Valence Electron Ionization Dynamics of Chromium by a Photoelectron Imaging Technique: $J^\pi$-Dependent State and Angular Distribution

Jeongmook Lee, Doo-Sik Ahn,* and Sang Kyu Kim*

Department of Chemistry (WCU), KAIST, Daejeon (305-701), Republic of Korea

Supporting Information

ABSTRACT: The photoionization of Cr at excited states is investigated using a velocity-map photoelectron imaging technique. Benzene chromium carbonyl or bis(η⁶-benzene) chromium was used as a precursor for the generation of excited Cr atoms. The a $^3S_2 \rightarrow x ^3P^0_3$ and a $^3D_3 \rightarrow y ^3D^0_2$ transitions are then employed for the preparation of resonant intermediate states in a two-color two-photon ionization process, in which an electronic configurational change from $3d^3(5D)4s^4p(1P^o)$ to $3d^4s^2(5P^o)$ occurs. The photoelectron kinetic energy distribution is found to be very sensitive to the ionization energy and the total angular momentum quantum number of the chromium ion ($J^\pi$). Anisotropy parameters associated with departing electrons also show significant variation depending on the energy and total angular momentum quantum number, suggesting that direct and/or indirect ionization should be quantum-mechanically mixed, manifesting the complicated nature of angular momentum couplings in the ionization continuum.

1. INTRODUCTION

Photoelectron angular distribution (PAD) provides important information about the nature of the quantum states involved in photoionization.¹ For alkali metal atoms, Berry et al. reported a complete study in which an angular momentum coupling model including radial dipole matrix elements and the relative phases of outgoing partial waves was successfully employed.²⁻⁷ Compared to alkali metal²⁻⁸ or alkaline earth metal atoms,⁹⁻¹² transition metals are intrinsically more complicated in terms of angular momentum coupling, clearly due to the existence of d-subshell electrons. Nonetheless, several beautiful studies have been carried out on several transition metals.⁹⁻¹² For instance, Weisshaar et al. reported state-resolved PADs and branching ratios in the two photon ionization of vanadium¹¹ and iron atoms. They found a strong correlation between the anisotropy parameters and the angular momentum coupling pattern. Several studies on the photoionization of chromium atom are also quite notable.¹³⁻¹⁹ Most previous transition metal studies, however, focused on the core–electron ionization process, in which the synchrotron radiation source is mainly used.¹⁶⁻¹⁹ The valence-electron ionization²⁰ and its photoelectron angular distribution have been less investigated thus far.

Here, we employed a photoelectron velocity-map imaging technique to measure the state-resolved PADs during the two-color two-photon ionization of Cr. For the generation of Cr in the gas phase, we photolyzed the transition metal complexes of benzene chromium carbonyl or bis(η⁶-benzene) chromium, as Armientrot et al. had initially employed for the generation of gas-phase metal atoms.²¹ The Cr atom is produced in many different quantum states. A specific atomic transition to the $^3P^0_3$ or $^3D^0_2$ state is exclusively selected here for the study of state-resolved ionization dynamics. The chromium cation eigenstates are identified by the kinetic energy of photoelectrons associated with the total angular momentum quantum number, $J^\pi$.¹⁰⁻¹² PADs and population branching ratios among $J^\pi$ are experimentally determined and their implications are discussed.

2. EXPERIMENT

The detailed experimental setup was described previously.²² Briefly, BCT (benzene chromium tricarbonyl) or BBC (bis(η⁶-benzene) chromium) (Aldrich) was heated to ∼130 °C in a small sample chamber, seeded in the Ar as a carrier gas, and expanded into a vacuum chamber through the orifice of a General Valve (Parker, 0.5 mm diameter) with a backing pressure of ∼2 atm. The molecular beam was skimmed (Beam Dynamics, 2 mm diameter) before it was perpendicularly intersected by two linearly polarized laser beams. The excitation laser ($\omega_1$) was the doubled output of a dye laser (Lumonics, Spectrummaster) pumped by the second harmonic output of a Nd:YAG laser (Continuum, Surelite), whereas the ionization laser ($\omega_2$) was generated by the frequency-doubling of the output of another dye laser (Lamda-Physik, Scanmate II) pumped by another Nd:YAG laser (Spectra-Physics, GCR-150). Two laser pulses were synchronized with the nozzle...
opening at 10 Hz and were spatiotemporally overlapped in counter-propagating manner.

In the two-color two-photon (\(\omega_1 + \omega_2\)) ionization experiment, the pulse energy of the excitation laser (\(\omega_1\)) was held below 10 \(\mu\)J to prevent the one-color two-photon ionization process. The photoelectron signal was practically absent when only one of two laser pulses was applied to the system. The Newton sphere of photoelectrons from the ionization of chromium was accelerated along the time-of-flight axis in the velocity mapping condition and was projected onto a position-sensitive detector equipped with microchannel plates and a P20 phosphor screen (Burle, 3040 FM CT, 40 mm diameter). The light emitted from the phosphor screen was monitored by a photomultiplier tube (PMT) to obtain the frequency-tuned excitation spectra. Images on the phosphor screen were taken by a charge-coupled device (CCD) camera (Sony XC-ST50, 768 \(\times\) 494 pixels) in conjunction with the IMACQ Megapixel acquisition program developed in the Suits’ group. Acquired images were reconstructed and analyzed using the basis-set expansion (BASEX) program.

3. RESULTS AND DISCUSSION

Low-lying excited-state chromium atoms are generated from the multiphoton dissociation of BCT at 298–301 nm (\(\omega_1\)). The nature of the excited quantum states of Cr is confirmed by photoelectron and photoion spectra taken as a function of the excitation wavelength (\(\omega_2\)) in the one-color two-photon excitation process (Figure 1). The two spectra are nearly identical to each other, indicating that photoelectrons are dominantly generated from the ionization of the excited chromium atom. Each peak in each spectrum is appropriately assigned on the basis of a comparison to well-established literature values for a number of transitions in Table S1 (Supporting Information). Specifically, atomic transitions of a \(5^S_f \rightarrow 3^P\) or a \(5^D_f \rightarrow 3^D\) intermediate states are also shown with proper assignments together with the statistical expectation of the Cr\(^{+}\) quantum states (\(6^D_{J'}\), where \(J'\) is the total angular momentum quantum number of the cation. Term energies associated with the final cationic states were precisely determined from the energetics involved in the ionization via \(5^S_2 \rightarrow 3^P\) or \(5^D_2 \rightarrow 3^D\) transitions (Table S2, Supporting Information). The intermediate state (x \(3^P\) or \(3^D\) mainly has the \(3d^44sp\) electron configuration (Table S3, Supporting Information). The core-conserving direct ionization of the \(3d^44sp(p^0) \rightarrow 3d^1(5D)4s(6D_{J'}) + e^-\) process seems to be the dominant ionizing mechanism. Branching ratios among different \(6^D_{J'}\) ion states during the ionization process via the \(3^P\) intermediate state are found to vary dramatically with the change of the ionization energy (\(\omega_2\)), as shown in Figure 3 and Table 1. At an ionization wavelength of 370.78 nm, where the kinetic energy of photoelectrons is as high as 0.95 eV, the \(J'\) distribution is estimated to be approximately 26:18:6:4 for \(6^D_3:6^D_2:6^D_1:6^D_0\). This is at least qualitatively consistent with the statistical expectation of 10:8:6:4 from the (2\(J' + 1\)) degeneracy factor though the \(6^D_3/2\) and \(6^D_2/2\) states are ~2.5 times more populated than predicted.

\[
E_{\text{int,ion}} = E_{\text{int,neutral}} + E_{\omega_1} + E_{\omega_2} - IP - eKE
\]
A statistical comparison, however, becomes less meaningful at $\omega_2 \sim 376$ nm as the relative ratio of $6D_{7/2}$ to $6D_{5/2}$ shows a large fluctuation over a minuscule energy range, as shown in Figure 3b–d. At an ionization wavelength of 384.282 nm, the ionization energy is not sufficient to access all $6D_{J+}$ ion states. Nonetheless, the fluctuation of the population with $J^+$ is clearly manifested, as shown in Figure 3e. The $J^+$-state distribution is found to be quite different for the ionization via $y 5D^0_2$, whereas the $6D_{7/2}$ state was found to be most populated at ionization wavelengths of 370.78, 376.042, 376.957 nm, whereas the relative populations among the other $6D_{J+}$ states at each ionization wavelength were found to vary significantly.

**Figure 3.** Raw photoelectron images (left) and $J^+$-state distributions (right) obtained from two-color two-photon ($\omega_1 + \omega_2$) excitation of Cr mediated by the $a 5S_2 \rightarrow x 5P^0_3$ transition ($\omega_1$) at ionization wavelengths ($\omega_2$) (a) 370.78, (b) 376.042, (c) 376.351, (d) 376.957, and (e) 384.282 nm. The double-headed arrow shows the polarization axes of the excitation and ionization lasers. The red vertical arrows in the spectra denote the maximum available internal energy at the given level of photon energy.

**Figure 4.** Raw photoelectron images (left) and $J^+$-state distributions (right) obtained from two-color two-photon ($\omega_1 + \omega_2$) excitation of Cr mediated by the $a 5D_3 \rightarrow y 5D^0_2$ transition ($\omega_1$) at ionization wavelengths ($\omega_2$) (a) 370.78, (b) 376.042, (c) 376.351, (d) 376.957, and (e) 384.282 nm. The double-headed arrow shows the polarization axes of the excitation and ionization lasers. The red vertical arrow in the spectra denotes the maximum available internal energy at the given level of photon energy.

**Table 1.** Branching Ratios over the Final Ion States from the Ionization of Chromium Using the Transition of $a 5S_2 \rightarrow x 5P^0_3$

<table>
<thead>
<tr>
<th>excitation wavelength (nm)</th>
<th>ionization wavelength (nm)</th>
<th>$^6D_{9/2}$</th>
<th>$^6D_{7/2}$</th>
<th>$^6D_{5/2}$</th>
<th>$^6D_{3/2}$</th>
<th>$^6D_{1/2}$</th>
</tr>
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<tr>
<td>298.868</td>
<td>370.78</td>
<td>48.3</td>
<td>34.0</td>
<td>10.3</td>
<td>7.4</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>376.042</td>
<td>41.6</td>
<td>25.9</td>
<td>25.7</td>
<td>6.8</td>
<td>~0</td>
</tr>
<tr>
<td>376.351</td>
<td></td>
<td>46.1</td>
<td>16.4</td>
<td>31.2</td>
<td>6.3</td>
<td>~0</td>
</tr>
<tr>
<td>376.957</td>
<td></td>
<td>49.8</td>
<td>17.9</td>
<td>28.3</td>
<td>4.0</td>
<td>~0</td>
</tr>
</tbody>
</table>

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be quite different. Interestingly, at $\omega = 384.282$ nm, the $^6D_{1/2}$ state population is most pronounced whereas the $^6D_{9/2}$ state was almost completely diminished, as shown in Figure 4e. The experimental finding that the $J'$-state distribution is highly sensitive to the ionization energy strongly indicates that phases of partial waves may interfere to result in a complicated intensity pattern in the photoelectron spectrum.

As expected from the energy-dependent variation of the $J'$-state distribution, the photoelectron angular distribution (PAD) also shows dramatic variations depending on the $^6D_{J'\sigma}$ state of the chromium ion. Generally, PAD for two-photon ionization using the linearly polarized light is described by the following equation:\textsuperscript{27--29}

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta)]$$

(2)

Here, $\theta$ is the angle between the direction of the outgoing electron and the electric vector of the linearly polarized light, $\sigma$ is the total ionization cross section, $P_2(\cos \theta)$ and $P_4(\cos \theta)$ are respectively the second and fourth Legendre polynomials, and $\beta_i$ is the anisotropy parameter. In Figures 5 and 6, PADs extracted from the photoelectron images are plotted in the polar coordinate with the corresponding fits using eq 2 with the $\beta_2$ and $\beta_4$ values listed in Table 2. Generally, PADs from the ionization via the $^1P_\ell$ result in large positive $\beta_2$ and $\beta_4$ values as the ionization converges to the $^6D_{9/2}$, $^6D_{5/2}$ or $^6D_{3/2}$ state whereas PAD associated with $^4D_{7/2}$ gives smaller positive $\beta_2$ and negative $\beta_4$ values. Large $\beta_2$ values observed in PADs from the $^1P_3$ ($L = 1$) intermediate state simply imply that the $d$-partial wave is heavily involved in the outgoing electron wave function. The relative phase of the $s$- and $d$-partial waves of the departing electron, according to the $\Delta l = \pm 1$ selection rule,\textsuperscript{2} therefore strongly depends on the final quantum state of the cation. PAD shows a large fluctuation of anisotropy parameters also with the change of the ionization energy, as clearly shown in Figure 5. During ionization via the $^1D_{3/2}$ state, on the other hand, PADs give very small $\beta_4$ values for all $J'$-states, indicating that the $p$-partial wave is dominant for the outgoing electron, which is again consistent with the $\Delta l = \pm 1$ selection rule, as $p$ and $f$ partial waves are expected from the $^1D_{3/2}$ state ($L = 2$). A large fluctuation of $\beta_2$ is also observed as a function of the ionization energy, as shown in Figure 6. It is noteworthy that $\beta_2$ becomes negative for photoelectrons associated with $^6D_{3/2}$ or $^6D_{1/2}$ at several ionization wavelengths. This, presumably results from the destructive interferences of partial waves with respect to the polarization vector axis, as observed for PAD from the oxygen anion.\textsuperscript{30,31}

It appears to be a formidable task to determine the ionization dynamics of Cr fully, as the electronic structure of the transition metal and interferences among many different partial waves are highly complicated due to the strong spin–orbit coupling. Electronic configurational mixing is one of the obstacles to understanding the interference mechanism acting during ionization process. For instance, the electronic characteristics of the $^1P_3$ or $^3D_2$ are scarcely described by the zeroth-order electronic configuration. The $^1P_3$ state consists of $\sim 55\%$ of $3d^2(4s4p^2(1P^0))$ and $\sim 8\%$ of $3d^3(4p^4)$ configurations whereas the remaining 37\% is not yet characterized.\textsuperscript{26} Similarly, the $^3D_2$ state is regarded as a mixture of $\sim 56\%$ of $3d^2(4s4p^4(1P^0))$ and $\sim 13\%$ of $3d^3(4p^4)$ configurations.\textsuperscript{26} A quantitative understanding of the Cr photionization dynamics thus requires multichannel quantum defect (MCQT) calculations based on a more comprehensive characterization of the quantum states involved in the optical excitation and ionization processed. In this report, we have not attempted theoretical calculations.

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**Figure 6.** Polar plots of photoelectrons associated with different $J'$ states of a chromium ion at various ionization wavelengths of (a) 370.78, (b) 376.042, (c) 376.351, (d) 376.957, and (e) 384.282 nm during two-color two-photon ionization via the $^1D_{3/2}$ intermediate state. The polarization axes of the ionization and excitation laser pulses are both vertical. The solid lines are fits to the experiment results (dots) from eq 2 with the $\beta_2$ and $\beta_4$ values listed in Table 2.
4. CONCLUSION

Excited chromium atoms are generated by the photolysis of benzene chromium carbonyl or bis(η⁶-benzene)chromium at 298–301 nm. Atomic transitions a 5S₂ → x 5P° and a 5D₃ → y 6D°₂ are employed to prepare specific intermediate states during the two-color two-photon ionization of Cr. The photoelectron kinetic energy and angular distributions associated with the final chromium cationic states are obtained by a velocity-map imaging technique. The ionization dynamics vary quite dramatically as the total ionization energy changes in terms of the intensity distributions among different J' states at the final 6D_J level and in terms of the phase differences of the outgoing partial waves, resulting in large fluctuations of β₂ and β₄ values over a small ionization energy range. Furthermore, the ionization processes via the x 5P° and y 6D°₂ intermediate states are very different in terms of the J'-dependent state and angular distributions. This experimental work, although it lacks a rigorous theoretical analysis, provides important information for regarding our understanding of the complex ionization dynamics of transition metals in the gas phase.

### ASSOCIATED CONTENT

**Supporting Information**

Tables summarizing the assignments of each peak in photoion spectrum in Figure 1, observed ion internal energy of final ion states from each ionization process, and electronic configurations, term symbols, energy levels, and leading percentage of each state. This information is available free of charge via the Internet at http://pubs.acs.org

**AUTHOR INFORMATION**

Corresponding Author

*Fax: (+82) 82-42-350-2810. Tel: (+82)-42-350-2843. E-mail: sangkyukim@kaist.ac.kr.*

Present Address

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.

Notes

The authors declare no competing financial interest.

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### REFERENCES


