Observation of Relative Population Change in the $^3P_0$ and $^3P_2$ States for Ar Glow Discharge Formation

Kohei Imura, Ryotarou Midorikawa, Toshio Kasai,* Hiroshi Ohoyama, and Dock-Chil Che†
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
†*Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei, Taiwan 107 Republic of China*

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The formation ratio of the two spin-orbit states, $^3P_0$ / $^3P_2$, of the metastable argon, Ar*, was investigated by the glow discharge of a pulsed Ar supersonic beam. The $^3P_0$ / $^3P_2$ ratio decreased with the increase of the glow discharge potential V_g, by which the electron bombardment initiates the discharge. The observed V_g-dependence clearly showed an inverse behavior against V_g as compared with that in the conventional electron impact by low beam densities.

It is desirable to select the single spin-orbit state of a metastable atom or molecule for studying 'state-to-state' chemistry. The energy transfer reactions such as Ar* + $N_2(X^1\Sigma_g^+)$ have been extensively studied by an afterglow technique by Setser and co-workers.[1] Spin-orbit state selection of the metastable atom has been also carried out by optical pumping.[2] In this letter, we demonstrate an useful and simple method for changing the population of the spin-orbit states of Ar* by changing a discharge potential V_g in the glow discharge using a pulsed Ar supersonic beam. The experimental evidence for the inverse V_g-dependence of a $^3P_0$ / $^3P_2$ formation ratio is presented.

Though the energy gap of the two spin-orbit states of Ar*, is only 0.17 eV (i.e. $^3P_0$ = 11.72 eV and $^3P_2$ = 11.55 eV, respectively), the Ar($^3P_0$) + N_2 reaction produces $N_2(C^3\Pi_u)$ in the vibrational states up to v′ = 3 but the Ar($^3P_2$) + N_2 reaction produces $N_2(C^3\Pi_u)$ in the vibrational states merely to v′ = 2.[2] Therefore, the population of $^3P_0$ and $^3P_2$ can be determined spectroscopically by monitoring the $N_2(C^3\Pi_u)$ emission from the Ar*($^3P_{0,2}$) + N_2 reaction.

A molecular beam machine with a collimated Ar* beam and an N_2 supersonic jet was employed. The $^3P_0$ and $^3P_2$ states of Ar* were generated by the glow discharge, where a coiled tungsten wire was heated by 7.0 A dc-current. 150-mA thermal electrons emit to a counter anode biased at V_g. Between these two electrodes, the Ar beam passes. The glow discharge was triggered when the 2-ms pulsed Ar (120 Torr stagnation pressure) was present. Then the Ar* beam crosses a 4-ms N_2 jet beam (40 Torr) in the reaction chamber after it was skimmed and collimated. The Ar* beam intensity was measured by a SEM (secondary electron multiplier). The N_2(C→B) chemiluminescence was observed through a monochromator (f = 30 cm) by a gated photon-counting system and the signal was accumulated by a micro-computer to improve the signal to noise ratio.[3]

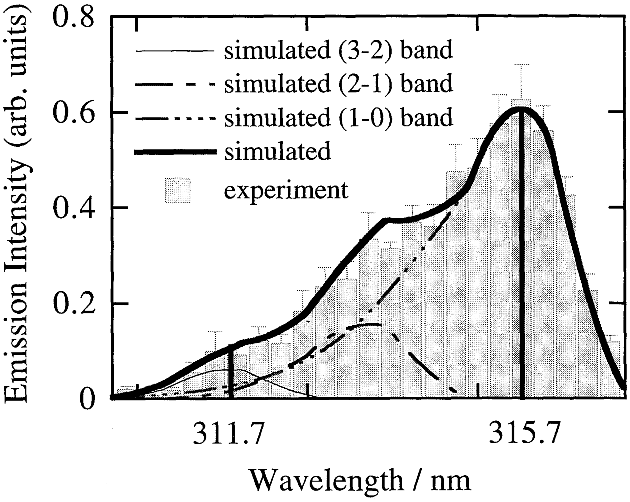

Figure 1. Chemiluminescent spectrum of the N_2(C→B) band in Ar* + N_2 reaction. The histogram and solid line show observed and simulated spectrum, respectively. Each dotted line corresponds to a simulated vibrational band.

Figure 1 shows the N_2(C→B) emission spectrum from the Ar* + N_2 reaction at V_g = 80 V. The spectral resolution was 1.28 nm due to an unavoidable weak emission in such a typical beam experiment. Even such a low resolution, it was sufficient to separate each vibrational band for vibrational population analysis. The N_2(C,v′=3) was produced only from the Ar($^3P_0$) + N_2 reaction as mentioned above, we can determine population of $^3P_0$ and $^3P_2$ by comparing the emission intensities of the corresponding vibrational bands. Thus the emission intensity of N_2(C,v′=3→B,v″=2) band was compared with that of N_2(C,v′=1→B,v″=0) band. These (3→2) and (1→0) bands correspond to the emissions at λ_0 = 312 and 316 nm, respectively. The former band is originated from the Ar($^3P_0$) reaction and the latter is originated from both Ar($^3P_2$) and Ar($^3P_0$) reactions. Practically, vibrational bands slightly overlap each other, therefore a computer simulation was necessary to determine the population of Ar*(^3P_j) (j = 0 or 2) and its V_g-dependence.

$$I(\lambda_0) \propto \sum_{v'} \sum_{J'J''} v^3 q_{v'v''} S_{J'J''} N_{v'} N_{J'} \rho(\lambda - \lambda_0) \tag{1}$$

Eq. 1 represents the emission intensity of the N_2 (C→B) transition at λ_0. In the equation, $q_{v';v''}$ is the Franck-Condon factor for the initial vibrational state v′ of the N_2(C) electronic state to the final vibrational state v″ of the N_2(B) electronic state. $S_{J'J''}$ is the line strength, ν is transition frequency, and $N_{v'}$ is the vibrational distribution of N_2(C) which is quoted from Reference 2. $N_{J'}$ is the rotational distribution of N_2(C,v′) which was assumed as a Boltzmann distribution, and the rotational temperatures were quoted from Reference 2. $\rho(\lambda-\lambda_0)$ is the slit function centered at λ_0, and it was approximated as a triangle function in the present simulation. The ratio of the emission intensities at λ_0 = 312 and 316 nm, corresponding to the (3→2) and (1→0) bands, is defined by Eq. 2.

$$R = \frac{I(312nm)}{I(316nm)} = \frac{A_0 Q + A_2}{B_0 Q + B_2} \tag{2}$$

where A_j and B_j are the simulated intensities at 312 and 316 nm contributed from each j spin-orbit state, respectively. Q is the $^3P_0$ / $^3P_2$ formation ratio. The V_g-dependence of the population of

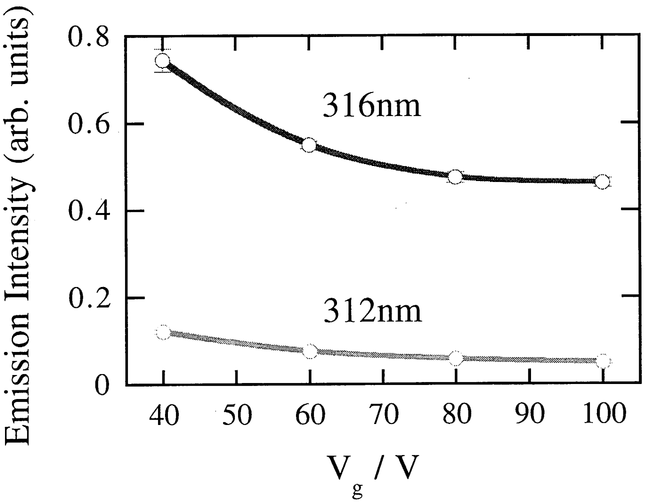

Figure 2. V_g-dependence of the emission intensity of the (3→2) and (1→0) vibrational bands. The *I(312 nm)* and *I(316 nm)* correspond to (3→2) and (1→0) vibrational bands, respectively.

the $^3P_2$ and $^3P_0$ states was thus calculated using Eq. 2. The simulated spectrum (the solid line) and the simulated vibrational bands (the dotted line) are shown in Figure 1 for $Q = 0.02$.

Figure 2 shows the V_g-dependences of *I(312nm)* and *I(316nm)* in the range of V_g = 40-100 V. As seen in the Figure, both emissions decrease as V_g increases. These decreasing behavior directly suggests that the number of the Ar* metastable atoms decreases with the increase of the discharge potential for $^3P_2$ and $^3P_0$ states. The same decreasing behavior was also confirmed by the SEM measurement in which the Ar* beam intensity was directly monitored. It was found that the Ar* intensity at 40 V showed 70% reduction at 100 V.

Now, the $^3P_0$ / $^3P_2$ formation ratio Q is defined by Eq. 3, which is simply derived from Eq. 2. R can be experimentally determined and Q is important in the later discussion.

$$Q=\left(\frac{^3P_0}{^3P_2}\right)=\frac{B_2R-A_2}{A_0-B_0R} \qquad (3)$$

Figure 3 shows the V_g-dependence of Q. This dependence clearly shows that Q decreases to one fifth with the increase of V_g between 40 and 100 V. This result is quite different from the one in a conventional electron impact using low beam densities, where Q increases with the increase of the electron impact energy.[4] Therefore, the present result is the first example which represents the clear inverse V_g-dependence.

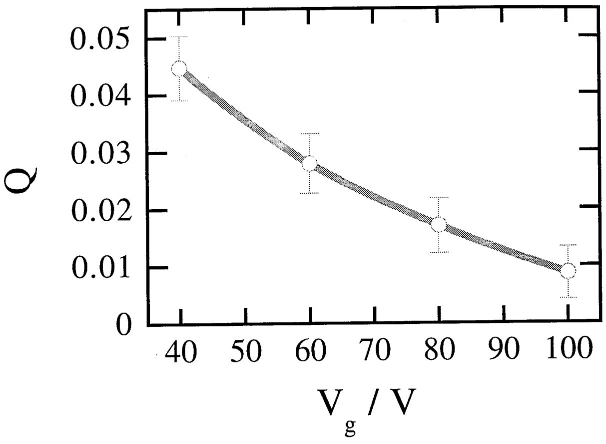

Figure 3. V_g-dependence of a $^3P_0$ / $^3P_2$ formation ratio Q.

Though the present glow discharge method would be regarded similar to the conventional electron impact method for the metastable formation, these methods are quite different in the following respects. First, the Ar* atoms are produced not only by electron impact but also by ion impact in the glow discharge, because plasma condition is preserved during the intense Ar pulse beam. Second, it is also likely that the produced Ar* will be quenched easily in the glow discharge zone due to relatively high density beam, and that the quenching rates might be different for different spin-orbit states. All these factors could change the formation ratio as the discharge potential is changed. Further studies, however, are expected for confirming the present V_g-dependence in more detail. From the view point of application, this method is practically very useful for studying the effect of spin-orbit states in chemical reactions.[5]

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References and Notes

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