Energy Transfer in the $2_u$ ($^1D_2$) Ion-Pair State of I$_2$ by Inelastic Collisions with Noble Gas Atoms

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ABSTRACT: We investigated the energy transfer in the $2_u$ ($^1D_2$) ion-pair state of I$_2$ by collision with noble gas atoms, Ar, Kr, and Xe, using an optical–optical double resonance/fluorescence detection technique. By analyzing the temporal profiles of the emission from the laser-excited $2_u$ ($^1D_2$) state at various noble gas pressures, the quenching rate constants $k_{q,Rg}$ were determined to be $(4.55 \pm 0.42) \times 10^{-10}$, $(4.23 \pm 0.11) \times 10^{-10}$, and $(6.83 \pm 0.16) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for quenching by Ar, Kr, and Xe, respectively. The $2_u$ ($^1D_2$) ion-pair state, lying in the vicinity of the $2_u$ ($^1D_2$) state, was identified as a destination state by collision with Ar and Kr. Collision with Xe provided a new reactive pathway forming the excimer XeI($^2B_1$). The rate constants were determined to be $k_{q,Xe}$ $(9.61 \pm 0.63) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{q,Kr}$ $(4.87 \pm 0.34) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the formation of the $2_u$ ($^1D_2$) state by collision with Ar and Kr, respectively, and $k_{q,Xe}$ $(6.55 \pm 0.19) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the formation of XeI($^2B_1$). The collisional cross sections calculated from the quenching rate constants were considerably larger than the molecular size, owing to the harpoon mechanism.

1. INTRODUCTION

The ion-pair states of halogen molecules are electronically excited charge-transfer states that correlate to positive and negative atomic ion pairs at the dissociation limits. In the I$_2$ molecule, a total of 20 ion-pair states are known, which are classified into four groups, or clusters, corresponding to the electronic states of $\Gamma$’ (P$_3/2$, P$_1/2$, 1D$_2$, 1S$_0$) + $\Gamma$’ (1S$_0$). Spectroscopic investigations of the ion-pair states have been actively carried out along with the establishment of laser excitation techniques. In particular, the development of the perturbation-facilitated optical–optical double resonance method has greatly advanced the study of ion-pair states, in which the two-step excitation is performed with the lower valence state as the intermediate state enabled the quantum-state selective excitation of the ion-pair states with large equilibrium internuclear distances. The development of these experimental techniques has provided rich spectroscopic parameters of ion-pair states, and their spectral features have been clarified in detail. Notable characteristics are that ion-pair states belonging to the same group are located energetically close to each other and that they have a strongly bounded potential curve with a longer equilibrium internuclear distance than that of the valence states.

Halogen molecules in the electronically excited states were known to exhibit a variety of curious radiative as well as nonradiative processes. For example, when the ICl molecule is excited to the $^3\Pi$ state in the gas phase, it undergoes an addition reaction with acetylene. This property has been used for the isotope separation of $^{35}$Cl and $^{37}$Cl. From our recent study on the ion-pair excited states of homonuclear halogen molecules, we successfully identified the coexistence of an optical process called amplified spontaneous emission (ASE) with fluorescence. The generation of ASE between the excited states, so far reported on a few molecular systems like NO and NH$_3$, requires an inversion of population between the upper and lower states for light amplification, which, in turn, provided us with a unique way of controlling the population transfer between the relevant states through on/off of the population inversion. As such, due to the coexistence of such novel processes with the rather classical behavior like spontaneous emission (fluorescence) and collisional energy transfer, the ion-pair states offer a benchmark for the dynamics in the charge-separated excited states. It is important to note here that the dynamic behavior sensitively depends on the individual ion-pair states, which
motivated the present state-to-state study in order to obtain a more detailed picture for the energy dissipation processes.

The collisional process of molecules with a change in quantum states before and after a collision is called inelastic collision, and many kinetic studies have been performed on such collisional processes. The collisional processes in the valence $B^1\Pi(0_u^+)$ state of $I_2$ with various atomic and molecular quenchers have been studied extensively for many years. It is known that collisions in the $B^1\Pi(0_u^+)$ state induce predissociation. For example, in the collisional process using noble gas atoms as quenchers, it has been confirmed that the rate constant of the collision-induced predissociation process increases as the vibrational quantum number increases.10

A non-adiabatic collisional process between ion-pair states of $I_2$ was first observed in 1924.11 They suggested the highly efficient collisional transfer from the $D^2\Pi$ ($^3P_g$) state to the $D^2\Pi$ ($^3P_u$) state, which was evidenced by the $D^2\Pi$ ($^3P_u$) → $A^2\Pi(2_u^+)$ fluorescence at 342 nm after the $D^2\Pi$ ($^3P_g$) excitation. In this early study, however, the selective excitation of a single state was not possible due to the lack of energy resolution of the spectroscopic system. Therefore, the rate constants reported at that time were only averaged effective parameters. In ref 12, it was shown that the energy transfer from the $D^2\Pi$ ($^3P_g$) state to the $D^2\Pi$ ($^3P_u$) state by collision with Ar was observed even at very low collisional energies. In the literature,13 they reported that when the $D^2\Pi$ ($^3P_g$) state was generated in an Ar atmosphere at 100 Torr, the energy transfer was so efficient that the emission from the $D^2\Pi$ ($^3P_u$) state was hardly observed because of the rapid energy transfer from the $D^2\Pi$ ($^3P_u$) state to the $D^2\Pi$ ($^3P_u$) state. The study of the collisions in a single rovibrational level of the ion-pair state was not possible until a more advanced laser excitation technique, such as the optical–optical double resonance method, became widespread.14

Regarding the self-quenching process in the ion-pair state of the $I_2$ molecule, Ubachs et al. first investigated the $E^2\Pi$ ($^3P_u$) state under single-collision conditions.15 Since then, the collisional process between the $E^2\Pi$ ($^3P_u$) and $D^2\Pi$ ($^3P_g$) states has been investigated in detail by Akopyan et al.16 and Fecko et al.17,18. In the second tier ion-pair states, the collisional process between the $f^2\Pi$ ($^3P_g$) and $F^2\Pi$ ($^3P_u$) states was found, and the vibrational distributions were evaluated.19,20 It has been explained both theoretically and experimentally that the vibrational distribution in the products due to collision-induced energy transfer depends on the energy gap between the initial and final states as well as on the magnitude of the Franck–Condon factor. We investigated the self-quenching processes in the $2_u^+ (1^D_g)$ state in the third tier ion-pair states. In this experiment, the production of the $2_u^+ (1^D_g)$ state, which was energetically located above the laser-prepared $2_u^+ (1^D_g)$ state, was identified. Interestingly, for each vibrational level ($v_u = 3–7$) in the $2_u^+ (1^D_g)$ state, vibrational levels with large Franck–Condon factors between the $2_u^+ (1^D_g)$ and $2_u^+ (1^D_g)$ states are generated. The large collisional cross sections calculated from the self-quenching rate constants are explained by the harpoon mechanism. The rate constant of the collision-induced energy-transfer process between the $2_u^+ (1^D_g)$ and $2_u^+ (1^D_g)$ states was found to be $\sim 15\%$ of the total collisional process in the $2_u^+ (2^D_g)$ state.21

In addition to the self-quenching process, studies on collisional processes using various simple molecules as collisional partners have been performed. In the collisional process of the $E^2\Pi$ ($^3P_u$) state with $N_2$, $N_2$, and CF$_4$ as collision partners, Akopyan et al. determined the reaction rate constants and the rovibrational distributions in the products by measuring the ratios of the $D^2\Pi$ ($^3P_u$) → $X^2\Sigma_g^+$ and the $E^2\Pi$ ($^3P_u$) → $B^2\Pi(0^+_u)$ emission intensities under various pressures.

Several studies on the collisional and reaction processes in the ion-pair states of $I_2$ molecules with noble gas atoms have been conducted. Akopyan et al. investigated the collisional process of $E^2\Pi$ ($^3P_u$) and $D^2\Pi$ ($^3P_u$) states in the first tier and the $f^2\Pi$ ($^3P_g$) state in the second tier with He, Ar, Kr, and Xe.23–25 Similar to the self-quenching process, transitions between the ion-pair states correlated to the same dissociation limit are observed primarily. However, the behavior for the first tier was different from that of the second tier. For example, in the first tier, the products are distributed in various electronic states of the same tier, whereas in the second tier, only energy transfer from the $f^2\Pi$ ($^3P_g$) state to the $F^2\Pi$ ($^3P_u$) states was recognized. Clarifying such differences in each tier would aid in understanding the nature of collisional energy relaxation in ion-pair states.

In the present study, we investigated the collisional process of the $2_u^+ (1^D_g)$ state in the third tier with noble gas atoms, Ar, Kr, and Xe. Selective excitation of $2_u^+ (1^D_g)$ ($v = 3$, $J = 23$) was performed using the optical–optical double-resonance method. The fluorescence at 247 nm from the initial $2_u^+ (1^D_g)$ single state was detected, and the temporal profiles were measured under various noble gas pressures. The quenching rate constants were calculated for each noble gas atom using the Stern–Volmer plots, and the collisional mechanism was discussed based on these values. Assuming that the collision between the excited iodine and noble gas atoms is due to the harpoon mechanism, the theoretical rate constants calculated by a simple model are compared with the experimental values. From the emission spectra obtained from the excitation of the $2_u^+ (1^D_g)$ state, it was found that the energy transfer between the $2_u^+ (1^D_g)$ and $2_u^+ (1^D_g)$ states is dominant in the case of Ar and Kr, while the reactive process of the XeI(5B) formation is dominant in the collisional process with Xe. By determining the rate constants of these processes, we report new insights into the collisional processes in the high-energy states of $I_2$.

2. RESULTS AND DISCUSSION

2.1. Temporal Profile and UV Fluorescence Spectra from the $2_u^+ (1^D_g)$ Ion-Pair State. Figure 1 shows the temporal profile and UV fluorescence spectra from the $2_u^+ (1^D_g)$ ion-pair state.

Figure 1. Temporal profiles of the (a) excitation laser pulse and (b) emission from the $2_u^+ (1^D_g)$ ($v = 3$) state. The sample pressure: $p(1_x) = 0.2$ Torr and $p(Xe) = 1.0$ Torr. The temporal profile of the measured fluorescence (b; open triangle) can be fitted by a convoluted waveform of the temporal profile of the excitation laser (a). The best fit is shown by the red curve.
profiles of the excitation laser (circle) and the fluorescence at 247 nm (triangle) belonging to the transition from the $2_u (^1D_2)$ ($v = 3, J = 23$) ion-pair state to the $^3\Pi(2_u)$ valence state, where sample pressures were $p(I_2) = 0.2$ Torr and $p(Xe) = 1.0$ Torr, respectively. The temporal profile of the measured fluorescence can be fitted by a convoluted waveform of the temporal profile of the excitation laser and a single exponential decay function with decay time $\tau$ as follows

$$F(t) = C \int_0^t P(t') \exp[\left( t' - t \right) / \tau] \, dt'$$

where $C$ and $P(t')$ are pre-exponential factors for adjusting the intensity and temporal profile of the excitation laser pulse. \cite{20, 21}

Least-squares fitting was performed to determine decay lifetime $\tau$. The convoluted waveform (solid red line in Figure 1), showing a satisfactory agreement with the observed temporal profile, corresponds to a decay time of $\tau \approx 13.4$ ns.

The temporal profile of the fluorescence from the $2_u (^1D_2)$ state is expressed by a kinetic model that considers the following processes

1. \( I(1\Pi) + h\nu \rightarrow I(2_u) \) \hspace{1cm} (2)
2. \( I(2_u) \rightarrow I(2_u) \text{(valence)} + h\nu: k_{Rg} \) \hspace{1cm} (3)
3. \( I(2_u) + I(2_u) \rightarrow \text{products}: k_{q22} \) \hspace{1cm} (4)
4. \( I(2_u) + Rg \rightarrow \text{products}: k_{q22}^{Rg} \) \hspace{1cm} (5)

By considering the competition of these processes, the inverse of the decay lifetime ($1/\tau$) can be expressed by the Stern–Volmer equation as

$$\frac{1}{\tau} = k_{Rg} + k_{q22}^{I(2_u)} + k_{q22}^{Rg}[Rg]$$

The decay lifetimes were measured under various noble gas pressures, and the rate constants of the total collisional decay of the $2_u (^1D_2)$ ($v = 3$) state are determined to be $k_{q22}^{Ar} = (4.55 \pm 0.42) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for Ar, $k_{q22}^{Kr} = (4.23 \pm 0.11) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for Kr, and $k_{q22}^{Xe} = (6.83 \pm 0.16) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for Xe, from the Stern–Volmer plots as shown in Figure 2. The intercepts of each plot are within the range of experimental error, which corresponds to the reciprocal of the fluorescence lifetime of the $2_u (^1D_2)$ ($v = 3$) state under the vapor pressure (0.2 Torr) of I$_2$. From our previously reported fluorescence lifetime $\tau$ ($= 1/k_{Rg,2_u}$) $(= 21.3 \pm 0.1)$ ns and the self-quenching constant $k_{q22}^{I(2_u)} = (1.30 \pm 0.01) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the $2_u (^1D_2)$ ($v = 3$) state, the inverse of the lifetime, $1/\tau$, at $p(I_2) = 0.2$ Torr is calculated to be $(5.54 \pm 0.03) \times 10^7$ s$^{-1}$. This value agrees with the intercepts shown in Figure 2 within the range of experimental error.

Figure 3 shows the dispersed fluorescence spectra of the emission from the $2_u (^1D_2)$ ($v = 3, J = 23$) state with Xe, Kr, and Ar (top panel: pure vapor I$_2$, second: I$_2$ with Kr 1.5 Torr, third: I$_2$ with Ar 1.5 Torr). The dispersed fluorescence spectrum of the pure I$_2$ sample consists of three band systems attributed to the $2_u (^1D_2) \rightarrow \DeltaP(2_u)$, $2_u (^1D_2) \rightarrow \PiP(2_u)$, and $2_u (^1D_2) \rightarrow \DeltaD(2_u)$ transitions from the shorter wavelength side. The $2_u (^1D_2)$ state, lying energetically adjacent to the laser-prepared $2_u (^1D_2)$ state, was generated by the same self-quenching process as in ref 21.

$$I(2_u) + I(2_u) \Rightarrow I(2_u) + I(2_u) : k_{q22}^{I(2_u)}$$

(6)

In the case of Kr and Ar inclusions, in addition to the emission bands, a weak emission system attributable to the $2_u (^1D_2) \rightarrow \DeltaD(2_u)$ transition was observed at 285–290 nm. The intensities of these two emission systems from $2_u (^1D_2)$ at 220–230 and 285–290 nm were found to increase compared with those from $2_u (^1D_2)$ without inserted noble gas pressures through the following quenching process

$$I(2_u) + Rg \Rightarrow I(2_u) + Rg : k_{Rg,2_u}^{I(2_u)}$$

(7)

We assume that the rate constants for the forward and reverse reactions in eqs 7 and 8 are equal.

In the case of Xe, only a slight increase in the fluorescence intensity was observed. Instead, the following reactive process was identified

$$I(2_u) + Xe \Rightarrow XeI(B) + I: k_{q22}^{Xe}$$

(8)

Again, as in processes 7 and 8, the rate constant of the forward and reverse reactions was assumed to be equal in the later analysis. When Xe is encapsulated, the emission around 253 nm was observed and assigned to the $B(1/2 3P_{3/2}) \rightarrow X(1/2 3\Sigma^+)$ transition of the XeI eximer produced by the process 9. A similar trend has been reported in previous studies on collision-induced processes in other ion-pair states. \cite{25}
Figure 4 shows the temporal profiles obtained by monitoring the emission from the 2g (1D2) state at 247 nm (triangle) and the
density: 607.4x800.9

2g (1D2) state at 230 nm (rhombus) of I2 and the B (1/2 2P3/2) state of XeI at 253 nm (square) under p(Xe) = 1.0 Torr. The
temporal profiles of the emission from the 2g (1D2) and XeI(B)
states can be reproduced by the convoluted curve of the temporal
profiles of the emission from the 2g (1D2) state, assuming a single
exponential decay function. This indicates that the temporal
profile of the emission from the 2g (1D2) state acts as the
excitation function of those from the 2g (1D2) state of I2 and B
(1/2 2P3/2) state of XeI, which are generated by the first-order
process from the 2g (1D2) state by collisions with iodine
molecules in the 2g (1D2) state. The decay time of the B (1/2
2P3/2) state of XeI was evaluated from the temporal analysis to be
13.4 ns, which concurs with the reported lifetime of the B (1/2
2P3/2) state, ~15 ns.18

2.2. Rate Constants for the Collision-Induced 2g (1D2)–
2g (1D2) Transition. The rate constants for the formation of the
2g (1D2) state indicated in reaction 8 were then determined. In
addition to reactions 7 and 8, the fluorescence relaxation of the
2g (1D2) state was considered as

I2(t) \rightarrow I2(valence) + hν: k_{R2g}

The net production rate of I2(2g) is described as

\[ \frac{dN_2(t)}{dt} = k_{R2g}N_2(t)[Rg] - k_{2g-2s}N_2(t)[Rg] + k_{2g-2s}N_2(t)[I_2(X)] - k_{R2g}N_2(t) \]

In the right-hand side of eq 11, the first and third terms
correspond to the dissociation of the laser-prepared 2g (1D2)
state, the second and fourth terms to the dissociation of the 2g
(1D2) state by collisions, and the fifth term to the fluorescence
decay of the 2g (1D2) state. Here, the emission intensity I2(t)
from the i state at time t can be expressed as I2(t) = k_{Ri}N(t)
using the number density N(t) and the radiative decay constant
k_{Ri}. From this relationship, the rate eq 11 can be transformed as

\[ \frac{dI_2(t)}{dt} = k_{R2g}I_2(t)[Rg] - k_{2g-2s}I_2(t)[Rg] + k_{2g-2s}I_2(t)[I_2(X)] - k_{R2g}I_2(t) \]

By integrating both sides of eq 12 from t = 0 to t = \infty, we obtain the relation,

\[ I_2(t) = I_2(0) = \frac{k_{R2g}I_2(t)[Rg]}{k_{2g-2s}[Rg]} \int_0^\infty I_2(t) dt \]

where I2 (t \to \infty) = I2 (t = 0) = 0. If we set \int_0^\infty I_2(t) dt = S_2, the
ratio of the emission intensities from the 2g (1D2) state to that
from the 2g (1D2) state, S2 / S2, can be written as

\[ \frac{S_2}{S_2} = \frac{k_{R2g}I_2(t)[Rg] + k_{2g-2s}[I_2(X)]}{k_{R2g}I_2(t)[Rg] + k_{2g-2s}[I_2(X)] + k_{R2s}} \]

When the pressure of the noble gas atoms is low, k_{Rg} \ll k_{R2g} and by ignoring the reverse reaction in reaction 8, eq 14
can be rewritten as

\[ \frac{S_2}{S_2} \approx \frac{k_{R2g}I_2(t)[Rg] + k_{2g-2s}[I_2(X)]}{k_{R2g}I_2(t)[Rg] + k_{2g-2s}[I_2(X)] + k_{R2s}} \]

Here, k_{R2g} and k_{R2s} are the reciprocals of the collision-free
fluorescence lifetimes of the 2g (1D2) and 2g (1D2) states, which
are k_{R2g} = (4.68 \pm 0.02) \times 10^{-10} s^{-1} and k_{R2s} = (2.24 \pm 0.04) \times 10^{-17} s^{-1}, respectively. k_{2g-2s} is the rate constant
due to the self-quenching 2g (1D2) – 2g (1D2) process, which is k_{2g-2s} = (1.89 \pm 0.01) \times 10^{-10} cm3 molecule^{-1} s^{-1} for 2g (1D2) \nu = 3.21
The integrated intensity ratio S2 / S2 is determined from the emission spectra under various noble gas pressures and is plotted
against the number density of noble gas atoms Ar and Kr.

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formation of XeI was determined to be constant of the XeI \((10 \times \sigma_{\text{number density of Xe}})\) excimer production process9 was then evaluated. In addition to reaction 9, the following radiative process must be considered in the rate equation.

\[
\text{XeI}(B) \rightarrow \text{XeI}(X) + \text{h}v: k_{\text{rel}}\text{XeI}
\]

In the present analysis, the process shown in reaction 17 is neglected because the number density of iodine molecules in the \(2^1_S\) \((^1D_2)\) state is much smaller than that in the \(2^3_S\) \((^1D_2)\) state.

\[
I_2(2^3_S) + \text{Xe} \rightarrow \text{XeI}(B) + I: \ k_{\text{rel}}\text{XeI} - \text{XeI}
\]

If we also ignore the reverse reaction in process 9, the rate equation can be written as

\[
\frac{dN_{\text{XeI}}(t)}{dt} = k_{\text{rel}}^{\text{XeI}} - k_{\text{rel}}^{\text{XeI}} X_{\text{XeI}} X_{\text{XeI}} (t) - X_{\text{XeI}} X_{\text{XeI}} (t)
\]

The integral intensity ratio \(S_{\text{XeI}}/S_{2_u}\) is obtained by integrating eq 18 as follows

\[
S_{\text{XeI}}/S_{2_u} = k_{\text{rel}}^{\text{XeI}}/k_{\text{rel}}^{\text{XeI}} [X_{\text{XeI}}]
\]

From the integrated intensity ratio \(S_{\text{XeI}}/S_{2_u}\) plotted against the number density of Xe (Figure 6), the rate constant of the formation of XeI was determined to be \(k_{\text{rel}}^{\text{XeI}} = (6.55 \pm 0.19) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The ratio of this value to the total deactivation rate by Xe was \(k_{\text{rel}}^{\text{XeI}} / k_{\text{rel}}^{\text{XeI}} = 0.096\). Thus, the collisional process 9 accounts for \(96.6\%\) of the total quenching process 5 by the Xe atom. Table 1 summarizes the rate constants determined in past studies were also included.

2.4. Harpoon Mechanism for the Quenching Process.

The quenching rate constant \(k_{\text{rel}}^{\text{Xe}}\) is related to the collisional cross-section \(\sigma\) as follows

\[
\sigma = \frac{k_{\text{rel}}^{\text{Xe}}}{c_{\text{rel}}} \quad \text{(20)}
\]

\[\text{Figure 5. Ratios of the integrated emission intensity from the } 2_u \text{ }(^1D_2) \text{ state to the emission from the } 2_g \text{ }(^1D_2) \text{ state, } S_{2_u}/S_{2_g}, \text{ against the quencher density, } [\text{Rg}]. \text{ The self-quenching rate constants can be derived using eq 15. Quencher; red circle (a): Ar, black square (b): Kr.}\]

\[\text{Figure 6. Ratios of the integrated emission intensity from the } 2_u \text{ }(^1D_2) \text{ state to the emission from the } B \text{ }(^3S_2) \text{ state of XeI, } S_{2_u}/S_{2_u}, \text{ against the Xe density, } [\text{Xe}]. \text{ The reaction rate constant can be derived using eq 19.}\]

where \(c_{\text{rel}}\) is the average relative velocity between excited iodine molecule and noble gas atom and is expressed from the gas molecule kinetics theory as follows

\[
c_{\text{rel}} = \sqrt{\frac{8RT}{\pi\mu}}
\]

\[\text{In eq 21, } R \text{ is the gas constant and } \mu \text{ is the reduced mass. The average relative velocities } c_{\text{rel}} \text{ between the excited iodine molecule and Ar, Kr, and Xe are } 426.1, 315.3, \text{ and } 269.1 \text{ m s}^{-1}, \text{ respectively, at } T = 296 \text{ K. The collisional cross-section } \sigma \text{ and collision radius } R_{\text{coll}} \text{ are listed in Table 2.}\]

It can be seen that the collisional cross sections shown in Table 2 are negatively correlated with the ionization energy of the quencher atoms and are considerably larger than the size of the excited iodine molecule and noble gas atoms. Such features indicate the harpoon mechanism to be responsible for the rapid progress of the reactions.\(^{27}\)

\[I_2(\text{IPS}) + \text{Rg} \rightarrow [I_2(\text{IPS}) \cdots \text{Rg}]* \rightarrow \text{products}\]

The harpoon mechanism is an electron-transfer reaction that occurs over a long distance. The formation of excimer-XeI shown in the diagram in Figure 7 is one example. The curve \(V_I(R)\) represents the electrically neutral potential curve between Xe and I\(_2\), given by

\[
V_I(R) = E(I_2^*) - \frac{C_6}{R^6}
\]

where \(E(I_2^*)\) and \(C_6\) are the energies of the \(2_u \text{ }(^1D_2) \text{ ion-pair state and proportional constant, respectively. In addition, } V_2(R) \text{ represents the Coulomb potential between } \text{Xe}' \text{ and } I_2^* \text{ given as}\)

\[
V_2(R) = E(I_2^*) + E_{\text{ip}}(\text{Rg}) - E_{\text{e}}(I_2^*) - \frac{e^2}{4\pi\epsilon_0 R}
\]

where \(E_{\text{ip}}(\text{Rg})\) is the ionization potential of the noble gas atoms, which is 15.8, 14.0, and 12.1 eV for Ar, Kr, and Xe, respectively.\(^{29-31}\) \(E_{\text{e}}(I_2^*)\) is the electron affinity of excited I\(_2\). The excited iodine molecules and noble gas atoms approach the potential curve \(V_I(R)\). When the distance \(R\) between the excited iodine molecule and the noble gas atom reaches critical reaction radius, \(R_{\text{harpoon}}\) the reaction proceeds along the Coulomb potential \(V_2(R)\), and excimer XeI(\(B\)) is produced. The produced XeI(\(B\)) emits 253 nm fluorescence and finally dissociates into Xe and I\(_2\) atoms. By neglecting the term of the covalent interaction
Table 1. Quenching Rate Constant, $k_{Q}^{c}$, Rate Constant of the $2_u (^1D_2) - 2_g (^1D_2)$ Collisional Transfer, $k_{Qg-2g}^{c}$, and Rate Constant of the Formation of XeI, $k_{Xe-2g}$,

| quencher | $k_{Q}^{c}$ (experimental)* | $k_{Qg-2g}^{c}$ (experimental)* | $k_{Xe-2g}$ (experimental)* |
|----------|-----------------------------|---------------------------------|-----------------------------|
| Ar       | $(4.55 \pm 0.42) \times 10^{-10}$ | $(9.61 \pm 0.63) \times 10^{-11}$ | $(6.55 \pm 0.19) \times 10^{-11}$ |
| Kr       | $(4.23 \pm 0.11) \times 10^{-10}$ | $(4.87 \pm 0.34) \times 10^{-11}$ | |
| Xe       | $(6.83 \pm 0.16) \times 10^{-10}$ | $(1.89 \pm 0.01) \times 10^{-10}$ | |

*cm$^{-3}$ molecule$^{-1}$ s$^{-1}$.

Table 2. Experimental and Theoretical Quenching Rate Constants, $k_{Q}^{R}$, Collisional Cross Section $\sigma$, and Collisional Radius, $R_{coll}$

| quencher | $k_{Q}^{R}$ (experimental)* | $\sigma$ a | $R_{coll}$ b | $k_{Q}^{R}$ (theoretical)* |
|----------|-----------------------------|-------------|--------------|-----------------------------|
| Ar       | $(4.55 \pm 0.42) \times 10^{-10}$ | $107 \pm 10$ | 5.84 | $(4.10 \pm 0.15) \times 10^{-10}$ |
| Kr       | $(4.23 \pm 0.11) \times 10^{-10}$ | $134 \pm 3$ | 6.55 | $(3.88 \pm 0.22) \times 10^{-10}$ |
| Xe       | $(6.83 \pm 0.16) \times 10^{-10}$ | $254 \pm 6$ | 9.01 | $(4.91 \pm 0.68) \times 10^{-10}$ |

*cm$^{-3}$ molecule$^{-1}$ s$^{-1}$. a)$^\circ$. A.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Schematic potential model for the harpoon mechanism. The right panel illustrates the potential energy curves of the $X'$ $\Sigma_{g}^{+}$, $B'$ $\Pi(0')$, $c'$ $\Pi_{u}$, and $2'$ $\Pi_{g}$ states of I$_2$. The central panel shows the schematic potentials of the activated complex, I$_2$-$\text{Xe}$, where $V_{1}(R)$ and $V_{2}(R)$ represent the potential energy curves of the neutral and ionic complexes, respectively. The left panel shows potentials of XeI. When the I$_2$ molecule in the 2' ($^1D_2$) state approaches the Xe atom, an activated complex is formed. The complex forms an ionic pair by electron transfer at the intersection of $V_{1}$ and $V_{2}$ to produce the electronically excited B (1/2 $^3P_{1/2}$) state of XeI. Then, XeI (B), emitting fluorescence, relaxes to the ground state and dissociates to Xe + I ($^1P_{1/2}$).

between I$_2^*$ and $R_{\text{harp}}$, the critical reaction radius is the distance between the two particles at the intersection of potentials $V_{1}(R)$ and $V_{2}(R)$ and is expressed as

$$R_{\text{harp}} = \frac{\epsilon^2}{4\pi\epsilon_0\varepsilon_0} \frac{1}{E_{\text{ip}}(R) - E_{\text{eI}}(I_2^*)}$$

(25)

It would be of interest to compare the theoretical $R_{\text{harp}}$ with the experimental values obtained in this study. To estimate the electron affinity $E_{\text{eI}}(I_2^*)$ of the 2' ($^1D_2$) state, we considered the energy of the anion I$_2^-$. The electronic configuration of the 2' ($^1D_2$) state is ($\sigma_g^2$)$^2$($\pi_g^2$)$^2$($\pi_u^2$)$^2$. The electronic configurations of the anionic states are ($\sigma_g^2$)$^2$($\pi_g^2$)$^2$($\pi_u^2$)$^2$: $^2\Pi_u$ and ($\sigma_g^2$)$^2$($\pi_g^2$)$^2$($\pi_u^2$)$^2$: $^3\Pi_c$. Ab initio calculations predict that the electronic states of $^2\Pi_{u,1/2}$, $^2\Pi_{g,1/2}$, $^2\Pi_{u,3/2}$, and $^2\Pi_{u,1/2}$ are located at $\sim 0.8$, $\sim 0.9$, $\sim 0.9$, and $\sim 1.7$ eV above the ground state of the I$_2^-$ anion, respectively. Then, $E_{\text{eI}}(I_2^*)$ of the 2' ($^1D_2$) state was estimated to be 7.6$\pm$8.5 eV. The critical reaction radius, $R_{\text{harp}}$, in eq 25 assumes two point-charge particles. Thus, the actual value of the collisional radius $R_{\text{coll}}$ can be expressed as

$$R_{\text{coll}} = R_{\text{harp}} + b$$

(26)

where $b$ is the impact parameter, estimated from the sum of half of the equilibrium internuclear distance of the 2' ($^1D_2$) state, $\sim 1.75$ Å, and the van der Waals radius of the noble gases (1.88, 2.02, and 2.16 Å for Ar, Kr, and Xe, respectively). The calculated quenching rate constants are listed in Table 2 and reflect the trend of the experimental rate constants, providing a strong support for the harpoon mechanism for the collisional process in the 2' ($^1D_2$) state.

3. CONCLUSIONS

In this work, we present a kinetic analysis of the collisional process between the 2' ($^1D_2$) ($v = 3$) ion-pair state of I$_2$ and noble gas atoms, Ar, Kr, and Xe, as quenchers. Approximately 21 and 12% of the quenching process by Ar and Kr, respectively, were found to be energy transferred to the energetically peripheral 2' ($^1D_2$) ion-pair state. The formation of excimer XeI(B) was observed in the collisional process with Xe, which accounted for 9.6% of the total quenching process by Xe. The collisional cross sections calculated from the quenching rate constants were considerably larger than the molecular size. The theoretical rate constants calculated from the ionization energy of the quencher atoms and the electron affinity of the 2' ($^1D_2$) state, assuming the harpoon mechanism, reflected the trend of the experimental rate constants.

4. EXPERIMENTAL METHODS

Excitation to the single rovibronic level of the 2' ($^1D_2$) state was performed by a perturbation-facilitated optical–optical double resonance technique through the $^2\Pi_u \sim B' \Pi(0')$ double-faceted valence state as the intermediate state. A schematic experimental setup is shown in Figure 8. Two dye lasers (Continuum ND6000) pumped by third (355 nm) and second
(532 nm) harmonic outputs of Nd:YAG lasers (Continuum Surelite I and II) were used as excitation light sources. The timing between the Q-switch and flash lamp of each laser was controlled by a pulse generator (Stanford Research System DG535). The output from the first dye laser (LD489, methanol solution) at ∼19885.0 cm⁻¹ was used as the excitation light for the c¹Π (νc = 13, Jc = 23) → B³Π(0) (νB = 59, JB = 22) ← X³Σ⁺ (νX = 0, JX = 23) transition. The second harmonic output at ∼34638.6 cm⁻¹ from the second dye laser (rhodamine 610 + rhodamine 590, methanol solution), frequency doubled by a KDP crystal (Inrad Optics), was employed as the excitation light for the 2νc (³D2) (ν = 3, J = 23) ← c¹Π (νc = 13, Jc = 23) transition. Both laser beams were spatially overlapped in a quartz cell filled with vapor I2 (∼0.2 Torr) at 23 °C and noble gas atoms (Ar, Kr, and Xe). The sample cell is made of synthetic fused silica. Both entrance and exit window surfaces are perpendicular to the laser propagation direction. The pulse width of the two laser pulses was typically ∼6 ns. The delay time between the two laser pulses was adjusted to 15 ns to eliminate their temporal overlap, avoiding any potential coherent process affecting the fluorescence decay profile. The sample pressure was measured using a capacitance manometer (Edwards Barocel). To minimize the effects of contamination, such as water, the sample cell was heated at a pressure of 10⁻⁴ Pa before sample installation. The samples were then sublimated multiple times under vacuum to remove any impurities.

To measure the dispersed fluorescence spectrum, the fluorescence from the electronically excited state of I2 was monitored from the side window of the cell and detected by a photomultiplier tube (PMT) (Hamamatsu Photonics R2496, time response: 0.7 ns) and directly transferred to an oscilloscope (Tektronix TDS7104). The captured temporal signals were integrated approximately 3000 times (∼5 min at a repetition rate of 10 Hz).

![Figure 8. Schematic experimental setup.](https://pubs.acs.org/10.1021/acsomega.1c06185)

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### Notes

The authors declare no competing financial interest.

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