Pulsed-field ionization spectroscopy of high Rydberg states (n=50–200) of bis(η⁶-benzene)chromium

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The ionization behavior of the high Rydberg states of bis(η⁶-benzene)chromium in the presence of ac and/or dc fields has been explored. The application of an ac scrambling field at the time of laser excitation lengthens the lifetime of the Rydberg state by almost two orders of magnitude. The lifetime enhancement by the scrambling field is much more effective for n<100 than it is for n>100 Rydberg states. The pulsed-field ionization of Rydberg states of n<100 shows the typical diabatic ionization behavior for low n. The two distinct ionization behaviors observed for the relatively low (n=50–100) and high (n=100–200) Rydberg states suggest that the former originate from the optically accessed nf Rydberg series, whereas the latter are due to np Rydberg series. Based on the understanding of the ionization behavior of bis(η⁶-benzene)chromium, the accurate ionization potential is deduced to give IP=5.4665±0.0003 eV. Optimization of the various electric field conditions greatly enhances the spectral sensitivity of the mass-analyzed threshold ionization (MATI) spectroscopy. The high-resolution MATI spectrum of the title molecule obtained here provides precise cationic vibrational frequencies for many skeletal and benzene ring modes. A number of vibrational modes are newly identified, and the ambiguity regarding to some mode assignments is now clearly resolved through the Frank-Condon analysis based on ab initio calculations. © 2007 American Institute of Physics. [DOI: 10.1063/1.2423022]

I. INTRODUCTION

Pulsed-field ionization (PFI) of high Rydberg states of atoms and molecules has been a hot topic especially in the late 1990s, since excellent spectroscopic tools such as zero-electron kinetic energy (ZEKE) or mass-analyzed threshold ionization (MATI) spectroscopy rely on the PFI of long-lived high n Rydberg states. The mechanism of the enormous lifetime lengthening of high Rydberg states has been subjected to intensive investigation for many chemical systems. Through a number of excellent experimental and theoretical studies, it is now well accepted that the lifetime lengthening is mainly due to the l mixing induced by a stray field which cannot be easily avoided in most laboratories. The l mixing from the optically prepared low-l state gives rise to the population in the nonpenetrating high-l states in which the electron orbits like that of hydrogen. The binding energy of an electron is expressed by the following relation:

\[ E_{nl} = - \frac{R_M}{(n + \delta_l)^2/2}. \]

Here, \(R_M\) is the Rydberg constant, \(n\) the principal quantum number, and \(\delta_l\) the l-dependent quantum defect. The higher l gives the smaller \(\delta_l\), implying that the corresponding electronic wave function is less overlapped with the ionic core to significantly slow down the dephasing processes of Rydberg states via predissociation, internal conversion, or autoionization.\(^\text{1,2,4,5}\)

Experimentally, an \(n^4\) dependence of the high \(n\) Rydberg state lifetime has been regarded as the evidence for the field-induced l mixing, while the collisional \(m_l\) mixing is considered to be responsible for an \(n^3\) dependence.\(^\text{1,5}\) Even though many experimental observations have been successfully explained by theoretical models developed by Levine and co-workers,\(^\text{6,7}\) the PFI behavior of high \(n\) Rydberg states of molecules is quite complex and it is not well understood yet. For example, in many cases, the application of a small dc field at the time of laser excitation is known to diminish the Rydberg state lifetime of molecules\(^\text{12–16}\), while the opposite cases have also been reported.\(^\text{17}\) The l mixing induced by a small dc field has been thoroughly studied for NO by Vrankking and Lee.\(^\text{5}\) They reported the minimum electric field required to induce the l mixing for nf or np Rydberg series of NO which are prepared by the (1+1') two-photon excitation. The np series of NO has the \(\delta\) value of 0.7286, whereas the quantum defect of nf series was found to be much smaller to give \(\delta=0.0101\). The more hydrogenic-like nature of the nf series has been manifested in the lower \(n\) and electric field values required for the l mixing to effectively occur compared with those for np series.\(^\text{5}\)

Compared to the case of NO, the ionization behavior of high Rydberg states of polyatomic molecules is much less understood. One of the reasons would be the increase of the number of degrees of freedom which results in the lifetime shortening of high \(n\) Rydberg states. Even though ZEKE spectroscopy has been widely used for accurate ionization...
potential (IP) measurements in the sense that it probes the Rydberg states of \( n \geq 250 \) using the small extraction field, the mechanism of mixing of high \( n \) states prior to PFI has little been studied for polyatomic molecules. Nonetheless, it should be noted that the long-lived Rydberg manifolds for Ar, HCl, N₂, C₆H₆, and O₂ were investigated by Hofstein et al.⁹ using the MATI spectroscopy. They pointed out the importance of the initially prepared Rydberg orbital for the understanding of the varying widths of Rydberg manifolds of different molecules. Additionally, it is also noteworthy that high Rydberg states (\( n > 50 \)) of 1,4-diazabicyclo[2,2,2]octane (DABCO) and DABCO-N₂ have been identified and their ionization behavior was studied using ZEKE and/or MATI spectroscopic techniques.⁹,¹¹

Here, we have studied the ionization behavior of high Rydberg states of bis(\( \eta^6 \)-benzene)chromium, Cr(Bz)₂. In spite of the large size of this molecule, the Rydberg transitions up to \( n = 35 \) had been clearly observed to give the quantum defect and extrapolated IP values.⁹ For Rydberg states of \( n > 35 \), presumably due to the overlap with intervalence transitions, no spectroscopic information is available to date. In this work, using the delayed pulsed-field ionization technique, Rydberg states of \( n = 50–200 \) are identified for the first time. The stray or ac scrambling field greatly enhances the Rydberg state lifetime, enabling one to observe high \( n \) Rydberg states and their ionization behavior. The high-resolution MATI spectrum is taken to give the detailed vibrational structure of the Cr(Bz)₂ cation. In this work, we greatly improved the spectral resolution of the MATI spectrum of Cr(Bz)₂ compared with other previous works, resolving the earlier ambiguity in the vibrational mode assignment. Furthermore, our MATI spectrum provides many newly found vibrational frequencies which are essential for understanding the nature of the metal-benzene \( \eta \) bonding.

II. EXPERIMENT

Bis(\( \eta^6 \)-benzene)chromium was purchased from Aldrich (97%) and used without further purification. The experimental setup has been described earlier¹⁹,²³ and is only briefly given here. The sample was heated to 120 °C, mixed with Ar carrier gas, and expanded into vacuum through a 0.8 mm diameter nozzle orifice (General Valve 9 Series). The supersonic jet was then skimmed though a 1 mm diameter skimmer (Precision Instrument) before it was collinearly overlapped with the UV laser pulse. The backing pressure was \( \sim 1.5 \) atm and the background pressure of \( \sim 10^{-7} \) Torr was maintained when the nozzle was on. A tunable laser pulse (1–2 mJ/pulse, \( \Delta t \approx 6 \) ns) in the 220–228 nm range was generated by the frequency doubling of the laser output from a dye laser (Lambda Physik, Scanmate 2) pumped by the third harmonic output of a Nd:YAG laser (Continuum, Precision II) through a BBO crystal placed on a homemade autotracker.

Molecules were excited to high \( n \) Rydberg states and allowed to stay for 10–200 \( \mu s \) before they were ionized by the pulsed field of 10–100 V/cm to give MATI ions. Because of the long delay time between the laser irradiation and pulsed-field ionization, the direct ions were spread out to be completely separated from the MATI ions. Resultant MATI ions were accelerated, drifted along the field-free region, and detected by dual microchannel plates. Ion signals were digitized by a digital oscilloscope (LeCroy, LTS84M) and stored in a personal computer using a data-taking program which controls the dye laser frequency tuning and homemade autotracker as well. Various electric field conditions were applied to explore the ionization behavior of high Rydberg states. For the ac scrambling field, the ac noise accompanied with the high-voltage pulser (DEI, PVM-4140) was used. The spoil field of 0.01–4 V/cm was applied when its effect on the MATI signal was investigated. For the high-resolution MATI spectrum, the electric field scheme in Fig. 1 was used. No spoil field was used, whereas the ac scrambling field was applied at the time of laser irradiation. The pulsed field of 10 V/cm was used to ionize and repel MATI ions into the accelerating field. Further acceleration was carried out in the upper electrodes for recording the frequency-dependent MATI signal.

Ab initio calculations were carried out by using the GAUSSIAN 03W program package.³⁰ The geometry and vibrational frequency of neutral and cationic states of bis(\( \eta^6 \)-benzene)chromium were calculated using the Möller-Plesset second-order perturbation theory and density functional theory (B3LYP) with the pseudo-core-potential LANL2DZ basis set. All harmonic frequencies reported here are not scaled. Frank-Condon overlap integrals using the Duschinsky transformation³¹ are calculated with a code developed by Peluso et al.²⁸ and Borrelli and Peluso.³³ Optimized structures and normal mode frequencies are used as inputs for both neutral and cationic states.

III. RESULTS AND DISCUSSION

One-photon MATI spectrum of Cr(Bz)₂ obtained in this work is compared with that previously reported by our group,²³ Fig. 2. The MATI spectrum in Fig. 2(a), which was taken with the pulsed field (\( F \)) of \( \sim 400 \) V/cm, shows broad spectral features, whereas the high-resolution MATI spectrum taken with \( F = 10 \) V/cm consists of sharp peaks with the narrow full width at half maximum bandwidth of \( \sim 5 \) cm⁻¹. The spectral narrowing by the smaller pulse-field strength is natural as the energy range of Stark states subjected to ionization becomes narrower with decreasing the pulse-field strength. However, the distinct structure observed
in the vibronic band in Fig. 2(a) is unusual and the origin of the structure needs to be investigated. The spectral structure observed in the red wing of the band in Fig. 2(a) had also been observed in the ZEKE spectrum reported in Ref. 9, in which it was ascribed to the autoionizing rotational states. Sohlein and Yang, in their recent ZEKE spectroscopic work, reported a similar-shaped band in which the structure was attributed to a low-frequency vibrational mode. Since they used laser ablation to produce the internally hot Cr(Bz)_2, however, the direct comparison with the MATI spectrum in Fig. 2(a) is not adequate.

Here, we examine spectral changes for various combinations of applied electric fields. The origin of the MATI spectral structure is associated with two distinct ionization behaviors of two different nl series. The high-resolution MATI spectrum, after resolving the issue of the ionization behavior of high n Rydberg states of Cr(Bz)_2, provides not only the most precise vibrational frequencies for the modes already identified before but also accurate frequency values for many other vibrational modes.

A. Ionization behavior of high Rydberg states (n=50–200) of the bis(η^6-benzene)chromium

The application of an ac scrambling field at the laser irradiation time greatly enhances the lifetime of Rydberg states. As the PFI strength (F) increases, according to the diabatic ionization mechanism, the ionization window becomes widened to ionize the Stark states down to IP ~ 4√F cm⁻¹. The MATI origin band obtained as a function of the PFI strength is shown in Fig. 3(a). The delay time between the laser and PFI is fixed at 14 μs. Interestingly, as the PFI strength increases the shoulder at the red wing starts to appear and it becomes a distinct peak at F > 30 V/cm. Consequently, for example, at F = 100 V/cm, two distinct peaks are observed over the energy range of ~ 50 cm⁻¹. A broad band centered at ~44 072 cm⁻¹ shows a gradual decrease of its bandwidth, accompanied by the blueshift of its red edge as the pulsed-field strength decreases. The shift of the red edge of the band with F (V/cm) follows the relation ΔIP ~ 4.54√F, giving an adiabatic IP value of 44 090±3 cm⁻¹, Fig. 3(b). The ionization behavior is consistent with a diabatic ionization model mechanism for low n. Meanwhile, the relatively sharp band located at 44 080 cm⁻¹ shows little change with the change of pulsed-field strength. At F = 10 V/cm, the broad band feature disappears while only a sharp band remains. Because of the long delay time between the laser excitation and pulsed-field ionization, no spoil field is used. It is clear that the band structure of the red shoulder in Fig. 2(a) is not due to the internal states of Cr(Bz)_2. Rather, it should be ascribed to the relatively low n Rydberg states of Cr(Bz)_2. Furthermore, it seems that the ionization behavior of Rydberg states is quite different for low and high n Rydberg states.

In order to investigate the origin for two distinct PFI behaviors, many different combinations of electric fields were explored. In Fig. 3(c), the pulsed field is fixed at 50 V/cm and the delay time between the laser and rising edge of the PFI voltage is changed to monitor the associated change of the MATI band shape. Although an accurate lifetime cannot be deduced from this measurement, it is obvious that the lifetime of the red shoulder is shorter than that of the peak at the blue edge. That is, the red-shoulder intensity
TABLE I. Experimental ionization potentials of bis(η²-benzene)chromium.

<table>
<thead>
<tr>
<th>IP (cm⁻¹)</th>
<th>Method</th>
<th>Ref./year</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 090± 3</td>
<td>High-resolution MATI spectroscopy</td>
<td>This work</td>
</tr>
<tr>
<td>44 081± 7</td>
<td>ZEKE spectroscopy</td>
<td>26/2006</td>
</tr>
<tr>
<td>44 087± 5</td>
<td>One-photon MATI spectroscopy</td>
<td>23/2004</td>
</tr>
<tr>
<td>44 087± 5</td>
<td>Two-photon MATI spectroscopy</td>
<td>28/2004</td>
</tr>
<tr>
<td>44 020±30</td>
<td>Gas-phase photoabsorption</td>
<td>35/1997</td>
</tr>
<tr>
<td>44 090 3±0.5</td>
<td>Rydberg states fitting</td>
<td>9/1994</td>
</tr>
</tbody>
</table>

In other words, the n=50–100 Rydberg states may belong to the nf series in which the initial l quantum number is 3, whereas the n=100–200 Rydberg states correspond to np series where the initial l is equal to 1. Similarly to the case of NO, the nf series is more hydrogenic and the l mixing occurs at the lower n compared with that of the np series. For the np series, because of the relatively large quantum defect of δ=1.38,9 the l mixing by the stray or ac field becomes significant only at high Rydberg states of n>100. Therefore, the diabatic ionization behavior of the ionization onset at low n, as a function of the pulsed-field strength, is hardly observed for the MATI peak at the long delay time of ~16 μs.

The one-photon excitation to an nf Rydberg series has rarely been reported for molecules to our best knowledge. This is because the optical selection rule is Δl=±1 and the angular momentum of the molecular orbital, which is poorly defined, is equal to or less than 1 for many organic molecules although it had been reported that the highest occupied molecular orbital (HOMO) of benzene correlates to a d atomic orbital and nf series is optically active in the MATI spectrum.18 For Cr(Bz)₂, however, the HOMO corresponds to the pure nonbonding d₂z orbital of the central metal atom and thus the angular momentum of l=2 is fairly well defined. The MATI signal represents long-lived high Rydberg states.
These states have high-\( l \) quantum numbers, and it results from the \( l \) mixing caused by the stray or ac field. However, the initial excitation to the high Rydberg states is governed by the optical selection rule of \( \Delta l = \pm 1 \). Therefore, the MATI spectrum could be interpreted using the optically bright and dark states with coupling between those as depicted in Fig. 4. Here, optically bright \( nf \) and \( np \) Rydberg states of \( \text{Cr(Bz)}_2 \) are strongly coupled to optically dark high-\( l \) Rydberg states through the \( l \) mixing in the presence of the stay and/or ac scrambling field to give the long-lived MATI states. The resultant MATI spectrum then reflects the long-lived high-\( l \) Rydberg states as well as optically accessible initial low-\( l \) quantum states.

In the overlapping region of \( n=80–120 \), the MATI signal originated from the \( nf \) series decreases as \( n \) increases. The lifetime modulation as a function of the principal quantum number had also been observed for NO and Ar.\(^5,\,\,\,8\) Even though the understanding of the origin for the lifetime modulation in Rydberg manifolds of the title molecule may need full consideration of multichannel interactions, a simple interpretation based on the one-electron atomic model could be conceived. That is, as the excitation energy increases, the density of states increases. The increase of the density of states should result in the coupling of the initially prepared \( f \) states to higher or lower \( l \) states according to the selection rule of \( \Delta l = \pm 1 \). The extent of the \( l \) coupling is strongly dependent on the external electric field, quantum defect, and principal quantum number with a relation of \( \Delta l = 3n^2Fl^{-1} \). Thus, at the given stray field of \( F \), the mixing of the \( nf \) states to high-\( l \) states with \( \Delta l = +1 \) may be activated early at the low \( n \)'s, whereas the coupling to low-\( l \) states with \( \Delta l = -1 \) becomes significant later at the relatively higher \( n \)'s. Therefore, in the \( n=80–120 \) region, the optically dark \( nd \) series could be effectively mixed with the optically bright \( f \) series, leading to the decrease of the lifetime because of the vulnerable nature of the \( nd \) series. At \( n > \sim 120 \), the \( np \) series undergoes the complete \( l \) mixing to give rise to the long-lived Rydberg manifolds. This simple picture, however, may need much improvement, especially in terms of the interaction of the Rydberg electron with the ionic core of this large molecule. High-resolution Rydberg spectroscopic work would be quite valuable for unraveling the dynamics involved in the \( l \)-mixing process in greater detail for this interesting molecule.

It should be noted that the \( l \) mixing by the ac scrambling field is much more effective for the \( n=50–100 \) Rydberg states. In Fig. 5(a), the MATI signal obtained in the absence of an ac scrambling field is shown as a function of the PFI field. The MATI signal due to \( n=50–100 \) states is significantly diminished, indicating that the corresponding lifetime gets shortened. Meanwhile, the MATI signal due to \( n=100–200 \) Rydberg states is found out to be less affected by the ac scrambling field. The application of the dc spoil field at the time of laser irradiation cuts off the high \( n \) Rydberg states. In Fig. 5(b), the MATI peak shows the redshift as the spoil field increases from 0.01 to 2.55 V/cm. The MATI peak shift due to the spoil field is found to be very significant. The energy shift from the adiabatic IP with increasing the spoil field is found out to be not systematic, and it seems to be nontrivial to extract quantitative values from the experiment carried out under the strong spoil field.

The \( \text{Cr(Bz)}_2 \) molecule provides the unique opportunity to investigate high \( n \) Rydberg states of the complex molecular system. However, at the same time it had been difficult to obtain a well-resolved MATI spectrum partly because of the lack of the knowledge about the ionization behavior of the optically accessible Rydberg states of \( \text{Cr(Bz)}_2 \). In the following section, using the most optimal experimental condition, the MATI spectroscopic characterization of the \( \text{Cr(Bz)}_2 \) cation is given.

### B. Vibrational structure of the bis(\( \eta^6 \)-benzene) chromium ion

The high-resolution MATI spectrum obtained in this work provides the detailed vibrational structure of the \( \text{Cr(Bz)}_2 \) cation. Since the HOMO is nearly pure \( d_{z^2} \) orbital of Cr which is not involved in the \( \pi \) bonding between benzene and Cr, the structural change of \( \text{Cr(Bz)}_2 \) induced by the first ionization is not expected to be drastic. The HOMO belongs to \( a_{1g} \), and the Jahn-Teller splitting is not expected for this highly symmetric molecular cation. The neutral and cationic structures are calculated using the density functional theory (DFT) (UB3LYP/LANL2DZ) method, Table II. The distance between chromium and benzene is predicted to be increased from 1.680 to 1.701 Å in the ionization process, while the structure of benzene moieties is little changed. The origin band is most strongly observed. The Bz–Cr–Bz symmetric bond is little changed.

![Image](https://example.com/figure5.png)

**FIG. 5.** (a) The MATI spectrum taken as a function of the PFI field in the absence of both ac scrambling and spoil fields. (b) The MATI origin band taken with the application of the various dc spoil fields without the ac scrambling field (see the text).

**TABLE II.** Structural parameters of bis(\( \eta^6 \)-benzene)chromium in the neutral and cationic ground states from the DFT calculation (UB3LYP/LANL2DZ level).

<table>
<thead>
<tr>
<th></th>
<th>( R(\text{Cr–Bz}) ) (Å)</th>
<th>( R(\text{C–C}) ) (Å)</th>
<th>( R(\text{C–H}) ) (Å)</th>
<th>( \angle(\text{CCCH}) ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral ground</td>
<td>1.680</td>
<td>1.430</td>
<td>1.085</td>
<td>1.23</td>
</tr>
<tr>
<td>Cationic ground</td>
<td>1.701</td>
<td>1.431</td>
<td>1.083</td>
<td>1.30</td>
</tr>
<tr>
<td>Difference</td>
<td>0.021</td>
<td>0.001</td>
<td>-0.002</td>
<td>0.07</td>
</tr>
</tbody>
</table>
stretching mode is found to be significantly active in the MATI spectrum, Fig. 6(a). Since the spectrum is very well resolved, vibrational frequencies are quite precisely determined. The Franck-Condon analysis based on ab initio molecular structures and vibrational frequencies is carried out to give the simulated MATI spectrum in Fig. 6(b).

Even though relative intensities and peak positions of the simulation do not match with the experiment extremely well, the Franck-Condon simulation leads to the reasonable assignments at least for low-frequency vibrational modes. Firstly, as stated above, the band strongly observed at the vibrational energy of 272 cm\(^{-1}\) certainly corresponds to the symmetric Bz–Cr–Bz stretching mode (\(v_{21}\)). This value is \(\sim 8\) cm\(^{-1}\) larger than the earlier reported ZEKE spectroscopic value.\(^{26}\) The corresponding ab initio frequency of 234 cm\(^{-1}\) is quite low compared to the experiment. Due to the ionization-driven structural change, the Bz–Cr–Bz stretching mode should be Franck-Condon active, as clearly depicted in Fig. 6(b). The band at 526 cm\(^{-1}\) is assigned as the first overtone of the \(v_{21}\) mode. As the fundamental \(v_{21}\) frequency is 272 cm\(^{-1}\), this assignment suggests that the Bz–Cr–Bz stretching mode is quite positively anharmonic. The vibrational band observed at 787 cm\(^{-1}\) cannot be ascribed to the second overtone of \(v_{21}\) since the fundamental and first overtone frequencies preclude this possibility which otherwise would give the negative anharmonicity for the \(v_{21}\) mode. The Franck-Condon analysis predicts that the \(v_{11}\) mode associated with C–H out-of-plane bending motion is active in the ionization spectrum, Figs. 6 and 7. The corresponding ab initio frequency is 799 cm\(^{-1}\), which is quite close to the experiment. This assignment is in accord with recent reports by Ketkov et al.,\(^{27,28}\) and Sohnlein and Yang.\(^{26}\)

Other weakly observed vibrational bands in the MATI spectrum are also well characterized. Because of the high quality of the spectrum, many new vibrational features of the Cr(Bz)\(_2\) ion could be identified. The 135 cm\(^{-1}\) band (\(v_{22}\)) is assigned to the asymmetric bending motion of benzene moieties of which the calculated value is 137 cm\(^{-1}\). Normal mode descriptions for \(v_{21}, v_{22},\) and \(v_{11}\) modes are given in Fig. 7. Other skeletal modes in which the benzene moiety moves like a rigid body along the intermoiety potential energy surfaces are observed in the vibration energy range of 100–500 cm\(^{-1}\). Even though ab initio values do not reproduce the experiment perfectly, reasonable assignments based on the Franck-Condon analysis are carried out and listed in Table III. Overall, the experimental vibrational frequencies are higher than those calculated, suggesting that the force constants associated with the Bz–Cr–Bz intermoiety motion are stronger than those predicted by the ab initio calculation at the level used in this work. A more reliable calculation at the higher level is desirable for the more thorough understanding of the \(\eta\)-bonding nature of the metal-benzene sandwich complex.

FIG. 6. (a) The MATI spectrum of the bis(\(\eta^6\)-benzene)chromium cation. (b) The simulated spectrum calculated by the Franck-Condon analysis based on DFT calculations for molecular structures and vibrational frequencies.

FIG. 7. Normal mode descriptions for \(v_{22}, v_{21},\) and \(v_{11}\) modes (see Table III).
The vibrational bands observed above 700 cm\(^{-1}\) are associated with the vibrational modes of benzene moieties. Nuclear motions of two benzene moieties are either symmetric or antisymmetric with respect to the inversion symmetry operation and corresponding vibrational modes are rather complicated in terms of associated nuclear motions. Based on the Franck-Condon analysis, the mode assignment is tentatively carried out, Table III. If our assignment is correct, it implies that the experimental frequencies for the vibrational modes of benzene moieties are also higher than predicted by the \textit{ab initio} calculation. High-level \textit{ab initio} calculations on this large metal-benzene sandwich complex system would be quite challenging but should be very valuable.

### TABLE III. Experimental and calculated vibrational frequencies of bis(\(\eta^6\)-benzene)chromium.

<table>
<thead>
<tr>
<th>Neutral ground</th>
<th>Rydberg</th>
<th>Cationic ground</th>
<th>MATI</th>
<th>Calc.</th>
<th>Normal mode description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZEKE(^a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0-0(^a)</td>
<td></td>
<td></td>
<td></td>
<td>Origin</td>
</tr>
<tr>
<td>135</td>
<td>137</td>
<td>(v_{22}^c)</td>
<td></td>
<td></td>
<td>Sym. Bz–Bz bend.</td>
</tr>
<tr>
<td>277</td>
<td>263</td>
<td>264</td>
<td>272</td>
<td>282</td>
<td>(v_{21}^c), (v_{18}^c)</td>
</tr>
<tr>
<td>400</td>
<td>366</td>
<td>(v_{16}^c)</td>
<td></td>
<td>424</td>
<td>(v_{21}^c), (v_{20}^c)</td>
</tr>
<tr>
<td>459</td>
<td>416</td>
<td>(v_{16}^c)</td>
<td></td>
<td>528</td>
<td>(v_{16}^c), (v_{24}^c)</td>
</tr>
<tr>
<td>526</td>
<td>537</td>
<td>(v_{11}^c)</td>
<td></td>
<td>791</td>
<td>(v_{11}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>791</td>
<td>790</td>
<td>786</td>
<td>787</td>
<td>862</td>
<td>(v_{10}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>910</td>
<td>915</td>
<td>931</td>
<td>968</td>
<td>1006</td>
<td>(v_{17}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>1050</td>
<td>977</td>
<td>(v_{1}^c)</td>
<td></td>
<td>1140</td>
<td>(v_{1}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>1140</td>
<td>1025</td>
<td>(v_{1}^c)</td>
<td></td>
<td>1152</td>
<td>(v_{1}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>1194</td>
<td>1183</td>
<td>(v_{10}^c)</td>
<td></td>
<td>1232</td>
<td>(v_{1}^c), (v_{19}^c)</td>
</tr>
<tr>
<td>1348</td>
<td>1338</td>
<td>(v_{10}^c)</td>
<td></td>
<td></td>
<td>(v_{10}^c), (v_{19}^c)</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) DFT (UB3LYP/LANL2DZ) not-scaled vibrational frequencies.
\(^b\) Raman spectroscopy (Ref. 36).
\(^c\) \(3d^2\text{-}R\alpha_n\), Rydberg transition (Ref. 34).
\(^d\) ZEKE spectroscopy (Ref. 26).
\(^e\) This work.
\(^f\) \(v_{1}−v_{20}\) Wilson numbering (Ref. 37) \(v_{21}−v_{22}\) skeletal vibrations (Ref. 34).
\(^g\) Symmetry species in \(D_{6h}\).

\(^h\) Accurately measured to be 44 090±3 cm\(^{-1}\). Vibrational frequencies of the Cr(Bz)\(_2\) cation are precisely measured and corresponding modes are assigned properly using the Franck-Condon analysis based on the DFT calculation. Since our spectrum is of high quality, it gives many newly found vibrational features which provide the detailed inter- and intramoiety vibrational structure of this important molecule. \textit{Ab initio} calculation at the level employed in this work was not satisfactory. High-level \textit{ab initio} calculations would be desirable for a more quantitative explanation of the experimental result.

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