Predissociation Dynamics of Br$_2$ in the [^{2}\Pi_{1/2}]_{c}5d; 0^+_g$ and [^{2}\Pi_{3/2}]_{c}6d; 0^+_g$ Rydberg States by Velocity Map Imaging Study

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ABSTRACT: We investigated the predissociation dynamics from the [^{2}\Pi_{1/2}]_{c}5d; 0^+_g$ and [^{2}\Pi_{3/2}]_{c}6d; 0^+_g$ Rydberg states of Br$_2$ using the velocity map imaging technique. Two-dimensional scattering images of the fragmented Br$^+$ exhibited an isotropic feature upon the excitation of these Rydberg states. Analysis of the total kinetic energy release suggested the existence of the predissociation pathways to the dissociation limits of Br(5s, 4p, $^2P_{3/2}$) + Br(4p, $^2P_{1/2}$) and Br(5s, $^4P_{5/2}$) + Br(4p, $^2P_{3/2}$) via the 0$^+_g$ ion-pair states that interact with the lower and/or excited-core Rydberg states lying at long internuclear distance regions thorough the avoided crossing.

1. INTRODUCTION

Since the widespread use of tunable dye lasers in the late 1970s, the development of powerful spectroscopic techniques, such as laser-induced fluorescence (LIF),$^1$ coherent anti-Stokes Raman spectroscopy (CARS)$^2$ and resonance-enhanced multiphoton ionization (REMPI),$^3$ has enabled us to investigate in detail the quantum state distributions of the internal states (rotational, vibrational, and electronic) of a wide range of products, resulting in dramatic advances in reaction dynamics research. However, spectroscopic approaches, in other words, measurements on the frequency axis, have the disadvantage that information about the translational motion (recoil velocity and anisotropy) is difficult to obtain, which is often essential for understanding reaction dynamics.

The ion imaging technique has been developed by Chandler and Houston to comprehensively elucidate the reaction mechanism, including information such as rate distribution and anisotropy parameters.$^4,5$ In contrast to spectroscopic methods, ion imaging has a tremendous advantage in which all of the information including two-dimensional (2D) images, velocities, and angular distributions associated with chemical reactions can be obtained.$^6$ Since then, techniques concerning ion imaging methods have been developed for a long time. As a result, the resolution of the images has been greatly improved,$^7$ and image processing and analysis methods have been well established.$^8$ The ion imaging technique is now recognized to be of high value in the field of chemical reaction dynamics.

Diatomic molecules, such as halogen molecules, are considered benchmarks for the study of reaction dynamics in the excited states due to their simple structures and have been studied both experimentally and theoretically for many years. In particular, the direct photodissociation and predissociation dynamics of the lower-valence electronic states of halogens have long been the subject of intensive research.$^9,10$ However, in the higher-energy region, where a number of highly excited states such as the Rydberg states exist, the density of states becomes high and the perturbations between these states are extremely complicated. In this energy region, there are many dark states with relatively short lifetimes due to the presence of the reaction processes such as predissociation and autoionization. For example, spectroscopic analysis of the non-fluorescent Rydberg states of the bromine molecule, Br$_2$, has been performed by Donovan et al.$^{11}$ They have analyzed the Rydberg series of $^{79}$Br$_2$ using resonance-enhanced multiphoton ionization (REMPI) spectroscopy and reported the spectra by monitoring $^{79}$Br$^+$ ions and $^{79}$Br$^+$ ions. However, the mechanism for production of Br$^+$ has not been discussed. The results show that the $^{79}$Br$^+$ signal is dominant in the Rydberg state with two-photon energy of around 76,000 cm$^{-1}$, suggesting that dissociation occurs more efficiently than in the other low-energy Rydberg states. Since the dissociation limit of Br$_2$ into Br$^+$(5s, $^4P_{5/2}$) + Br(4p, $^2P_{3/2}$) is $\sim$79,331 cm$^{-1}$ from the lowest rovibrational level of the $X^3\Sigma_g^+$ ground state,$^{12}$ the

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dissociation channel to that limit might be observed from electronic states located in this energy region.

Rapid expansion of computational resources in recent years has made it possible to construct an overall picture of the potential energy of relatively small molecules. In particular, high-precision quantum chemical calculations of valence excited states, including ion-pair states of halogen molecules with many electrons, have been extensively performed, and calculation results with an accuracy satisfactorily enough to reproduce experimental data have been reported. However, quantum chemical calculations for highly excited levels, such as Rydberg states, located in the high-energy region are still challenging. One of the reasons that hinder the development of calculations is the lack of experimental data to be compared with the calculation results. In this respect, experimental investigations on the electronic structure and reaction dynamics in the high-energy region would be also indispensable for the future improvement of theoretical techniques.

In the present work, the dissociation processes in the $^3\Pi_{1/2},5d; ^5\Pi_{3/2},6d; ^6\Pi_{5/2}$ Rydberg states at excitation energies of around 81,000 cm$^{-1}$ were investigated using the velocity map imaging (VMI) method.

2. EXPERIMENTAL SECTION

Experiments described in this work have been performed with an Eppink–Parker-type velocity map imaging (VMI) system. The schematic of the experimental setup is shown in Figure 1. The apparatus consists of two differentially pumped chambers, namely, for molecular beam source and ionization/VMI detection. The source chamber is evacuated by a 2400 L/s turbo molecular pump (Osaka Vacuum, TG2400F), while the ionization/VMI chamber is equipped with an 1100 L/s turbo molecular pump (Osaka Vacuum, TG1100F). Each turbo molecular pump was backed up by 35 L/s scroll pumps (Mizutani, K-35) and a 2400 L/s turbo molecular pump (Osaka Vacuum, TG2400F). A molecular pump was backed up by the third harmonic output of a Q-switched Nd$^3$:YAG laser (Continuum, Surelite II) operating at 10 Hz was used as the excitation/ionization light source. The UV laser power and pulse width were typically $\sim$0.05 mJ/pulse and $\sim$7 ns, respectively. UV laser pulse was focused by an $f = 170$ mm lens and introduced at the interaction region between the repeller and extractor electrodes in the VMI chamber.

The product ions are collinearly accelerated by a DC electric field into the 45 cm long flight region and detected by a chevron-type 42 mm imaging MCP detector (Hamamatsu Photonics, ORCA-spark) and stored in a PC using image acquisition and accumulation software (Hamamatsu Photonics, HiPic 9). Camera frames were accumulated for 60,000 shots to form a scattering image. Corrections for the radial distribution and translational energy of the fragment ions were performed by acquiring a photodissociation image of O$_2$ at around 225.655 nm.

3. RESULTS AND DISCUSSION

3.1. Excitation of the Rydberg States of Br$_2$. Rydberg states of Br$_2$ were excited from the $X^1\Sigma_g^+$ ground state by one-color two-photon absorption. Figure 2 shows the mass spectrum obtained when the two-photon wavenumber was adjusted to be $\sim$81,405 cm$^{-1}$. The mass peak group at around $m/z = 160$ was attributed to Br$_2^+$, which has three isotopes,
mass channels, respectively. Four peaks are observed in the 81,000–81,500 cm⁻¹ region, which are assigned to the transition to the [3Π_{1/2}],5d; 0⁺ (ν = 0), [3Π_{3/2}],6d; 2⁺ (ν = 2), [3Π_{3/2}],6d; 0⁺ (ν = 2), and [3Π_{1/2}],5d; 0⁺ (ν = 1) Rydberg states from the lower wavenumber side.

The Br⁺ cation is undoubtedly generated from the subsequent one-photon absorption after two-photon excitation to the Rydberg state from the X 1Σ⁺ ground state, i.e.,

excitation: Br₂(X) + 2hν → Br₂(Ry)

ionization: Br₂(Ry) + hν → Br⁺

Though the intensity ratios differ, the fact that a similar REMPI spectrum with the same transition wavenumbers is recorded when the 79Br⁺ mass channel was monitored indicates that the dissociation of Br₂ is occurring within the laser pulse width in the Rydberg states. Although there are several possible processes for the formation of Br⁺, the following process is most likely in this study.

predissociation: Br₂(Ry) → Br⁺ + Br

ionization: Br⁺ + hν → Br⁺

3.2. Velocity Map Images. The scattering image of 79Br⁺ was acquired by applying a fast, high-voltage pulse, ∼100 ns, which is much shorter than the difference between 79Br⁺ and 81Br⁺ in the arrival time to the MCP. As mentioned before, the transition wavenumbers of the three isotopes of Br₂ are very close to each other. At the transition wavenumbers used in this study, the excitation of 79Br₂ is dominant with simultaneous minor contributions from 81Br⁺Br and 83Br₂. Therefore, the ion image obtained here is not only due to the dissociated fragment from pure 79Br₂, although the interference of minor species is not critical enough to hamper the derivation of parameters such as translational energy. Figure 4a,b shows the fragmented Br⁺ ion images obtained by the excitation to the [3Π_{1/2}],5d; 0⁺ (ν = 1) and [3Π_{3/2}],6d; 0⁺ (ν = 2) Rydberg states, respectively. The left side of each picture is the raw image, while the right side is the Abel-inverted image reconstructed by the polar basis function expansion (pBASEX) method. A broad signal was observed at the center of the image in Figure 4. This signal centered at TKER ≈ 0 is thought to originate from the dissociation of (Br₂)₂ clusters possibly produced in a supersonic jet, which is not the main subject of this paper. In both Rydberg states, isotropic rings (anisotropy parameter β ≈ 0) with two different kinetic energies were observed (C1 and C2 in Figure 4). The radial intensity distributions were determined by integrating the obtained images over the entire angle, as shown in Figure 5. The left side (a) of Figure 5 corresponds to the [3Π_{1/2}],5d; 0⁺ (ν = 1) state, and the right side (b) corresponds to the [3Π_{3/2}],6d; 0⁺ (ν = 2) state. The solid black traces correspond to the experimental total kinetic energy release (TKER). The recoil energy was determined using the distance from the center of the image to the ring corresponding to each dissociation path and the time of flight for the detection of 79Br⁺ in the TOF-MS spectrum (Figure 2).

TKER can be determined using the two-photon energy used for excitation to the Rydberg state, the binding energy ΔE_{bind}(X),¹ and internal energy E_{int} in the X 1Σ⁺ ground state of the Br₂ molecule, and the energy E_d of the electronic state of the excited Br atom correlated to the dissociation limit as follows

TKER = 2hν − ΔE_{bind}(X) − E_d + E_{int}

In this study, the internal energy E_{int} is assumed to be zero because the experiment was conducted under supersonic jet-cooled conditions. The rotational temperature of Br₂ in the molecular beam produced in this experiment is about 25 K (see Section 3.3). The internal energy (rotational energy) at this temperature is estimated to be approximately 9 cm⁻¹ (∼10⁻³ eV), which is negligibly small. Each of the two observed peaks can be well reproduced by the calculated values (vertical blue dashed lines) assuming the following dissociation and ionization pathways.¹²
dissociation, C1:
\[ \text{Br}_2(\text{Ry}) \rightarrow \text{Br}^*(5s, 4P_{3/2}) + \text{Br}(4p, 2P_{3/2}) \]  \hspace{1cm} (6a)

dissociation, C2:
\[ \text{Br}_2(\text{Ry}) \rightarrow \text{Br}^*(5s, 4P_{1/2}) + \text{Br}(4p, 2P_{1/2}) \]  \hspace{1cm} (6b)

ionization: \[ \text{Br}^*(5s, 4P_{5/2, 3/2}) + h\nu \rightarrow \text{Br}^+ \]  \hspace{1cm} (6c)

The calculated kinetic energy of the dissociated fragment from the \[^2\Pi_{1/2}], 5d; 0^+_g (\nu = 1)\) state is 0.258 eV for Channel 1 and 0.0753 eV for Channel 2. For the \[^2\Pi_{3/2}], 6d; 0^+_g (\nu = 2)\) state, TKERs of 0.249 and 0.0664 eV are expected for C1 and C2, respectively. The ionization energy of Br is \(IE(\text{Br}) = 95284.8 \text{ cm}^{-1}\) and the energies of \(\text{Br}(5s, 4P_{5/2})\) and \(\text{Br}(5s, 4P_{3/2})\) from the ground state of \(\text{Br}(4p, 2P_{3/2})\) are 63436.5 and 64907.2 cm\(^{-1}\), respectively. The one-photon energies of the UV laser are 40702.5 cm\(^{-1}\) for the excitation to \[^2\Pi_{1/2}], 5d; 0^+_g (\nu = 1)\) and 40666.5 cm\(^{-1}\) for \[^2\Pi_{3/2}], 6d; 0^+_g (\nu = 2)\), which are sufficient for one-photon ionization of the \(\text{Br}(5s)\) atoms. Figure 6 illustrates the dissociation scheme of \(\text{Br}_2\) excited to the \[^2\Pi_{1/2}], 5d; 0^+_g\) and \[^2\Pi_{3/2}], 6d; 0^+_g\) Rydberg states. The two dissociation paths identified in this study are energetically correlated to the lowest \((5s, 4P_{5/2})\) and second-lowest \((5s, 4P_{3/2})\) Rydberg states.
4P\textsubscript{3/2}) excited Rydberg configurations of Br atoms. The predissociation limits correlating the ground state (4P, 3P\textsubscript{3/2}) and its spin-orbit excited state (4P, 3P\textsubscript{1/2}) are located in much lower energy regions and the laser wavelength used in this study is insufficient for one-photon ionization from 4P, 3P\textsubscript{3/2}, and 3P\textsubscript{1/2}. Therefore, even if the dissociation pathways to the lower energy limits exist, it will not be observed in the ion images. However, since the repulsive walls of the valence states are independent of the \([\tilde{\Sigma}_{u,1/2}], 6d; 0^+_g\) and \([\tilde{\Sigma}_{u,1/2}], 6d; 0^+_h\) Rydberg states and there is no avoided crossing, such a dissociation process is unlikely to occur.

3.3. Mechanism of Predissociation from the Rydberg States of Br\textsubscript{2}. The \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) and \([\tilde{\Pi}_{3/2}], 6d; 0^+_g\) Rydberg states converge with the ground state of the ion core (X \(\tilde{\Pi}_{1/2, 3/2}\) of Br\textsuperscript{+}) and exist in the region of shorter internuclear distances than the ground state of neutral Br\textsubscript{2}. The 5s Rydberg states correlated with the dissociation limit Br\textsuperscript{+}(5s) + Br(4p) exist in the lower-energy region. In general, the potential energy curves of the Rydberg states are similar to each other, so in the region around the equilibrium internuclear distance, the interaction of these lower Rydberg states with the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) and \([\tilde{\Pi}_{3/2}], 6d; 0^+_g\) Rydberg states seems to be negligible. However, the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e/\tilde{\Pi}_{3/2}], 6d; 0^+_g\) states may be connected with lower 0\textsuperscript{+} \(\text{Rydberg states by a relay of the 0^+_h \text{ ion-pair states, as shown in Figure 7. It is known that the}

![Figure 7](https://pubs.acs.org/journal/acsodf)

higher vibrational levels of the ion-pair states of halogen molecules interact with the Rydberg states at a shorter internuclear distance. Kalemos et al. reported several avoided crossings on the inner and outer part of the E 0\textsuperscript{+} \(\text{Br}_2 \) ion-pair state of \(I_2\) by \textit{ab initio} multireference configuration interaction methods.\textsuperscript{19} Although the interaction of the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) and \([\tilde{\Pi}_{3/2}], 6d; 0^+_g\) Rydberg states with the ion-pair states of Br\textsubscript{2} has not been studied so far, the mixing of the ion-pair and Rydberg states is a commonly observed phenomenon.\textsuperscript{20} In Figure 7, the potential of the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) Rydberg state is drawn using the parameter of the X \(\tilde{\Pi}_{1/2}\) state of Br\textsuperscript{+} cation.\textsuperscript{21} Although there may be several Rydberg states correlated to Br\textsuperscript{+}(5s) + Br(4p), only the 5s; 0\textsuperscript{+} Rydberg state is illustrated with a blue curve to avoid complexity. Br\textsubscript{2} has four 0\textsuperscript{+} ion-pair states: \(E 0^+_e (\tilde{\Pi}_3), f 0^+_e (\tilde{\Pi}_3), f 0^+_g (\tilde{\Pi}_2), \) and \(0^+_g (\tilde{\Pi}_2)\). Among them, the 0\textsuperscript{+} \(\text{Br}_2\) state has not been observed experimentally while \textit{ab initio} calculation estimates its location in an energy region about \(79,000 \text{ cm}^{-1}\) above the \(X^1\Sigma^+\) ground state.\textsuperscript{22} Since the ion-pair states have a longer internuclear distance than the Rydberg states, the interaction of the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e/\tilde{\Pi}_{3/2}], 6d; 0^+_g\) states with the 0\textsuperscript{+} \(\text{Br}_2\) state is unlikely. The potential minima of the \(E 0^+_e (\tilde{\Pi}_3), f 0^+_e (\tilde{\Pi}_3), \) and \(f 0^+_g (\tilde{\Pi}_2)\) states are located at \(\sim 97,777.9, \sim 53,101.7, \) and \(\sim 65,512.0 \text{ cm}^{-1}\) from the ground state, respectively, which are lower than the energy region surveyed in this study. The highly vibrational levels of these ion-pair states have not been experimentally investigated, and an accurate potential energy curve cannot be drawn over a wide range of internuclear distances. Therefore, in the potential energy curves shown in Figure 7, the \(E 0^+_e (\tilde{\Pi}_3)\) potential was adopted for the experimentally investigated region (near the potential minimum) and the inner potential wall was adjusted to reproduce the \(E 0^+_e (\tilde{\Pi}_3)\) potential in the low-energy region based on the results of \textit{ab initio} calculation.\textsuperscript{22} Since the potential energy curves of the ion-pair states have similar shapes to each other, we referred to the known parameters of the \(D 0^+_e (\tilde{\Pi}_3)\) state of Br\textsubscript{2} for the long-range Coulomb potential dominating the outer branch of the ion-pair potential energy curves.\textsuperscript{23} As a result, the \(E 0^+_e (\tilde{\Pi}_3)\) state intersects the asymptote to the dissociation limits observed in the current experiment, Br\textsuperscript{+}(5s, 4P\textsubscript{5/2, 3/2}) + Br(4p, 3P\textsubscript{3/2}), at \(\sim 38\) and \(\sim 26 \text{ Å}, \) respectively. The \(f 0^+_g (\tilde{\Pi}_2)\) states intersect the asymptote at \(\sim 18\) and \(\sim 15 \text{ Å}\) and at \(\sim 8\) and \(\sim 7 \text{ Å}\) for the \(f 0^+_g (\tilde{\Pi}_2)\) state, respectively.

On the other hand, it is known that halogen molecules have shallow Rydberg states (excited-core Rydberg states) in the long internuclear distance region. For example, the \([\tilde{\Sigma}_{u,1/2}], 6s; 0^+_e\) and \([\tilde{\Sigma}_{u,1/2}], 6s; 0^+_g\) states of the \(I_2\) molecule, correlated with the \(1^1(P_{3/2}) + 1^1(6s, 4p_{3/2}) + 1^1(P_{3/2}) + 1^1(6s, 5p_{3/2})\) dissociation limits, respectively, have been identified as an excited-core Rydberg state by the optical-triple resonance spectroscopy via the ion-pair states.\textsuperscript{24,25} Although no spectroscopic analysis of such shallow Rydberg states is currently available for the Br\textsubscript{2} molecule, the shallow excited-core \(0^+_e\) Rydberg states may exist in the same energy region as the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) and \([\tilde{\Pi}_{3/2}], 6d; 0^+_g\) Rydberg states. The energetic positional relationship and structure of the electronic state of Br\textsubscript{2} are very similar to those of \(I_2\). For various valence, Rydberg, and ion-pair states, the \(I_2\) potential agrees well with the Br\textsubscript{2} potential if the energy is multiplied by a factor of 1.135 and the internuclear distance by a factor of 0.86 relative to the ground-state dissociation limit. The excited-core Rydberg state of Br\textsubscript{2} in Figure 7 is drawn by modifying the potential curves reported for \(I_2\). While the Br\textsubscript{2} molecule is most likely to dissociate via the Rydberg ion-pair perturbation at the inner wall as discussed earlier, the possibility of the ion-pair-excited-core Rydberg and/or ion-pair-lower Rydberg perturbation at the relatively longer internuclear distances may not be discriminated. There seems to be no significant difference in the intensity ratios of C1 and C2, C2/C1, of 0.45 ± 0.05 and 0.31 ± 0.21 for the \([\tilde{\Pi}_{1/2}], 5d; 0^+_e\) and \([\tilde{\Pi}_{3/2}], 6d; 0^+_g\) states, respectively. The value of C2/C1 may be correlated to the magnitude of the interactions between the intermediate ion-pair state and the excited-core states; similar intensity ratios for
the $^{[\Pi_{2/3}]_{5d}}$, $^{[\Pi_{1/3}]_{6d}}$, and $^{[\Pi_{2/3}]_{6d}}$ states may imply the presence of an identical dissociation mechanism.

Next, we discuss the anisotropy of the obtained scattering distribution. As mentioned above, two isotropic rings, corresponding to dissociation paths (6a) and (6b) with different kinetic energies, were observed clearly in the experimental images. Since the rotational constants of the $^{[\Pi_{2/3}]_{5d}}$, $^{[\Pi_{1/3}]_{6d}}$, and $^{[\Pi_{2/3}]_{6d}}$ Rydberg states have not been reported, the rotational contours of the REMPI spectra were analyzed by the Pgor program, assuming the same rotational constant as the $^{[\Pi_{2/3}]_{4d}}$ Rydberg state. The rotational temperature was found to be about 2.5 K. Assuming Boltzmann distribution at this rotational temperature, the rotational quantum number $J_{\text{max}}$ giving the maximum population, is estimated to be about 10. Thus, the rotational period of a molecule in the Rydberg states shall be presumed to be approximately 20 ps at $J = 10$. On the other hand, an obvious line broadening in the rotational contour of the REMPI spectrum was seen. The linewidth of the dye laser used in the experiment, determined from the measurement of the fringe pattern of a Fabry–Perot Etalon, was $\sim 0.15$ cm$^{-1}$ for the fundamental (visible) output. Considering that the linewidth increases by a factor of $\sqrt{2}$ upon second harmonics generation, the resolution of the spectrum is expected to be about 0.21 cm$^{-1}$. Assuming this laser linewidth, the homogeneous width (lifetime width) estimated from the profile simulation is $\sim 0.5$ cm$^{-1}$, which corresponds to 10 ps for the lifetime of the excited states. Therefore, in the $^{[\Pi_{2/3}]_{5d}}$, $^{[\Pi_{1/3}]_{6d}}$, and $^{[\Pi_{2/3}]_{6d}}$ Rydberg states, the predissociation process proceeds on a time scale comparable to or shorter than the rotational period. In such cases, the angular distribution of fragments is expected to show anisotropic behavior. In general, in photodissociation of diatomic molecules, should the molecule rotate before dissociation, the degree of correlation between the electric field vector of the light and the fragment recoil direction will be lowered but not completely to zero. The limiting values for anisotropy parameters for parallel and perpendicular transitions are $\beta_{\parallel} = 0.5$ and $\beta_{\perp} = -0.25$, respectively. Therefore, the anisotropy of the observed images in the present work cannot be interpreted from the perspective of the lifetime of the excited state. One possible explanation for the isotropic pattern in Figure 4 despite the short lifetime in the Rydberg state is that two-photon absorption occurs through the inner walls of various valence states lying in the one-photon energy region. Current experiments do not allow us to confirm whether the two-photon excitation to the Rydberg state occurs under nonresonance or via a sequence of two steps. In the latter case, $\Omega = 0$ or $\Omega_1$ valence states can behave as intermediate states. Dixon derived expressions for recoil anisotropy following multiphoton processes via near-resonant intermediate states.

Ab initio calculations have revealed the existence of repulsive walls of various valence states of Br$_2$ in the one-photon energy region in this experiment, and indeed, the corresponding weak absorption has been observed. The presence of such valence states may be responsible for the isotropy of fragments produced by the predissociation in the Rydberg state. In this study, we have not observed a direct dissociation process in the valence states following one-photon absorption, but dissociative fragments in the one-photon energy region have been observed upon Rydberg state excitation of the iodine molecule. A similar excitation/predissociation scheme may apply for the Rydberg state of Br$_2$.

Another possibility is the involvement of relatively long-lived ($\sim$ns) ion-pair states in the dissociation pathway. It is possible that dissociating molecules are trapped in the bound state for longer than the rotational period, resulting in the loss of anisotropy of the final fragments.

4. CONCLUSIONS

In this study, velocity map imaging of the charged photofragments technique was applied to study the predissociation dynamics in the $^{[\Pi_{2/3}]_{5d}}$, $^{[\Pi_{1/3}]_{6d}}$, and $^{[\Pi_{2/3}]_{6d}}$ Rydberg states of Br$_2$. For each Rydberg state, two isotropic fragment images with different kinetic energies were observed. Analysis of the distribution of the total kinetic energy release indicates that these two dissociation paths originate from the predissociation paths of Br$_2$(Ry) → Br$^+$(5s, $^3P_{3/2}$) + Br(4p, $^3P_{3/2}$) and Br$_2$(Ry) → Br$^+$(5s, $^3P_{3/2}$) + Br(4p, $^3P_{3/2}$). These dissociation processes are thought to be mediated by the $^{[\Pi_{2/3}]_{6d}}$ ion-pair and lower and/or excited-core Rydberg states, which are expected to exist at longer internuclear distances. According to the analysis of REMPI spectra, the lifetime of the excited Rydberg state is about 10 ps, which is comparable to or shorter than the rotational period of the excited molecule. It can be interpreted that two-photon excitation is a sequential process via repulsive walls of various valence states, and the anisotropy is averaged out, resulting in an isotropic fragment image. The analysis of perturbations between the ion-pair states and the Rydberg states and collaboration with theoretical researchers will be necessary to further investigate the predissociation dynamics of the Rydberg states of Br$_2$.

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