expected on the basis of the IE shift caused by the substitution of one deuterium atom in **2** with hydrogen (0.0004 eV). This can be due to deviations from additivity in the influence of deuteration on the zero-point energy in the neutral molecule **1** and cation **1**$^+$. The **1** ZPE value estimated on the basis of the DFT calculations[39] exceeds 5 eV. Since this energy is subtracted from the ZPE of **1**$^+$ when determining the IE value, even relatively small deviations from linearity in the dependence of ZPE on the number of deuterium atoms can produce noticeable nonadditivity in the influence of the deuteration extent on the IE of **1**.

The difference between the IE and the frequency corresponding to the R4p$_{x,y}$ 0_0^0 peak maximum represents the term value *T* equal to the binding energy of the R4p$_{x,y}$ electron to the cationic core. The shapes of the potential energy surfaces of a Rydberg-state neutral molecule and of a cation in the corresponding electronic state are very similar.[49] One should expect, therefore, that the shifts of the **1** R4p$_{x,y}$ state and the **1**$^+$ ground state on deuteration are parallel, and consequently, the R4p$_{x,y}$ term values of **1** and **2** are equal. Table 2 shows, however, that the *T* magnitude changes from 17 333 to 17 308 cm^{-1} on going from **1** to **2**. This decrease arises from the Jahn−Teller effect in the degenerate R4p$_{x,y}$ state ($^1E_{1u}$). The presence of the Jahn−Teller instability has been revealed recently during analysis of the 3d$_{z^2}$ → R4p$_{x,y}$ vibronic structure.[31] The higher term value of **1** as compared to **2** is a result of a stronger Jahn−Teller energy decrease in **1**. Interestingly, the Jahn−Teller activity observed in this case arises exclusively from degeneracy of the Rydberg 4p$_{x,y}$ orbital. The bis(η^6-benzene)chromium ionic core interacting with the R4p$_{x,y}$ electron is nondegenerate ($^2A_{1g}$), so the core does not contribute to the Jahn−Teller instability of the Rydberg state.

The MATI peak observed for **2** and **3** at 17 308 and 17 311 cm^{-1}, respectively, (Figure 4) corresponds to the vibrationless level of the cation $^2A_{1g}$ (...[3d,Bz(e$_{2g}$)]^4[3d(a$_{1g}$)]^1) ground electronic state. The signal obtained with a constant spoiling potential is, however, too weak to reveal the ZEKE states lying

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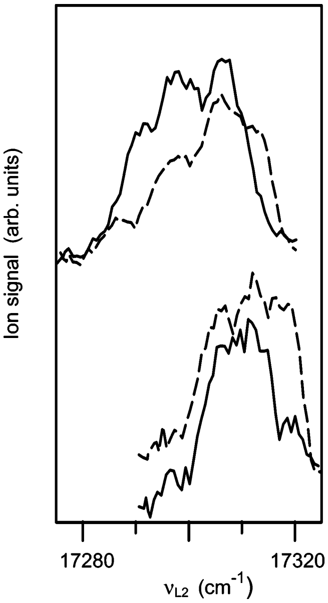

Figure 5. MATI spectra of **2** (full line) and **3** (dashed line) with the L1 wavenumber corresponding to the $[21]_0^1$ component, $\nu_{L1} = 26\,941$ cm^{-1} (top), and the $[11as]_0^1$ component, $\nu_{L1} = 27\,279$ cm^{-1} (bottom), of the R4p$_{x,y}$ transition.

near excited vibrational levels of the cations 2^+ and 3^+. To increase the signal/noise ratio, the pulse of a zero-potential stabilizing field can be applied shortly after excitation.[38] As a result, the MATI peak becomes substantially stronger and broader (Figure 4). However, the wavenumber corresponding to the beginning of the signal decrease remains practically unchanged. The peak broadening has, therefore, no influence on the IE determination.

Even with the stabilized-ZEKE setup the excitation of the molecules **2** and **3** via the 0_0^0 component of the Rydberg transition gives no clearly defined signals corresponding to the 1^+ vibrational states. This is indicative of small Franck−Condon factors for the electronic transitions from the vibrationless R4p$_{x,y}$ state to the ZEKE states with a vibrationally excited cationic core. A two-color MATI scheme gives, however, another possibility to determine vibrational level energies of a free cation. The 1^+-3^+ vibrational frequencies can be found with the ZEKE stabilizing technique when using the R4p$_{x,y}$ vibronic levels of **1**−**3** as intermediate states in the multiphoton excitation. For 1^+, the ν_{21} and ν_{21} frequencies (262 and 788 cm^{-1}, respectively) have been determined recently in such an experiment.[29,30] Notice that the results of the two-color[30] and one-photon[47] MATI spectroscopy for ν_{21} coincide (Table 2).

The MATI signals obtained with the L1 frequency corresponding to the $[21]_0^1$ and $[11as]_0^1$ components of the Rydberg transition in **2** and **3** are given in Figure 5. Each spectrum shows a peak arising from the ZEKE states lying under a corresponding cationic vibrational level. The vibrational quantum numbers remain, therefore, unchanged on the excitation from the R4p$_{x,y}$ state to the ZEKE states and on the subsequent ionization. As with the vibrationless cationic state, the vibrational level energies correspond to the region of a sharp decrease in the MATI signal. This gives the cationic vibrational frequencies $\nu_{21} = 249 \pm 3$ cm^{-1}, $\nu_{11as} = 594 \pm 3$ cm^{-1} for 2^+ and $\nu_{21} = 251 \pm 3$ cm^{-1}, $\nu_{11as} = 595 \pm 3$ cm^{-1} for 3^+. Comparison with the Rydberg-state frequencies (Table 2) shows that the ionization of the R4p$_{x,y}$ state does not lead to noticeable changes in ν_{21} and ν_{11as} of the **1**−**3** molecules. The ν_{21} and ν_{11as} frequencies in the ground-state neutral **1** molecule (277 and 791 cm^{-1}, respectively, as determined from the solid-state Raman spectrum)[41−43] are also close to the values obtained from the REMPI[28] and MATI[29,30] spectra (Table 2).

Conclusion

In this work we have used for the first time two-color MATI spectroscopy in combination with a REMPI experiment to study fine effects caused by deuteration of bis(η^6-benzene)chromium. The ionization energy of $(\eta^6\text{-}C_6D_6)_2Cr$ and $(\eta^6\text{-}C_6D_5H)(\eta^6\text{-}C_6D_6)Cr$ has been determined as 5.4558 ± 0.0004 and 5.4562 ± 0.0004 eV, respectively. The unprecedented MATI resolution makes it possible to reveal even the IE increase arising from substitution of one deuterium atom with hydrogen. The influence of deuteration on the ionization energy of bis(η^6-benzene)chromium appears to be nonadditive. The R4p$_{x,y}$ term value determined on the basis of the REMPI-MATI experiments decreases on going from $(\eta^6\text{-}C_6H_6)_2Cr$ to $(\eta^6\text{-}C_6D_6)_2Cr$ as a result of the Jahn−Teller instability of the Rydberg state. The MATI spectra give the frequencies of the totally symmetric Cr−C_6H_6 stretch and C−D out-of-plane bend for sandwich ions. These frequencies correspond to the free gas-phase ground-state cations, so they can serve, together with the ionization energies determined in the present work, as good experimental references for high-accuracy computational studies of bis(η^6-benzene)chromium and its derivatives.

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