

Atomic Alignment Effect on the Branching to ArCl* and CCl₂* Formation in the Reaction of Oriented Ar(³P₂, M_J=2) + CCl₄

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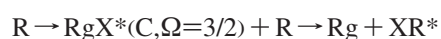
Atomic alignment effects for the formation of ArCl*(C) and CCl₂*(\tilde{A}) in the reaction of Ar(³P₂) + CCl₄ have been measured by using an oriented Ar(³P₂, M_J=2) beam at a collision energy of 0.08 eV. The emission intensity for ArCl*(C) and CCl₂*(\tilde{A}) has been measured as a function of the magnetic orientation field direction in the collision frame. A significant atomic alignment effect is observed for the atom transfer process [ArCl*(C) formation]. Formation of ArCl*(C) is modestly enhanced when the electron angular momentum of the Ar(³P₂) reactant is aligned along the relative velocity vector, while the excitation transfer process [CCl₂*(\tilde{A}) formation] shows little alignment effect.

Introduction

The effect of reactant approach geometry on chemical reactions is an important field of dynamical stereochemistry. Some studies have employed external fields and a polarized laser to prepare oriented or aligned molecules.^{1–3} The influence of atomic orbital alignment on reaction dynamics was first studied by Hertel et al. using an aligned Na(3²P) prepared by optical pumping method.⁴ Since then, significant alignment dependences have been reported for the naked outer atomic orbital prepared by optical pumping.^{5–12} However, the direct interrogation of reactive geometric requirements for the multiplet atoms is difficult by optical pumping method, and almost nothing is known about the stereoselectivity on the triplet system like metastable rare gas atoms Rg*(np⁵(n+1)s¹) that has the unpaired inner atomic orbital shielded by the outer extended orbital.

It is well-known that the reaction of Rg* with polyatomic halogen-containing molecules RX are similar to reactions of alkali metal atoms M. This similarity is due to the analogous outer valence electron configuration between Rg*(np⁵(n+1)s¹) and M(np⁶(n+1)s¹).¹³ As with the formation of metal halide MX for the alkali-metal atoms,¹⁴ the reaction of Rg* generating electronically excited rare-gas halides RgX* is known to proceed via the harpooning mechanism. The potential of the excited-state pair is the Coulombic potential of an ion-pair V(Rg⁺, RX⁻). However, unlike the alkali-metal atoms, excitation transfer may compete with the atom transfer channels. Since the ion-pair potential of the excited system is far above the ground-state of the collision pair, the attractive ion-pair potential V(Rg⁺, RX⁻) must pass through the sequence of electronically excited states of the reagent V(Rg, RX*). Coupling between the ion-pair state V(Rg⁺, RX⁻) and some of these excited states V(Rg, RX*) diverts trajectories from the ion-pair potential to products correlating to the excited reagent state RX*.

The collision of metastable rare-gas with the halogen-containing molecules leads both to atom transfer (excimer, RgX*) and to excitation transfer (electronically excited molecules, XR*).^{15,16}



X = halogen, R = any group

The nonclosed shell of Rg⁺ gives rise to two different excited rare gas halide product states, RgX*(B) and RgX*(C), that correlate with Rg⁺(³P_{3/2}) and X⁻(¹S₀).

Since the ion-pair potential differs from that of the alkali metal atom case in terms of the number of states and other effects related to the nonclosed shell nature of the positive ion-core Rg⁺, these ion-cores should affect exit channel potential and give an important role to control the branching to each reaction channel. Despite the numerous studies on Rg* reactions, many of the details of the reaction dynamics still remain obscure; especially, the steric effect due to the ion-core is still an unresolved problem.

It is well-known that the reactions of excited alkaline earth metal atoms M*(np⁶(n+1)s¹(n+1)p¹) with polyatomic halogen-containing molecules also produce the electronically excited metal halide via the harpooning mechanism.

Rettner and Zare first studied the effect of atomic reagent approach geometry on reactivity with polarized laser for the reaction of Ca(¹P₁) with HCl, Cl₂, and CCl₄.⁶ Young et al. studied the orbital alignment effect for the reaction of Ca(¹P₁) with CH_{4-n}Cl_n (n = 1–4) reactions.¹¹ It was reported that the reaction of Ca(¹P₁) atom having a naked outer atomic p orbital with CCl₄ displays no significant dependence on approach geometry. The difference in the orbital configuration between Rg*(np⁵(n+1)s¹) and excited alkaline earth metal atoms M*(np⁶(n+1)s¹(n+1)p¹) provides interesting contrast on the stereoselectivity.

In the present study, we measured the atomic alignment effect for the formation of ArCl*(C) and CCl₂*(\tilde{A}) in the reaction of Ar(³P₂) + CCl₄ by using an oriented Ar(³P₂, M_J=2) beam. In contrast with the Ca(¹P₁) + CCl₄ reaction, a significant atomic alignment effect was observed for the atom transfer process (ArCl*(C) excimer formation), while the excitation transfer process (CCl₂*(\tilde{A}) formation) displays no significant dependence on approach geometry.

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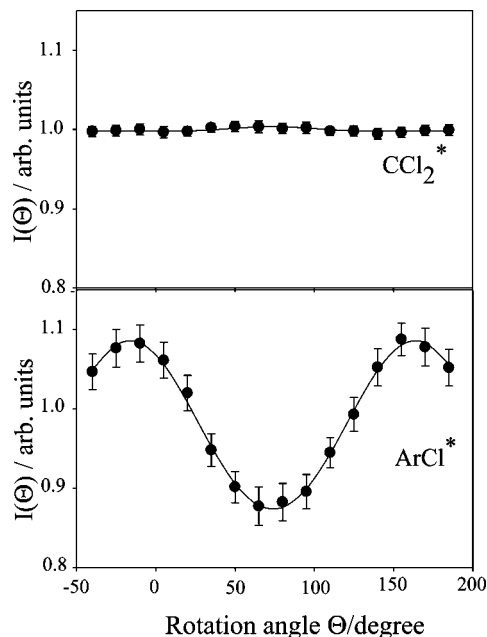


Figure 1. The chemiluminescence intensity as a function of rotation angle Θ of the magnetic orientation field direction for $\text{ArCl}^*(\text{C})$ (a) and $\text{CCl}_2^*(\tilde{\text{A}})$ (b). Experimental (closed circle), Θ -dependence represented by the fittings with using eq 3 (solid lines). The origin of the rotational angle Θ is the direction of the $\text{Ar}(^3\text{P}_2)$ beam axis:

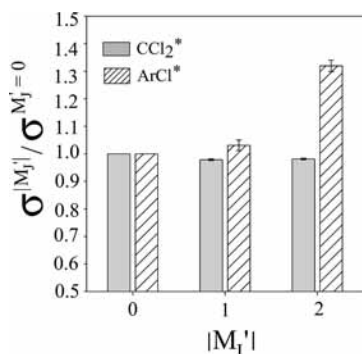


Figure 2. The relative cross-sections for each M_j' state in the collision frame, $\sigma^{M_j'=0}$, $\sigma^{M_j'=1}$, and $\sigma^{M_j'=2}$ for $\text{CCl}_2^*(\tilde{\text{A}})$ (shaded bar) and $\text{ArCl}^*(\text{C})$ (dashed bar).

2. Experimental Section

The experimental apparatus and procedures were almost same as the previous one.^{17,18} Briefly, a metastable $\text{Ar}(^3\text{P}_{0,2})$ beam was generated by a pulsed glow discharge with a pulse width of 100 μs , and then state-selected by a magnetic hexapole. An almost pure $\text{Ar}(^3\text{P}_2, M_J=2)$ beam with a velocity of 700 ms^{-1} collides with the CCl_4 beam in a homogeneous magnetic orientation field \mathbf{B} . The CCl_4 beam was injected with a stagnation pressure of 10 Torr from a pulsed valve that was placed at a distance of 8 cm from the beam crossing point. The signal from the photomultiplier was counted by a multichannel scaler (Stanford SR430). The ArCl^* and CCl_2^* chemiluminescences were measured as a function of the direction of the magnetic orientation field in the laboratory frame (rotation angle Θ). The origin of Θ is the direction of the $\text{Ar}(^3\text{P}_2)$ beam axis. The homogeneous magnetic orientation field was generated by the four pieces of ferrite magnet mounted on a motor-driven rotatable stage, and its direction \mathbf{B} was rotated around the beam crossing point over the angle region $-45^\circ \leq \Theta \leq 180^\circ$ by an interval of 15° . Although the $\text{Ar}(^3\text{P}_2, M_J=2)$ beam is oriented in the homogeneous magnetic orientation field \mathbf{B} , we can only

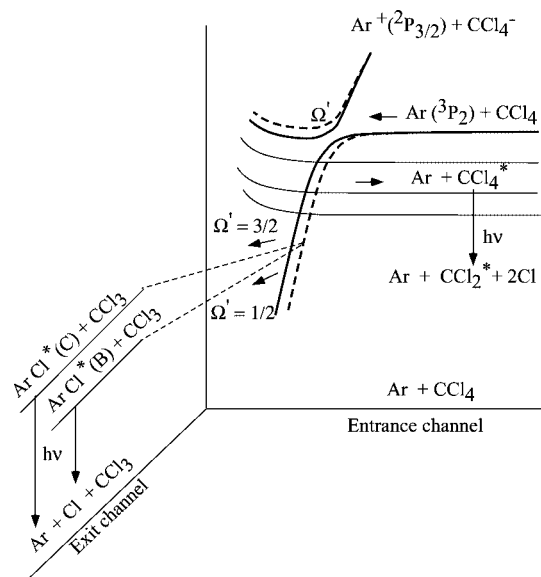


Figure 3. A schematic potential diagram for the reaction of $\text{Ar}(^3\text{P}_2) + \text{CCl}_4$. The entrance potential $V(\text{Ar}(^3\text{P}_2) + \text{CCl}_4)$ crosses with the ion-pair potential $V(\text{Ar}^+ - \text{CCl}_4^-)$ via an electron jump. The attractive ion-pair potential $V(\text{Ar}^+ - \text{CCl}_4^-)$ passes through a continuum of electronically excited states of the reagent $V(\text{Ar}-\text{CCl}_4^*)$. Coupling between the ion-pair state $V(\text{Ar}^+ - \text{CCl}_4^-)$ and some of these excited states $V(\text{Ar}-\text{CCl}_4^*)$ diverts trajectories from the ion-pair potential to products correlating to the excited reagent states CCl_4^* that result in the production of CCl_2^* . The nonclosed shell of Ar^+ gives rise to two different excited rare gas halide product states, $\text{ArCl}^*(\text{B})$ and $\text{ArCl}^*(\text{C})$, which correlate with the $\text{Ar}^+(^3\text{P}_{3/2})$ and $\text{Cl}(^1\text{S}_0)$.

observe the alignment effect in the present study. The orientation effect cannot be observable due to the experimental condition with cylindrical symmetry.¹⁷

The chemiluminescences from the products $\text{ArCl}^*(\text{C})$ (175 $\text{nm} < \lambda < 300 \text{ nm}$) and $\text{CCl}_2^*(\tilde{\text{A}})$ ($\lambda > 400 \text{ nm}$) were selectively collected and detected by a photomultiplier (Hamamatsu R943-02) through a suitable band-pass filter [Monotech MT-BF2000IF13 ($\lambda_{\text{center}} = 200 \text{ nm}$, $\lambda_{\text{bandwidth}} = 13 \text{ nm}$), HOYA L-42, respectively]. Unfortunately, we cannot observe the VUV emission from $\text{ArCl}^*(\text{B})$ ($\lambda < 180 \text{ nm}$). Since the emission within this wavelength region is in the absorption band of O_2 molecule, the so-called ‘‘Schuman–Rung continuum’’, the emission is almost completely absorbed by O_2 in air before detection.

3. Results and Discussion

3–1. M_j' -Dependent Cross-Section in the Collision Frame, $\sigma^{M_j'}$. Figure 1 shows the chemiluminescence intensity of $\text{ArCl}^*(\text{C})$ and $\text{CCl}_2^*(\tilde{\text{A}})$ as a function of the rotation angle Θ of the direction of magnetic orientation field \mathbf{B} . A significant difference of Θ -dependence was observed between two reaction channels. Formation of $\text{ArCl}^*(\text{C})$ is modestly enhanced when the electron angular momentum of the $\text{Ar}(^3\text{P}_2)$ reactant is aligned along the relative velocity vector, while the excitation transfer process [$\text{CCl}_2^*(\tilde{\text{A}})$ formation] displays no significant dependence on approach geometry.

These Θ -dependences can be analyzed using an irreducible representation of the density matrix.¹⁷ In the present study, to determine the total cross section, only the even moments can be observed due to the experimental condition with cylindrical symmetry.

The chemiluminescence intensity, $I(\Theta)$, can be written as follows by using the relative cross-section, $\sigma^{M_j'}$, in the collision frame.

$$I(\Theta) = \frac{1}{280}(39\sigma^{M_j'=0} + 88\sigma^{M_j'=1} + 153\sigma^{M_j'=2}) + \frac{1}{16}(-3\sigma^{M_j'=0} - 4\sigma^{M_j'=1} + 7\sigma^{M_j'=2})\cos 2\theta + \frac{1}{64}(3\sigma^{M_j'=0} - 4\sigma^{M_j'=1} + \sigma^{M_j'=2})\cos 4\theta \quad (1)$$

This equation is equivalent to the general multipole moment's form

$$I(\Theta) = a_0 + a_2 \cos 2\theta + a_4 \cos 4\theta \quad (2)$$

where θ is the angle between the relative velocity v_R and the direction of the orientation magnetic field \mathbf{B} . It is defined as $\theta \equiv \Theta_{v_R} - \Theta$ using the direction of the relative velocity v_R in the laboratory coordinate Θ_{v_R} . Since θ has a distribution by the misalignment caused by the velocity distribution of CCl_4 beam, we must use the $\cos 2n\theta$ factors averaged over the Maxwell-Boltzmann velocity distribution of CCl_4 beam at room temperature, $\langle \cos(2n(\Theta_{v_R} - \Theta)) \rangle$. We finally use the following equation for the evaluation of the experimental results,

$$I_{\text{obs}}(\Theta) = a_0 + a_2 \langle \cos(2(\Theta_{v_R} - \Theta)) \rangle + a_4 \langle \cos(4(\Theta_{v_R} - \Theta)) \rangle \quad (3)$$

The coefficients a_n were determined as the fitting parameters by using eq 3 by means of χ^2 analysis. They are summarized as follows:

$$a_2/a_0 = 0.1115 \pm 0.0026, \quad a_4/a_0 = 0.0026 \pm 0.0035 \quad \text{for ArCl}^* \text{ channel} \quad (4)$$

$$a_2/a_0 = -0.0029 \pm 0.0007, \quad a_4/a_0 = 0.0011 \pm 0.0008 \quad \text{for CCl}_2^* \text{ channel} \quad (5)$$

No notable contribution of rank 4 moment (a_4) was recognized. This result suggests that the dynamics in these reaction systems are dominantly controlled by the alignment of the unpaired inner 4p orbital of $\text{Ar}(^3\text{P}_2)$. These coefficient ratios were used to derive the relative cross-sections for each M_j' state, $\sigma^{M_j'=0}$, $\sigma^{M_j'=1}$, and $\sigma^{M_j'=2}$.

The resultant relative cross-sections, $\sigma^{M_j'}$, were determined to be as follows.

$$\sigma^{M_j'=0}:\sigma^{M_j'=1}:\sigma^{M_j'=2} = 1:(1.031 \pm 0.019):(1.320 \pm 0.020) \quad \text{for ArCl}^* \text{ channel} \quad (6)$$

$$\sigma^{M_j'=0}:\sigma^{M_j'=1}:\sigma^{M_j'=2} = 1:(0.979 \pm 0.003):(0.981 \pm 0.003) \quad \text{for CCl}_2^* \text{ channel} \quad (7)$$

They are summarized in Figure 2. From Figure 2, it is found that the two reaction channels show different atomic alignment dependence. A significant atomic alignment effect was observed for the ArCl^* excimer formation, while the CCl_2^* formation via energy transfer process is almost isotropic with negligible alignment effect.

3-2. Atomic Alignment Effect on CCl_2^* and ArCl^* Formation. A schematic potential diagram for the reaction of $\text{Ar}(^3\text{P}_2) + \text{CCl}_4$ is shown in Figure 3. The excitation energy of $\text{Ar}(^3\text{P}_2)$ is 11.55 eV. The ionization potential (IP) of $\text{Ar}(^3\text{P}_2)$ is estimated to be 4.2 eV from the IP (15.76 eV) of Ar. The electron affinity of CCl_4 has been reported to be 0.8 ± 0.34 eV.¹⁹ The reaction of $\text{Ar}(^3\text{P}_2) + \text{CCl}_4$ is expected to be initiated by an electron jump to generate the ion-pair ($\text{Ar}^+ - \text{CCl}_4^-$). Since the ion-pair potential of $V(\text{Ar}^+ - \text{CCl}_4^-)$ is far above the ground-state of the collision pair, the attractive ion-pair potential $V(\text{Ar}^+ - \text{CCl}_4^-)$ passes through the sequence of excited states of the reagent $V(\text{Ar} - \text{CCl}_4^*)$. Coupling between the ion-pair state

$V(\text{Ar}^+ - \text{CCl}_4^-)$ and some of these excited states $V(\text{Ar} - \text{CCl}_4^*)$ diverts trajectories from the ion-pair potential to products correlating to the excited reagent state CCl_4^* . The $\text{CCl}_2^*(\tilde{\text{A}})$ formation proceeds via the back-electron-transfer from the ion-pair ($\text{Ar}^+ - \text{CCl}_4^-$) to the excited state ($\text{Ar} - \text{CCl}_4^*$).

The valence shell configuration of CCl_4 was reported to be $(6t_2)^6(2e)^4(7t_2)^6(2t_1)^6$.²⁰ (Another assignment of $(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$ has been sometimes used for the same configuration).²¹ The orbital energy was reported to be 11.69, 12.62, 13.44, and 16.58 eV for the $2t_1$, $7t_2$, $2e$, and $6t_2$ orbital, respectively.²² The formation of $\text{CCl}_2^*(\tilde{\text{A}})$ is known to proceed via the following two reactions from the excited states CCl_4^* .



The onsets for two reactions were reported to be 6.1 and 8.6 eV, respectively. Reaction b is known to be the dominant process.^{21,23} Three transitions peaked at 9.42, 9.70, and 11.08 eV were reported for the excited states of CCl_4 related to the $\text{CCl}_2^*(\tilde{\text{A}})$ formation. These transitions have been assigned to be $(2t_1)^{-1}4p$, $(7t_2)^{-1}4p$, and $(2e)^{-1}4p$, respectively.²⁴ Therefore, the sequence of excited states related to the $\text{CCl}_2^*(\tilde{\text{A}})$ formation should be characterized by the promotion of an electron from the $2e$ (and/or $7t_2$, $2t_1$) molecular orbital to the $4p$ Rydberg orbital, $\text{Ryd}(4p)$.²⁵ In order for the energy transfer to occur, the set of orbitals, $[3p + 2e \text{ (and } 7t_2, 2t_1)]$ and $[4s + \text{Ryd}(4p)]$, must overlap.

The electron transfer from the $4s$ orbital of Ar to the $\text{Ryd}(4p)$ orbital of CCl_4 should be related to the ion-pair formation. Generally speaking, it is unlikely that ion-pair formation gives a clear atomic alignment effect, because this is the electron transfer process from the widespread outer $4s$ orbital of $\text{Ar}(^3\text{P}_2)$ to the widespread empty $\text{Ryd}(4p)$ orbital of CCl_4 .

The electron transfer from the $2e$ (and $7t_2$, $2t_1$) orbital to the hole of the $3p$ orbital of Ar should correspond to the back-electron-transfer. It is also unlikely that the electron transfer probability from the $2e$ (and $7t_2$, $2t_1$) orbital to the hole of the $3p$ shell of Ar has a clear atomic alignment effect because the $2e$ (and $7t_2$, $2t_1$) molecular orbital is dominantly characterized by the degenerated $2p$ atomic orbitals on the four Cl atoms that overlap each other and are not easy to distinguish.

No significant atomic alignment effect being observed for $\text{CCl}_2^*(\tilde{\text{A}})$ formation via excitation transfer indicates that the electron transfer process for both the formation of ion-pair ($\text{Ar}^+ - \text{CCl}_4^-$) and the back-electron-transfer from the ($\text{Ar}^+ - \text{CCl}_4^-$) has little alignment effect.

In contrast with the negligible alignment effect for the excitation transfer process (CCl_2^* formation), we observed a significant atomic alignment effect for the atom transfer process (ArCl^* excimer formation). The formation of ArCl^* is known to proceed via the harpooning mechanism. The effect of ion-cores on the exit channel potential and/or on the branching to each reaction channel is directly confirmed. In order to explain the clear M_j' effect for the ArCl^* formation, we must assume that the configuration of the $3p$ orbital of $\text{Ar}(^3\text{P}_2)$ in collision frame experimentally prepared before collision must be conserved as the configuration of the $3p$ electron of the ion-core of $\text{Ar}^+(^2\text{P}_j)$ in the ion-pair ($\text{Ar}^+ - \text{CCl}_4^-$) after the electron jump. This assumption seems to be reasonable, because the coupling between the ion-core of $\text{Ar}^+(^2\text{P}_j)$ and the $4s$ electron is known to be weak for $\text{Ar}(^3\text{P}_2)$ and can be expressed as $4s[3/2]_j^2$ by $j-1$ coupling. Indeed, the conservation of the spin-orbit state in the ion-core ($\text{Ar}^+(^2\text{P}_{1/2})$) was reported in the $\text{Ar}(^3\text{P}_0) + \text{RX}$ reaction.¹⁶ On the basis of the assumption that the angular

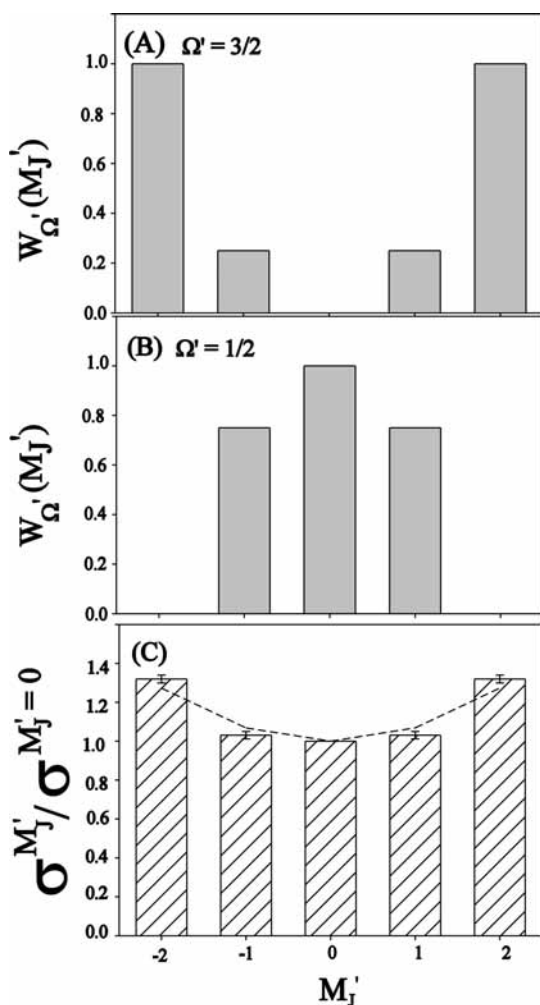


Figure 4. (a, b) Calculated M_J' state dependence of each Ω' component, $\Omega' = 3/2$ (A), $\Omega' = 1/2$ (B), by using a standard recoupling procedure of angular momentum through the Clebsch–Gordan coefficients under the assumption that the angular momentum of the $\text{Ar}^+(\text{}^2\text{P}_1)$ is conserved after the electron jump of the 4s electron. (c) The experimental M_J' state dependence of the cross section for $\text{ArCl}^*(\text{C})$ (dashed bars), the calculated M_J' state dependence of the cross section for $\text{ArCl}^*(\text{C})$ by $0.56W_{3/2}(M_J') + 0.44W_{1/2}(M_J')$ (solid line).

momentum of the $\text{Ar}^+(\text{}^2\text{P}_1)$ is conserved after the electron jump of the 4s electron, the electronic state of $\text{Ar}^+(\text{}^2\text{P}_1)$ should become $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ state. Moreover, the observed clear atomic alignment effect in the collision frame implies that the quantum number of Ω' in the collision frame is also conserved in the ion-pair ($\text{Ar}^+-\text{CCl}_4^-$) through the whole course. In this case, the configuration of angular momentum of $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ provides two spin–orbit states, $\Omega' = 3/2$ and $\Omega' = 1/2$, in the collision frame,



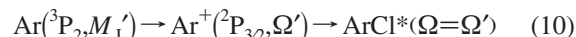
where m_s' is the magnetic spin quantum state of 4s electron in the $\text{Ar}(\text{}^3\text{P}_2, M_J')$.

The fraction of each Ω' component $W_{\Omega'}(M_J')$ in the M_J' state can be calculated by using a standard recoupling procedure of angular momentum through the Clebsch–Gordan coefficients as follows,²⁶

$$W_{\Omega'}(M_J') = |\langle 2, M_J' | 3/2, \Omega' = (M_J' - M_s'), 1/2, M_s' \rangle|^2 \quad (9)$$

They were summarized in Figure 4a,b. If the electronic configuration of the inner 3p electron in the $\text{Ar}(\text{}^3\text{P}_2)$ is conserved

as the electronic configuration of the 3p electron of the ion-core of $\text{Ar}^+(\text{}^2\text{P}_{3/2})$ in the ion-pair ($\text{Ar}^+-\text{CCl}_4^-$) after the electron jump, it is expected that the M_J' dependence for $\text{ArCl}^*(\text{B}, \Omega = 1/2)$ and $\text{ArCl}^*(\text{C}, \Omega = 3/2)$ formation in the reaction of $\text{Ar}(\text{}^3\text{P}_2) + \text{CCl}_4$ can be directly correlated to the Ω' distribution in collision frame for the collinear approach, $W_{\Omega'}(M_J')$.



In this case, the M_J' dependence of $\text{ArCl}^*(\text{C}, \Omega = 3/2)$ formation can be expressed in terms of $W_{3/2}(M_J')$ for the collinear approach. The experimental M_J' state dependence of the cross section for $\text{ArCl}^*(\text{C})$ can be well reproduced by the summation of $0.56W_{3/2}(M_J') + 0.44W_{1/2}(M_J')$. Although the large fraction of $W_{1/2}(M_J')$ is inconsistent with the M_J' selectivity under the collinear correlation, this consistency is reasonable because the M_J' selectivity at the noncollinear approach should be disturbed by the change of the configuration of Ar^+-Cl^- axis due to impact parameter.

In conclusion, the effect of ion-core (and/or the effect of the angular momentum Ω' of the ion-core in the collision frame) on the exit channel potential is directly revealed for the atom transfer reaction of $\text{Rg}^*(\text{}^3\text{P}_2) + \text{XR}$.

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