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Active Control of the Relative Population of $^3P_0$ Fine-State in the Glow Discharge of a Supersonic Ar Beam

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An active control for changing the relative population of the $^3P_0$ fine-state of Ar* in a supersonic beam was investigated in a glow discharge by adding a small amount of foreign gases to pure Ar gas. The Ar* mean velocity was determined to be constant at major positions of the time profile, except for a rise and the decay of the beam for all gas mixtures, and also pure Ar. The relative population of $^3P_0$ decreased with the discharge potential for the addition of ethylene, cyclohexane, and benzene. However, the addition of N_2 and CH_4 and pure Ar, did not show such a $^3P_0$ decrease. These dissimilar behaviors of the foreign mixed gases could be interpreted based on a difference in the ionization potential of the molecules. A useful application of this population control is discussed.

It has been widely acknowledged that it is important for "state-to-state" chemistry to investigate chemical reactions with a single fine-state (or spin-orbit state) of the reagent.[1,2] Such a fine-state selection has been achieved by laser optical pumping of the metastable Ar atom.[3] We have recently demonstrated a simple method for changing the relative population of the $^3P_0$ fine-state of Ar* with respect to $^3P_2$ in a d.c.-electric glow discharge of a pulsed supersonic beam.[4] The $^3P_0$ relative population was decreased along with an increase in the discharge potential, (V_g) which was applied during the discharge. Such a V_g-dependence appears to be different from the V_g-dependence for conventional electron-impact excitation with a low-density molecular beam[5,6]

In the glow discharge, the Ar* atoms can be produced by not only the electrons, but also ions under plasma conditions. It is likely that with a high-density beam the two fine-states of Ar* would be quenched at different rates in a high-density atomic beam in the glow-discharge region. These factors concerning collisions in the beam would be effective to the fine-state relative populations. Moreover, our recent study has suggested that hydrocarbon contaminants in the vacuum chamber would effectively affect the glow-discharge conditions.[4] It is therefore useful to clarify those possible effects of gas impurity and/or vacuum contamination on the fine-state population in the glow-discharge. In this work we added a small amount of foreign gases to pure Ar, such as nitrogen and hydrocarbons, to see whether they might give such effects upon the glow-discharge conditions. The V_g-dependences of the Ar* velocity distribution and the beam-profile have been measured in detail. A useful application of the present method for studying the CF_3* chemiluminescence reaction is briefly discussed.

Experimental

Figure 1 schematically shows the apparatus for Ar* beam formation with a glow discharge. The apparatus consists of three differential pumped vacuum chambers, where C1 and C2 are beam collimators. The 1-ms pulsed Ar beam is produced by a pulse valve (V1) with 1-mm diameter. The glow discharge is ignited at the first filament (F1) zone when the pulse beam passes through from the pulse valve to a skimmer (SK). The second filament (F2) zone was made for ensuring efficient Ar* formation. The filaments of a coiled tungsten with 1% thorium were activated with a d.c.-current of 7.0 A for thermal-electron generation. The stainless-steel anode grids (G1 & G2) were biased at +25 — +120 V with respect to the filaments at zero volt. The Ar* beam was detected by a ceratron (secondary electron multiplier, Murata MFG, EMT-6081B) and the output signals were recorded by a digital oscilloscope followed by computer accumulation.[8] In order to remove unnecessary ions, a pair of deflecting plates (EF, 100 V cm^{-1}) were set in the buffer chamber. A TOF (time-of-flight) measurement was carried out with a 100-Hz mechanical chopper mounted near to C1 with a 750 mm flight length. The ceratron was active to both the Ar* metastable

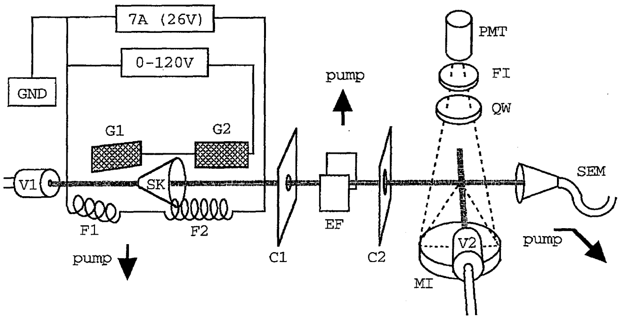

Fig. 1. Schematic view of the experimental setup for the Ar* glow discharge. V1, Ar pulse valve; SK, skimmer; F1 & F2, filaments for glow discharge; G1 & G2, anode grids; C1 & C2, Ar* beam collimators; EF, ion deflecting plates; SEM, Ar* detector (Ceratron); V2, N_2 pulse valve; MI, collection mirror; QW, quartz window; FI, bandpass light filter; PMT, photomultiplier.

atoms and VUV (vacuum ultraviolet) stray light of the glow discharge. Thus, since a flight length of 750 mm was not sufficient for separating the Ar* signal from the VUV light signal, we extended the flight length to 1500 mm for measuring the total Ar* beam intensity, in which the TOF chopper was not used. The energy gap of the two spin-orbit state of Ar* is 0.17 eV (i.e. $^3P_0 = 11.72$ eV and $^3P_2 = 11.55$ eV, respectively) and the $Ar(^3P_0)+N_2$ reaction produces $N_2(C^3\Pi_u)$ in the vibrational states up to $v' = 3$; however, the $Ar(^3P_2)+N_2$ reaction produces $N_2(C^3\Pi_u)$ in the vibrational states only up to $v' = 2$. Because of this, the relative population of the $^3P_0$ fine-state can be determined by monitoring the $N_2(C \rightarrow B)$ emission from the crossed-beam reaction of $Ar^* + N_2$, in which Ar* is a mixture of $^3P_0$ and $^3P_2$.[4)] Thus, the emission intensity of the $N_2(C, v' = 3 \rightarrow B, v'' = 2)$ band was compared with that of the $N_2(C, v' = 1 \rightarrow B, v'' = 0)$ band. As can be seen in the fluorescent spectra of nitrogen molecules of Fig. 6 of Ref. 3, measured by Nguyen and Sadeghi, the (3→2) band is located in the 310—312 nm region, and the (1→0) band origin is located at 316 nm. The former band originated from the $Ar(^3P_0)$ reaction, and the latter from both the $Ar(^3P_0)$ and $Ar(^3P_2)$ reactions. The chemiluminescence was collected by a concave mirror (MI) and separated by a bandpass light filter (FI) centered at 311 nm with a 2-nm bandwidth, which was sufficiently narrow to isolate the (3→2) band; it was detected by a photomultiplier (PMT). Therefore, only the emission of the $N_2(3 \rightarrow 2)$ band was observed, from which the $^3P_0$ relative population could be determined.[4,7)] The radiation lifetime of $N_2(C \rightarrow B)$ varies around 40 ns, depending upon the upper vibrational states.[9,10)] The gate-width of the photon counter was set at 2.5 ms in order to cover the central portion of the cross-beam signal. The 5% gas mixtures of Ar were prepared before use by mixing pure Ar with pure gases of N_2, CH_4, C_2H_4, C_6H_{12}, and C_6H_6, which were commercially available.

Results and Discussion

Ignition for the glow discharge, in a general sense, depends upon the product of the effective pressure of the reagent gas and the applied potential (V_g) in the discharge region in the vacuum chamber.[6)] In order to separate and clarify the V_g-dependence, V_g was varied over 30—120 V, while the stagnation pressure of Ar was held constant at 120±5 Torr (1 Torr = 133.322 Pa). Therefore, the Ar beam intensity, and equivalently the local pressure in the discharge region, was held constant. The V_g-dependence of the time-profile of the Ar* beam is shown in Fig. 2. The Ar* intensity was measured by the ceratron with a 750 mm flight length. A glow discharge did not occur below $V_g = 27 \pm 2$ V, and four values of V_g (30, 40, 60, and 120 V) were selected. The Ar* beam-width, which corresponds to the discharge duration, becomes wider along with V_g, as the figure shows. This tendency simply indicates that the glow discharge depends upon the product of the pressure and V_g in the discharge region.

Figure 3 shows the dependences of the mean velocity of the Ar* beam upon the position of the beam profile at various V_g. As can be seen, those dependences clearly indicate that the mean velocities of the beam can be regarded as being almost constant at all positions of the beam profile, although there are unstable regions at the rise and decay of the beam profile. It is also noteworthy that the mean beam velocities do not vary, even if V_g is changed. This result suggests that a glow discharge may not influential to the beam velocity, though not a few collisions are expected to take place during the discharge.

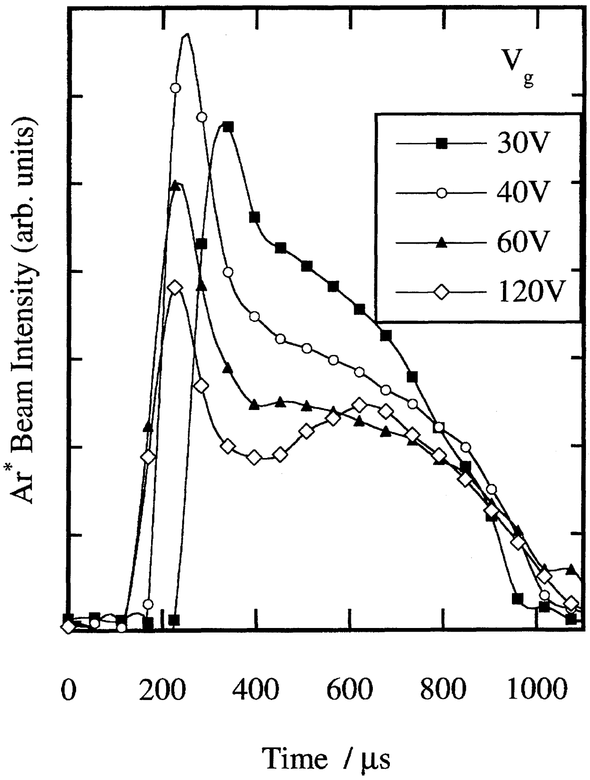

Fig. 2. Time profiles of the Ar* beam produced at various V_g. The Ar* intensity was measured by the ceratron with 75 cm flight length. The origin of arriving time is arbitrary (the horizontal scale).

A typical TOF signal of the Ar* beam with a 750 mm flight length is shown in Fig. 4. The solid line is the experimental result for a pure Ar beam; the open squares are the simulated points. The first peak on the left along the time axis is due to stray light from the glow discharge. This light peak could therefore be utilized as the origin in the TOF measurement. The stream velocity (v_s) was determined by fitting the TOF profiles to the shifted Maxwellian velocity distribution for a supersonic molecular beam, as given by[11)]

$$f(v) = \left(\frac{v}{\alpha_s}\right)^3 \exp\left(-\frac{(v-v_s)^2}{\alpha_s^2}\right),$$
$$kT_s = (1/2)m\alpha_s^2, \qquad (1)$$

where α_s is the transverse velocity, T_s is related to the translational temperature, k is the Boltzmann constant, and m is the mass of Ar. The best-fit simulation gave the most probable values of v_s and α_s to be 610±10 $m\,s^{-1}$ and 100±10 $m\,s^{-1}$ for a pure Ar* beam, respectively. The stream velocity and the transverse velocity of Ar* for all mixture gas reagents employed in this work were found to be the same, suggesting that the added gas (5%) did not alter the Ar* beam character, itself, very much.

Figure 5 shows the V_g-dependence of the total intensity of the Ar* beam. The vertical scale is normalized to the

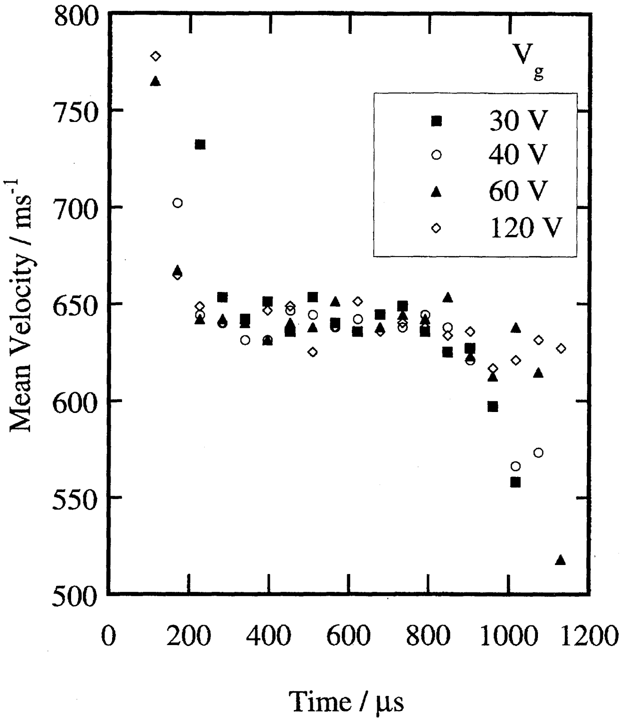

Fig. 3. Dependence of the mean velocity of the Ar* beam upon the position of the beam profile at various V_g.

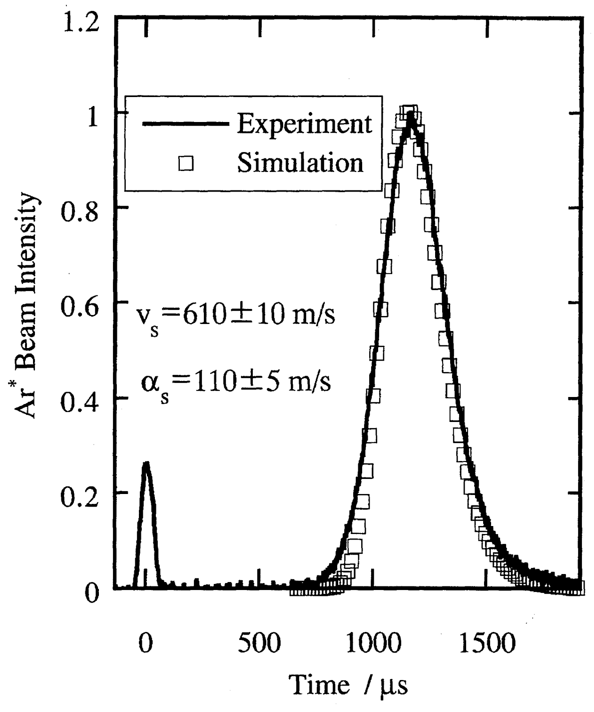

Fig. 4. A typical TOF signal for the Ar* beam. The solid line is experimental data, and the open squares stand for the simulated points by using Eq. 1 (see text).

beam intensity at V_g=40 V for all regents. The Ar* beam intensity gave the maximum near to a threshold potential of ca. 30 V. The beam intensity then considerably decreases as V_g increases up to 60 V, resulting in an ca. 15% reduction of the maximum intensity. Over V_g=60 V, the Ar* beam

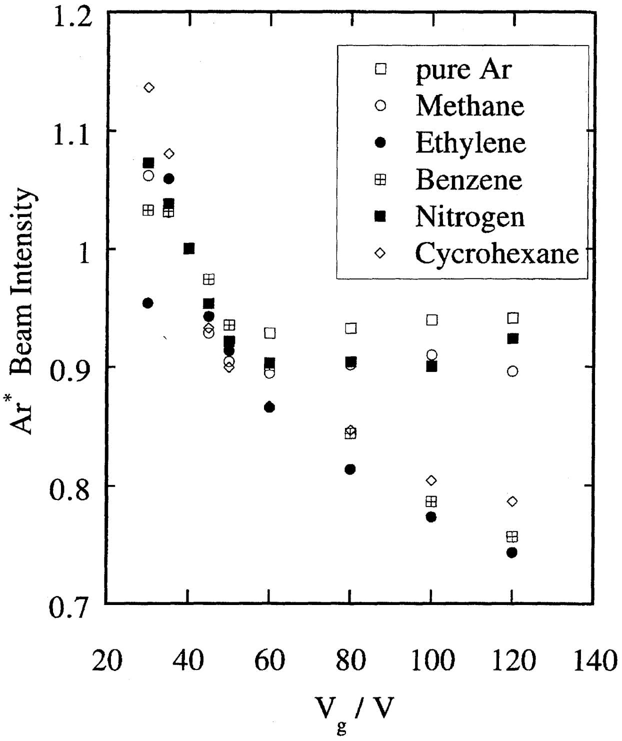

Fig. 5. V_g-dependence of the beam intensity of the Ar* beam of various mixture gases of Ar. Pure Ar, □; 5% methane/Ar, ○; 5%N$_2$/Ar, ■; 5%ethylene/Ar, ●; 5%cyclohexane/Ar, ◇; 5%benzene/Ar, ⊞. The beam intensity is normalized at 40 V for each reagent gas.

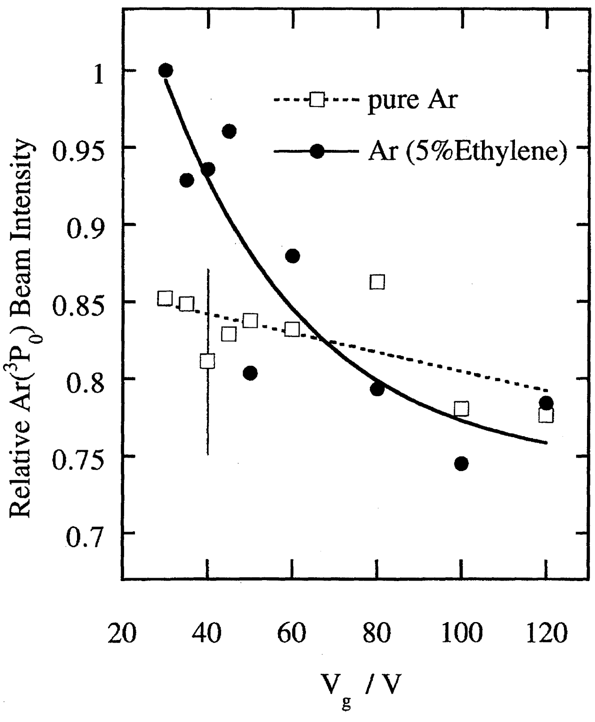

Fig. 6. V_g-dependence of the $^3P_0$ relative population for pure Ar and 5% mixture gas of C_2H_2/Ar. The open squares are the experimental data for pure Ar, and the solid ones are those for the 5% mixture gas of C_2H_2/Ar. The curves were obtained by the least-square fitting. The vertical bar stands for the estimated experimental error.

Table 1. Ionization Potentials (I.P.) of Molecules in Gas Phase

Group	Adiabatic I.P./eV	Vertical I.P./eV
Group I:		
Nitrogen (N_2)	15.59	15.59
Methane (CH_4)	12.57	14.0
Group II.:		
Ethylene (C_2H_4)	10.51	10.51
Cyclohexane (C_6H_{12})	9.89	
Benzene (C_6H_6)	9.24	

The excitation energies for producing Ar* are 11.55 eV to Ar($^3P_0$), and 11.72 eV to Ar($^3P_2$), respectively. These data are quoted from "JCS Handbook of Chemistry," Part II, 3rd ed, Maruzen, Tokyo (1984), p. 576.

intensity begins to show two different tendencies. The pure Ar gas and the Ar gas mixed with 5% of CH_4 or N_2 (these will be classified as group I in Table 1 in later) showed no changes, giving a plateau up to V_g=120 V. Group II for the Ar gas mixed with 5% of either ethylene, cyclohexane, or benzene, on the other hand, was found to give a continuous slow decrease up to 120 V.

The V_g-dependence of the Ar* beam intensity in Fig. 5 could be interpreted in two ways: one is that the excitation function (i.e. the excitation cross section of the reagent gas to Ar*) is a function of V_g, whose general shape shows an initial sharp rise in the small-V_g region, followed by a tailing decrease after giving a maximum peak. The second aspect is that the density of the charged particles in the discharge field, such as the thermal electrons and secondarily produced ions, increases as V_g is raised, due to the ohmic relation between the electrodes of the filament cathode and the anode. This current rise in the discharge field could be qualitatively observed as we raised V_g. However, a quantitative measurement and an analysis were not possible in the present pulsed beam experiment under the glow-discharge conditions.

If we take a gas mixture of pure Ar and a foreign gas (M) as an example for the discharge reagent, the initial step of the electron-bombardment process produces neutral excited species of Ar* and M* and their ions, Ar^+ and M^+, in the glow-discharge region. Then, the excited species other than the metastable argon (Ar*) could be a secondary source for Ar* formation. We would therefore expect that the current rise is not linear with respect to V_g, unlike in the case of normal electron-bombardment excitation with a low electron-beam density. Another factor which could change the V_g-dependence of Ar* formation is the de-excitation, or quenching, of the produced metastable argon (Ar*) by collisions with the mixed gas (M). A major de-excitation process for Ar* would be Penning ionization,

$$Ar^* + M \longrightarrow Ar + M^+ + e. \tag{2}$$

We may therefore be able to characterize the observed two different V_g-dependences of Ar* formation in Fig. 5 to be a result of combining those effects mentioned above. Namely, it is plausible that both changes in the field current and in the Ar* de-excitation probability would provide two sets of the observed V_g-dependences as the change of M, which is classified either as group I or group II. Suppose that the Ar* de-excitation process (2) would play a significant role in the overall process of Ar* formation; the ionization potential (I.P.) of the mixed gases (M) would be a reasonable measure, because the probability of such a resonant quenching process would be relevant to I.P. Table 1 lists the ionization potentials of the molecules used as mixing gas. The excitation energies to Ar* are footnoted at the bottom of the table, compared with the energies which Ar* possesses, i.e. ca. 11 eV.[12] I.P.s of N_2 and CH_4 (group I) are larger than the energy of Ar* and those of C_2H_4, C_6H_{12}, and C_6H_6 (group II) are smaller than the energy of Ar*. Therefore, it is plausible that the addition of molecules of group II would quench the Ar* atoms more efficiently than the molecules of group I, since the transferred energy from Ar* is sufficient for Penning ionization.[12,13] This quenching process could occur efficiently in glow-discharge formation because of its relatively intense beam intensity. Ionic reactions in the glow-discharge, however, must be taken into account as additional quenching processes for further discussion.

The Ar($^3P_0$)+N_2 reaction produces the excited $N_2(C^3\Pi_u)$ in the $v' \leq 3$ vibrational states. In contrast, the Ar($^3P_2$)+N_2 reaction produces only the excited N_2 in the $v' \leq 2$ vibrational states.[7] Therefore, the relative population of the $^3P_0$ and $^3P_2$ fine-states can be determined by monitoring the emission spectrum of $N_2(C^3\Pi_u)$ in the Ar*+N_2 reaction. The V_g-dependence of the relative population for the $^3P_0$ state of Ar*, namely [Ar($^3P_0$)]/([Ar($^3P_0$)]+[Ar($^3P_2$)]), was thus determined by a comparison of the 312-nm emission intensity due to the N_2(C, v'=3)→N_2(B, v''=2) transition, [N_2(C,v'=3)], with the total Ar* beam intensity. [Ar($^3P_{2,0}$)], i.e. the sum intensity of [Ar($^3P_0$)] and [Ar($^3P_2$)], which was directly measured by the ceratron. This relationship is represented by Eq. 3. The quantity of the left-hand side of Eq. 3 may be called the $^3P_0$ fraction in the beam, and the quantity of the right hand side of the equation is experimentally determined, which is called the relative Ar($^3P_0$) beam intensity.

$$\frac{[\mathrm{Ar}(^3\mathrm{P}_0)]}{[\mathrm{Ar}(^3\mathrm{P}_2) + \mathrm{Ar}(^3\mathrm{P}_0)]} \propto \frac{[\mathrm{N}_2(\mathrm{C}, v' = 3)]}{[\mathrm{Ar}(^3\mathrm{P}_{2,0})]} \tag{3}$$

Figure 6 shows the V_g-dependence of the relative Ar($^3P_0$) beam intensity for pure Ar, and the 5% mixture gas of C_2H_4/Ar, which was chosen from group II. The open squares are the experimental data for pure Ar, and the solid ones are those for the 5% mixture gas of C_2H_4/Ar. The curves with the solid and broken lines were obtained by a least-squares fitting. The absolute value of the vertical scale, which corresponds to the $^3P_0$ fraction in the beam, can be estimated from Fig. 6 if we utilize the previously obtained value of 0.045 for the $^3P_0/^3P_2$ fine-state population ratio, as defined in Ref. 4.[4] After this conversion, one unit of the vertical scale of Fig. 6 corresponds to 0.043, which may be regarded as the absolute of the $^3P_0$ fraction. (As we have pointed out, this correction needs to be substantiated due the fact that the curve of the $^3P_0/^3P_2$ fine-state population ratio for nominally-pure Ar gas in the previous study turned out to represent the curve for accidentally-not-pure Ar as the result of contamination from diffusion oil in the nozzle chamber.)

As can be seen in Fig. 6, there is no noticeable change with V_g for pure Ar. However, for the ethylene mixture, there is a significant change with V_g. This result suggests that we are able to prepare an Ar* beam in which the $^3P_0$ fine-state is dominantly populated by setting the glow-discharge potential at low V_g. Inversely, a relatively smaller population for the $^3P_0$ fine-state can be obtained at high V_g. Though we do not exactly understand the reason for this V_g-dependence of the relative Ar($^3P_0$) beam intensity, this method will provide the simplest way to investigate the fine-state effects. A preliminary application of this method to study the A($^3P_{0,2}$)+ $CF_3H \rightarrow Ar+CF_3+H$ reaction indicates such a fine-state effect when V_g is varied.[14] The details concerning the application will be presented elsewhere. The practical usefulness of the present method of changing the relative fine-state populations of the metastable atoms or molecules would be promising.

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