ARTICLES

Steric Effect in the Energy Transfer Reaction of N_2 + Rg ($^3P_2$) (Rg = Kr, Ar)

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Received: July 29, 2008; Revised Manuscript Received: August 27, 2008

Steric effect for the formation of N_2 (B, $^3\Pi_u$) in the energy transfer reaction of Kr ($^3P_2$) + N_2 has been measured using an oriented Kr ($^3P_2$, $M_J = 2$) beam at a collision energy of 0.07 eV. The N_2 (B, $^3\Pi_u$) emission intensity was measured as a function of the magnetic orientation field direction in the collision frame. A significant atomic alignment effect on the energy transfer probability was observed. This result was compared with that for the formation of N_2 (C, $^3\Pi_g$) in the Ar ($^3P_2$) + N_2 reaction. Despite the large difference on the energy transfer cross-section, the atomic alignment dependence for Kr ($^3P_2$) + N_2 is found to be analogous to that for Ar ($^3P_2$) + N_2. It is revealed that the configuration of inner 4p (3p) orbital in the collision frame gives an important role for the stereoselectivity on electron transfer process via the curve-crossing mechanism.

1. Introduction

The excitation transfer reaction of metastable rare gas Rg (^3P) with N_2 is one of the simplest reaction systems widely investigated as a benchmark system so far.[1−12] For the Rg (^3P) + N_2 reaction, detailed experimental information such as the fully resolved state-to-state data is now available.[11−13] The reaction has provided detailed information about the collisional energy transfer process. It has been recognized that this reaction proceeds via the curve-crossing mechanism.[11] The intermediate state has been identified as $Rg^+ + N_2^-(X^2\Pi_g)$. Despite numerous experimental studies, the process of excitation transfer is not fully understood, because the complexity of excited atom-heavy molecular systems is still almost prohibitive for large-scale calculation of the interaction potentials, coupling, and scattering cross-sections. No theoretical information is available, and only semiempirical potentials exist for Rg (^3P) + N_2.[11,14]

For the Rg ($^3P_2$) + N_2 reaction, the importance of the steric requirement was predicted. From the π^+ states preference of the product N_2 (C, $^3\Pi_u$), Setser et al.[2] and Derouard et al.[4] proposed an energy transfer mechanism via the formation of a linear complex, ArN_2*. They proposed that the in-plane approach of the Ar (^3P) with its half-filled *p*-orbital parallel to this plane should favor the reaction. In addition, from the rotational alignment of N_2 (C, $^3\Pi_u$), Tyndall et al. also suggested a similar model that the reaction occurs preferentially in the plane of rotation of N_2 via an electron exchange mechanism.[5] In spite of the recognition that the steric effect is an important factor for the control of the title reaction, nothing has been directly studied about the steric aspect of the title reaction. Recently, we developed an oriented Ar ($^3P_2$, $M_J = 2$) beam and applied it to the energy transfer reactions.[15−21]

For the Ar ($^3P_2$) + N_2 reaction, we observed a significant steric effect in the Ar ($^3P_2$) + N_2 reaction by using an oriented Ar ($^3P_2$) beam,[15] and the observed steric effect supports the mechanism proposed by Setser et al.[2,4] that the energy transfer process proceeds via ArN_2* complex formation. We tentatively assigned the observed steric effect as the favorable configuration of the 3p orbital for the efficient overlap with $2\sigma_u$ molecular orbital of N_2. However, the origin of the stereoselectivity is still unobvious because the energy transfer reaction of Ar ($^3P_2$) + $N_2 \rightarrow N_2$ (C, $^3\Pi_u$) + Ar is known to proceed via the formation of an ion-pair intermediate $Ar^+ + N_2^-(X^2\Pi_g)$ in the curve-crossing mechanism.

To make clear the stereoselectivity in the course of the energy transfer process, it is interesting to compare the analogous reaction systems that have different reaction probability. In the present study, the atomic alignment effect for the formation of N_2 (B, $^3\Pi_u$) in the energy transfer reaction of Kr ($^3P_2$) + N_2 has been measured and compared with that for the formation of N_2 (C, $^3\Pi_g$) in the Ar ($^3P_2$) + N_2. Despite the large difference on the energy transfer cross-section, an analogous atomic alignment dependence was observed for these reaction systems.

2. Experimental Section

The experimental apparatus and procedure were almost the same as the previous one.[15,21] A metastable Rg ($^3P_{0,2}$) beam generated by a pulsed glow discharge with a pulse width of 100 μs was state-selected by a magnetic hexapole. The almost pure Kr (and Ar) ($^3P_2$, $M_J = 2$) beam with the velocity of 490 (and 700) ms^{-1} collides with the N_2 beam in a homogeneous magnetic orientation field. The N_2 beam was injected with a stagnation pressure of 8 torr from a pulsed valve that was placed at a distance of 8 cm from the beam crossing point. The chemiluminescence from the product N_2 (B, $^3\Pi_{u}$,) for Kr ($^3P_2$, $M_J = 2$) and N_2 (C, $^3\Pi_g$) for Ar ($^3P_2$, $M_J = 2$) was selectively collected and detected by through a suitable band-pass filter (HOYA L42, U340). The signal from the photomultiplier was counted by a multichannel scaler (Stanford SR430). The chemiluminescence was 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 Rg ($^3P_2$) beam axis. The homogeneous magnetic orientation field was generated by the four pieces of ferrite magnets mounted on a motor-driven rotatable stage, and its direction **B** was rotated around the beam

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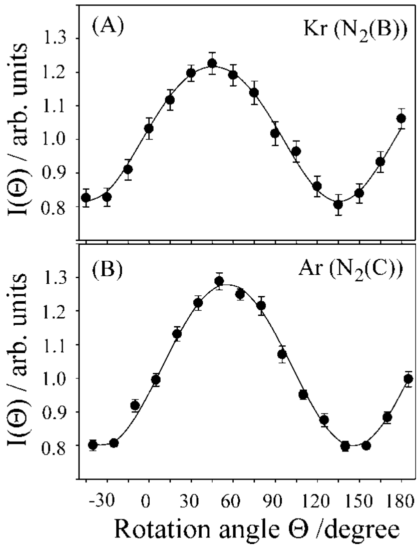

Figure 1. N_2 (B, C) chemiluminescence intensity as the function of rotation angle Θ of the magnetic orientation field direction. The origin of the rotational angle Θ is the direction of the Rg ($^3P_2$) beam axis: N_2 (B) formation from the Kr ($^3P_2$) + N_2 reaction (A), N_2 (C) formation from the Ar ($^3P_2$) + N_2 reaction (B). Experimental values (closed circles) and Θ-dependence represented by the fittings with using eq 3 (solid lines).

crossing point over the angle region $-45 \leq \Theta \leq 180°$ by an interval of 15°.

3. Results and Discussion

3.1. M'_J-Dependent Cross-section in the Collision Frame, $\sigma^{|M'_J|}$.

Figure 1 shows the Θ-dependence of the chemiluminescence intensity of N_2 (B, $^3\Pi_u$) for Rg = Kr and N_2 (C, $^3\Pi_g$) for Rg = Ar as a function of the rotation angle Θ of the direction of magnetic orientation field **B**. The difference of the maximum peak position for two reaction systems is due to the difference of the relative velocity direction between two reaction systems. These Θ-dependencies can be analyzed using the evolution procedure based on an irreducible representation of the density matrix.[15−20] The chemiluminescence intensity, $I_{obs}(\Theta)$, can be written as follows by using the relative cross-section, $\sigma^{|M'_J|}$, in the collision frame.

$$I_{obs}(\Theta) = \frac{I(\Theta)}{D\bar{I}} = \frac{1}{280}(39\sigma^{M'_J=0} + 88\sigma^{|M'_J|=1} + 153\sigma^{|M'_J|=2}) + \frac{1}{16}(-3\sigma^{M'_J=0} - 4\sigma^{|M'_J|=1} + 7\sigma^{|M'_J|=2})\cos 2\theta + \frac{1}{64}(3\sigma^{M'_J=0} - 4\sigma^{|M'_J|=1} + \sigma^{|M'_J|=2})\cos 4\theta \quad (1)$$

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 **B**. It is defined as $\theta \equiv \Theta_{v_R} - \Theta$ using the direction of the relative velocity V_R in the laboratory coordinate. Because θ has a distribution by the misalignment caused by the velocity distribution of the N_2 beam, we must use the cos $2n\theta$ factors averaged over the Maxwell−Boltzmann velocity distribution of the N_2 beam at room temperature, $\langle\cos(2n(\Theta_{v_R} - \Theta))\rangle$. Finally, we use the following equation for the evaluation of the experimental results,

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

The coefficients (a_n) were determined as the fitting parameters by the use of eq 3 through a χ^2 analysis. They are summarized as follows:

$$a_2/a_0 = -0.214 \pm 0.006, \quad a_4/a_0 = -0.015 \pm 0.008 \text{ for Kr}(^3P_2)$$

$$a_2/a_0 = -0.249 \pm 0.006, \quad a_4/a_0 = -0.004 \pm 0.007 \text{ for Ar}(^3P_2)$$

A notable contribution of rank 4 moment (a_4) was recognized for the Kr ($^3P_2$) reaction. This result suggests that the unpaired inner orbital of the triplet species interacts with the outer extended orbital in the course of energy transfer process. 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.

$$\sigma^{M'_J=0} : \sigma^{|M'_J|=1} : \sigma^{|M'_J|=2} = 1 : 1.116 \pm 0.035 : 0.652 \pm 0.018 \text{ for Kr}(^3P_2)$$

$$\sigma^{M'_J=0} : \sigma^{|M'_J|=1} : \sigma^{|M'_J|=2} = 1 : 0.934 \pm 0.025 : 0.546 \pm 0.012 \text{ for Ar}(^3P_2)$$

They are summarized in Figure 2. As a reference, the expected $\sigma^{|M'_J|}$ from the Percival−Seaton hypothesis were also shown in Figure 2, as a broken line, that were calculated by using the standard recoupling procedure of angular momentum through the Clebsch−Gordan coefficients.[15,22] At a glance, it is recognized that the experimental $\sigma^{|M'_J|}$, does not follow the Percival−Seaton hypothesis. From the Figure 2, it is found that the title two reactions show similar atomic alignment dependence despite the two reactions systems having different orders of cross section.

3.2. Atomic Alignment Effect on the Energy Transfer Probability.

The electron configuration for the excited N_2 (B, $^3\Pi_g$) state is represented by $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(2\sigma_u)^2$ $(1\pi_u)^4$ $(3\sigma_g)^1$ $(1\pi_g)^1$.[23] The N_2 (B, $^3\Pi_g$) state is formed by promotion of an electron from $3\sigma_g$ to $1\pi_g$. This takes place by the exchange process; the 5s electron of Kr ($^3P_2$) transfers to an empty $1\pi_g$ orbital and a $3\sigma_g$ electron transfers to the half-filled 4p orbital. Similarly, the electron configuration for the excited N_2 (C, $^3\Pi_u$) state is represented by $(1\sigma_g)^2$ $(1\sigma_u)^2$ $(2\sigma_g)^2$ $(2\sigma_u)^1$ $(1\pi_u)^4$ $(3\sigma_g)^2$

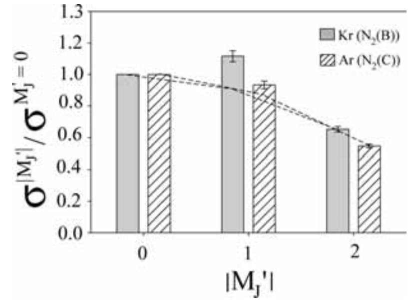

Figure 2. The relative cross-sections for each M'_J state in the collision frame, $\sigma^{M'_J=0}$, $\sigma^{|M'_J|=1}$, and $\sigma^{|M'_J|=2}$. N_2 (B) formation for the Kr ($^3P_2$) + N_2 reaction (shaded bar), N_2 (C) formation for the Ar ($^3P_2$) + N_2 reaction (dashed bar). The broken line indicates the cross-section estimated on the basis of the Percival−Seaton hypothesis.

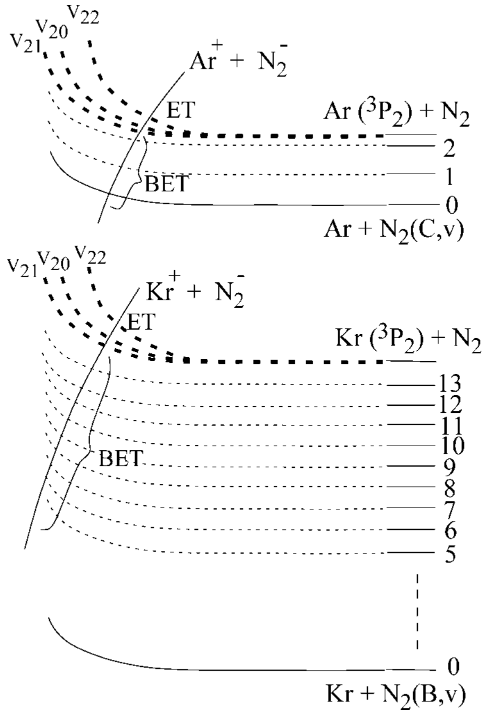

Figure 3. A schematic drawing of the energy transfer mechanism via the curve-crossing mechanism. The electrostatic induction terms that were caused by the penetration of the N_2 molecule into the diffuse 5s (4s) orbital of the Kr ($^3P_2$) (Ar ($^3P_2$)) atom should contribute in the entrance channels. The open shell character of the Rg^+ (^2P_j) ion core splits the entrance surface into three branches (V_J)—designated as V_{22}, V_{21}, and V_{20}—that correlate with Rg ($^3P_2$). The spin−orbit interaction in the Rg ($^3P_2$) affects the adiabatic potential energy curves of the entrance channels by partially mixing their Σ and Π electrostatic characters at intermediate and large intermolecular distance. “ET” designates the electron transfer in step 1, and “BET” designates the back electron transfer in step 2.

$(1\pi_g)^1$.[23] The N_2 (C, $^3\Pi_u$) state is formed by promotion of an electron from $2\sigma_u$ to $1\pi_g$. This takes place by the exchange process; the 4s electron of Ar ($^3P_2$) transfers to an empty $1\pi_g$ orbital, and the $2\sigma_u$ electron transfers to the half-filled 3p orbital.

The excitation transfer reaction of Rg ($^3P_2$) + N_2 has been recognized as the reaction that proceeds via the curve-crossing mechanism. The intermediate state has been identified as $Rg^+ + N_2^-$ ($X^2\Pi_g$).[12] The process proceeds via the following two electron transfer processes.

Step 1: electron transfer (ET) from the 5s (4s) orbital of Kr ($^3P_2$) (Ar ($^3P_2$)) to the empty $1\pi_g$ orbital of N_2.

Step 2: Back electron transfer (BET) from the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^- to the half-filled 4p (3p) orbital of Kr^+ (Ar^+).

The mechanism was schematically shown in Figure 3. Generally speaking, it is unlikely that the configuration of the inner 4p (3p) orbital gives a significant effect on the electron transfer probability in step 1, because step 1 is the electron transfer process from the widespread outer 5s (4s) orbital of Kr ($^3P_2$) (Ar ($^3P_2$)) to the widespread empty $1\pi_g$ orbital of N_2. The$1\pi_g$ orbital has two nodal planes (see Figure 4). One bisects the N−N axis. The other coincides with the N−N axis. On the basis of the symmetry for the$1\pi_g$ orbital, this electron transfer should be favorable for the bent configuration of N_2 along the relative velocity (V_a and V_b) as shown in Figure 4. According to the semiempirical potential energy surface reported by Vredenbregt et al.,[12] the electron transfer is expected to take place at a rather short internuclear distance (ca. <3 Å). At such closer intermolecular distances, the steric requirement of the orbital overlap at step 1 might become less important because of the distortion of the diffuse 5s (4s) orbital, caused by the penetration of the N_2 molecule into the diffuse 5s (4s) orbital of the Kr ($^3P_2$) (Ar ($^3P_2$)) atom. On the contrary, in such case, the open shell nature of the Rg^+ (^2P_j) ion core should give an important role on the effective adiabatic potentials. In other word, electrostatic induction terms should contribute in the entrance channels. A schematic drawing of the entrance surfaces is shown in Figure 3. As formulated by Aquilanti et al.,[24] the open shell character of the Rg^+ (^2P_j) ion core splits the entrance surface into three branches $V_{J\Omega}$—V_{22}, V_{21}, and V_{20}—that correlate with Rg ($^3P_2$) (Ω is the absolute projection of the total electronic angular momentum J along the intermolecular axis. In the present study, Ω directly corresponds to $|M'_J|$). These three effective adiabatic potentials $V_{J\Omega}$ have the different weight of Σ and Π characters.

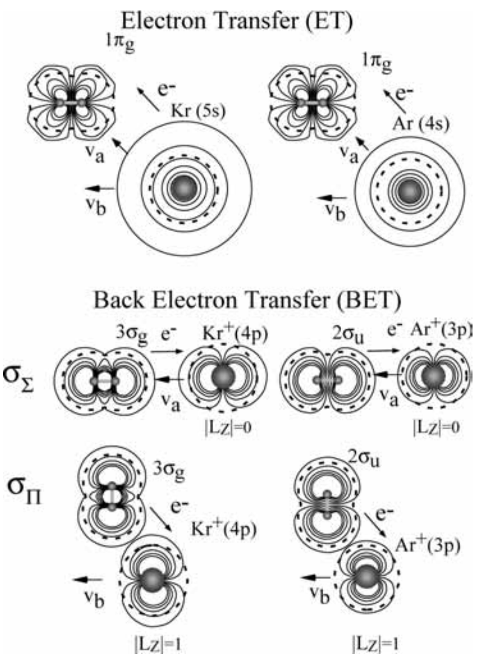

Figure 4. A schematic drawing of the energy transfer mechanism. The two representative configurations between the $3\sigma_g$ ($2\sigma_u$) molecular orbital of N_2 and the 4p (3p) atomic orbital of Rg ($^3P_2$): Σ-configuration ($L_Z = 0$), Π-configuration ($L_Z = 1$). The electron density distributions of the $3\sigma_g$ ($2\sigma_u$) orbital of N_2 and the 4p (3p) atomic orbital of Kr (Ar) were calculated using the GAUSSIAN 98 ab initio program package with 6−311G (3df, 2pd) basis set. Dashed lines indicate the van der Waals surface of molecule as an approximate position of the repulsive wall. The arrows of υ_a and υ_b show the relative velocity direction that is favorable for the electron transfer.

$$V_{J\Omega} = W_\Pi(J\Omega)V_\Pi + W_\Sigma(J\Omega)V_\Sigma$$

where W_Σ and W_Π are the weights of the two electrostatic characters in the entrance channels at each crossing point.

$$W_\Pi(2,2) = 1, \quad W_\Sigma(2,2) = 0$$

$$W_\Pi(2,1) = \frac{2}{3}\cos^2 \alpha, \quad W_\Sigma(2,1) = 1 - \frac{2}{3}\cos^2 \alpha$$

$$W_\Pi(2,0) = \sin^2 \alpha, \quad W_\Sigma(2,0) = \cos^2 \alpha$$

where

$$\cos^2 \alpha = \frac{1}{2}\frac{3\beta}{10(1 + \frac{9}{25}\beta^2)^{1/2}}$$

where $\beta = V_2/\varepsilon$, and V_2 is the anisotropic component of the interaction that was obtained by a spherical harmonics expansion of the potential around the P-state atom, and ε is the spin−orbit term. The spin−orbit interaction in the Rg ($^3P_2$) affects the adiabatic potential energy curves of the entrance channels by partially mixing their Σ and Π electrostatic characters at intermediate and large intermolecular distance. On the basis of this treatment, the relative reactivity for each magnetic substate in the collision frame ($\sigma^{|M_J'|}$) can be expressed as follows,

$$\sigma^{|M_J'|} = W_\Pi(|M_J'|)\sigma_\Pi + W_\Sigma(|M_J'|)\sigma_\Sigma$$

where σ_Π and σ_Σ are the cross-section for the two electrostatic characters in the entrance channels at each crossing point. The experimental results can be represented by using the two parameters $\cos^2 \alpha$ and $R \equiv \sigma_\Sigma/\sigma_\Pi$. They were summarized as follows,

$$\cos^2 \alpha = 0.4 \quad \left(\beta \equiv \frac{V_2}{\varepsilon} \approx -0.3\right) \text{ and } \frac{\sigma_\Sigma}{\sigma_\Pi} = 2.4 \text{ for Kr } (^3P_2)$$

$$\cos^2 \alpha = 0.5 \quad \left(\beta \equiv \frac{V_2}{\varepsilon} \approx -0\right) \text{ and } \frac{\sigma_\Sigma}{\sigma_\Pi} = 2.7 \text{ for Kr } (^3P_2)$$

The parameter of $\cos^2 \alpha$ is found to be almost equal to ~0.5. This result means that the curve-crossing occurs at the intermolecular distance where the spin−orbit interaction is dominant as compared with the anisotropic term, $|V_2| < \varepsilon$. We observed a slight difference of $\cos^2 \alpha$ between the two reaction systems. This difference can be attributed to the difference of the crossing point between two reaction systems. Kr ($^3P_2$) + N_2 experiences the curve-crossing at the shorter intermolecular distance as compared with that for Ar ($^3P_2$) + N_2. In addition, we observed a large difference on the cross section for the two electrostatic characters $R \equiv \sigma_\Sigma/\sigma_\Pi \approx 2.5$. The values of $R \equiv \sigma_\Sigma/\sigma_\Pi$ for the two reaction systems are also found to be slightly different. We can expect the three orientation of the half-filled 4p (3p) orbital of Rg ($^3P_2$) for entrance channels: (1) pointing toward the center of the N_2 molecule ($L_Z = 0$); (2) oriented perpendicularly to the plane of the three atoms ($|L_Z| = 1$); and (3) orthogonal to the two previous orientations ($|L_Z| = 1$). On general grounds for the correlation of potential surface of the collisional complex, it is expected that when a Rg ($^3P_2$) atom collides with its filled orbitals pointing toward the N_2 center of mass ($|L_Z| = 1$), the energy transfer processes will be more effective, since here the entrance and exit channels exhibit the same character under several different symmetries.[24] However, this expectation is in conflict with the present result. Because it is expected that Σ entrance states ($L_Z = 0$) lead to Π exit states by Coriolis coupling for the $C_{\infty V}$ symmetry, the present result $R \equiv \sigma_\Sigma/\sigma_\Pi \approx 2.5$ means the importance of the $C_{\infty V}$ symmetry with the half-filled 4p (3p) orbital of Rg ($^3P_2$) is pointing toward the center of the N_2 molecule.

Vecchiocattivi et al. have reported another scheme to evaluate the weight of Σ and Π character in the effective adiabatic potential curve $V_{j\Omega}$ for the Rg$^+$ (^2P_j) neutral system where the coupling due to the inner shell vacancy of the metastable atom is also considered.[25] According to this scheme, two effective adiabatic potentials $V_{j\Omega}$ can be expressed as follows,

$$V_{3/2,3/2} = V_\Pi, \; V_{3/2,1/2} = W_\Pi V_\Pi + W_\Sigma V_\Sigma$$

We assume that the coupling between the ion core of Kr$^+$ (^2P_j) and the 5s electron is negligibly weak. In this case, the fraction of Ω component in ion core Rg$^+$($^2P_{3/2}$) produced from each M_J' state of Rg ($^3P_2$) can be calculated using a standard recoupling procedure of angular momentum through the Clebsch−Gordan coefficients.[22] The relative reactivity for each magnetic substate in the collision frame, $\sigma^{|M_J'|}$, can be expressed as follows,

$$\sigma^{|M_J'|=2} = \sigma_{3/2,3/2} = \sigma_\Pi$$

$$\sigma^{|M_J'|=1} = \frac{1}{4}\sigma_{3/2,3/2} + \frac{3}{4}\sigma_{3/2,1/2} = \frac{(1+3W_\Pi)}{4}\sigma_\Pi + \frac{3}{4}W_\Sigma\sigma_\Sigma$$

$$\sigma^{|M_J'|=0} = \sigma_{3/2,1/2} = W_\Pi\sigma_\Pi + W_\Sigma\sigma_\Sigma$$

Unfortunately, this scheme can not reproduce the qualitative relationship among the experimental relative cross-sections; $\sigma^{M_{J=0}'} < \sigma^{|M_{J=1}'|}, \approx \sigma^{|M_{J=2}'|}$. It is found that the picture of Rg$^+$ (^2P_j) $-N_2$ can not suitable to express the effective adiabatic potential in step 1.

To understand the large difference between σ_Π and σ_Σ, we must consider the steric effect in step 2 (BET). We calculate the electron density distributions of the $3\sigma_g$ ($2\sigma_u$) orbital of N_2 and 4p (3p) atomic orbital of Kr (Ar) using the GAUSSIAN 98 ab initio program package with 6−311G (3df, 2pd) basis set. The mechanism is schematically shown in Figure 4. As can be expected from the similarity of the molecular orbital related to the energy transfer, the atomic alignment dependence for two reaction systems are analogous despite the extreme difference of cross-section. A clear M_J' dependence observed in the title reactions indicates that the configuration of inner atomic orbital with spin interaction gives a significant effect on the electron and/or back-electron transfer process.

Because step 2 is the electron transfer process from the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^- to the half-filled 4p (3p) orbital of Kr$^+$ (Ar$^+$), the configuration of the half-filled 4p (3p) orbital of Kr$^+$ (^2P_J) (Ar$^+$ (^2P_J)) should give a significant effect on the back-electron transfer in step 2. To explain the clear atomic alignment effect experimentally observed, however, we must assume that the configuration of the inner 4p (3p) orbital of Kr ($^3P_2$) (Ar ($^3P_2$)) experimentally prepared before collision must be conserved as the configuration of the 3p orbital of ion core of Ar$^+$ (^2P_j) during a long-duration time of step 2 after the energy transfer has occurred (step 1). If this is the case, the efficiency for the orbital interaction can be qualitatively estimated from a simple consideration about the orbital overlap efficiency based on the symmetry of the relevant orbital. The similarity of atomic alignment dependence for two reaction systems should be attributed to the analogous spatial distribution of the molecular orbital related to the energy transfer for two reaction systems. On the basis of the symmetry of the related orbital, we can expect two favorable configurations, Σ-configuration and Π-configuration, between the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^- and the half-filled 4p (3p) orbital of Kr$^+$ (Ar$^+$) for the back-electron transfer, as shown in Figure 4. The Σ-configuration ($L_Z = 0$) is favorable for collisions with a wide range of the impact parameters, whereas the Π-configuration ($|L_Z| = 1$) is favorable only for the collision with a large impact parameter. The steric effect observed in the present study, $R \equiv \sigma_\Sigma/\sigma_\Pi = \sigma(L_Z = 0)/\sigma(|L_Z| = 1) \approx 2.5$, means that the Σ-configuration ($L_Z = 0$) is 2.5 times more favorable than the Π-configuration ($|L_Z| = 1$).

It is hard to exactly evaluate the orbital overlap by taking the interaction potential into consideration. Here, we roughly estimate the orbital overlap efficiency based on a simple model shown in Figure 5. The exterior electron for the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^- is localized near the molecular axis, and the distribution seems to be spherical near the molecular axis. Therfore, it is not unreasonable to assume that the efficient orbital overlap only occurs within the limited Rg$^+$−N_2^- configuration. Here, θ is the angle between the N_2^- molecular axis and the direction of Rg$^+$ from the center of mass of N_2^-. The intermolecular distance

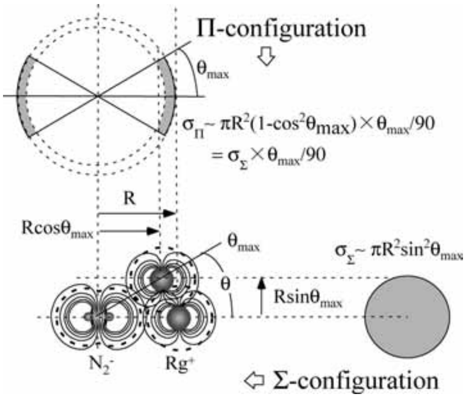

Figure 5. A schematic drawing of the orbital overlap efficiency for the back electron transfer. The exterior electron for the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^- is localized near the molecular axis, and the distribution was assumed to be spherical near the molecular axis. θ is the angle between the N_2^- molecular axis and the direction of Rg^+ from the center of mass of N_2^-. R is the $Rg^+-N_2^-$ distance for the efficient orbital overlap at $0 = \theta$. The efficient orbital overlap is assumed to only occur within the $Rg^+-N_2^-$ configuration limited by $0 \le \theta \le \theta_{max}$. Shaded regions show the cross-section to reach the favorable $Rg^+-N_2^-$ configuration for the approach under Σ- and Π-configuration. The cross-section for the approach under Σ- and Π-configuration is estimated to be $\sigma_\Sigma \approx \pi R^2 \sin^2 \theta$ and $\sigma_\Pi \approx \pi R^2(1 - \cos^2 \theta)\theta_{max}/90$, respectively. The cross-section ratio between Σ- and Π-configuration is simply expressed as $R = \sigma_\Sigma/\sigma_\Pi \approx 90/\theta_{max}$.

for the efficient orbital overlap at $0 = \theta$ is expressed by R. Because the orbital overlap is a function of the $Rg^+-N_2^-$ configuration, the efficiency of the orbital overlap for Σ- and Π-configurations can be attributed to the probability to reach the reactive $Rg^+-N_2^-$ configuration. If we assume the straight trajectories, the cross-section for the approach with Σ- and Π-configuration can be estimated as follows (see the shaded region in Figure 5),

$$\sigma_\Sigma \approx \pi R^2 \sin^2\theta, \quad \sigma_\Pi \approx \pi R^2(1 - \cos^2\theta)\theta_{max}/90$$

As a result, the cross-section ratio between Σ- and Π-configuration is simply expressed by $R = \sigma_\Sigma/\sigma_\Pi \approx 90/\theta_{max}$. This estimation seems to be in accord with the experimental value of $R \approx 2.5$ because the θ_{max} is expected to be less than 45° on the basis of the exterior electron distribution for the $3\sigma_g$ ($2\sigma_u$) orbital of N_2^-.

Conclusions

It is suggested that the observed steric effect is primarily due to the favorable configuration of the 4p (3p)-orbital of Kr ($^3P_2$) (Ar ($^3P_2$)) for the efficient overlap with the $3\sigma_g$ ($2\sigma_u$) molecular orbital of N_2 and due to the steric effect on the entrance surface caused by the open shell character of the Rg^+ (^2P_j) ion core and the spin−orbit interaction.

References and Notes

(1) Sadeghi, N.; Setser, D. W. *Chem. Phys. Lett.* **1981**, *82*, 44.
(2) Setser, D. W.; Stedman, D. H.; Coxon, J. A. *J. Chem. Phys.* **1970**, *53*, 1004.
(3) Piper, L. G.; Velazco, J. E.; Setser, D. W. *J. Chem. Phys.* **1973**, *59*, 3323.
(4) Derouard, J.; Nguyen, T. D.; Sedeghi, N. *J. Chem. Phys.* **1980**, *72*, 6698.
(5) Tyndall, G. W.; de Vries, M. S.; Cobb, C. L.; Martin, R. M. *J. Chem. Phys.* **1987**, *87*, 5830.
(6) Krenos, J.; Bruno, J. B. *Chem. Phys. Lett.* **1977**, *49*, 447.
(7) Lee, W.; Martin, R. M. *J. Chem. Phys.* **1975**, *63*, 962.
(8) Schweid, A. N.; Fluendy, M A. D.; Muschlitz, E. E., Jr. *Chem. Phys. Lett.* **1976**, *42*, 103.
(9) Sanders, R. A.; Schweid, A. N.; Weiss, M.; Muschlitz, E. E., Jr. *J. Chem. Phys.* **1976**, *65*, 2700.
(10) Cutshall, E R., Jr; Muschlitz, E. E., Jr *J. Chem. Phys.* **1979**, *70*, 3171.
(11) van Vliemergen, E. J. W.; Vredenbregt, E. J. D.; Kaashoek, G. H.; Jaspar, J. P. M. J.; Van Lanen, M. M. M.; Janssens, M. F. M.; Verheyen, M. J.; Beijerrinck, H. C. W. *Chem. Phys.* **1987**, *114*, 117.
(12) Vredenbregt, E. J. D.; Boom, W.; van Gerwen, R. J. F.; Beijerinck, H. C. W. *Chem. Phys.* **1990**, *145*, 267.
(13) ChowChiu, L.-Y.; Chiu, Y. N.; Krumpelmann, T.; Ottinger, C. *Chem. Phys. Lett.* **1988**, *151*, 220.
(14) van Gerwen, R. J. F.; Vredenbregt, E. J. D.; Kerstel, E. R. T.; Beijerinck, H. C. W. *Chem. Phys.* **1987**, *118*, 407.
(15) Watanabe, D.; Ohoyama, H.; Matsumura, T.; Kasai, T. *J. Chem. Phys.* **2006**, *125*, 084316.
(16) Watanabe, D.; Ohoyama, H.; Matsumura, T.; Kasai, T. *J. Chem. Phys.* **2006**, *125*, 224301.
(17) Matsumura, T.; Ohoyama, H.; Watanabe, D.; Yasuda, K.; Kasai, T. *J. Phys. Chem. A* **2007**, *111*, 3069.
(18) Matsumura, T.; Ohoyama, H.; Watanabe, D; Yasuda, K.; Kasai, T. *J. Phys. Chem. A* **2007**, *111*, 6945.
(19) Watanabe, D.; Ohoyama, H.; Matsumura, T.; Kasai, T. *J. Phys. Chem. A* **2007**, *111*, 6915.
(20) Ohoyama, H.; Matsumura, T.; Yasuda, K.; Watanabe, D.; Kasai, T. *J. Chem. Phys.* **2007**, *127*, 024303.
(21) Watanabe, D.; Ohoyama, H.; Matsumura, T.; Kasai, T. *Phys. Rev. Lett.* **2007**, *99*, 043201.
(22) Zare, R. N. *Angular Momentum*; Wiley: New York, 1998.
(23) Lewis, B. R.; Gibson, S. T.; Zhang, W.; Brion, H. L.; Robbe, J.-M. *J. Chem. Phys.* **2005**, *122*, 144302.
(24) Aquilanti, V.; Candori, R.; Pirani, F. Ottinger, C. *Chem. Phys.* **1994**, *187*, 171.
(25) Brunetti, B.; Candori, P.; Falcinelli, S.; Lescop, B; Linti, G.; Pirani, F.; Vecchiocattivi, F. *Eur. Phys. J. D.* **2006**, *38*, 21.

JP806745G