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Chemi-ionization of Cs*($8^2P_{1/2}$) with Cs and Foreign Gases

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Chemi-ionization has been studied by the collision of the excited atom of cesium ($8^2P_{1/2}$), whose energy is lower by 0.7 eV than its ionization energy, with cesium, rare gases or simple molecules. The mechanisms for the chemi-ionization, and quenching processes occurring simultaneously were set up and the cross sections of the processes have been determined. Since the pressure effects of added gases to the absorption coefficient of Cs at 3888 Å from the He lamp could not be neglected, suitalbe corrections were made.

It has long been known that the vapor of cesium or rubidium[1] can be photoionized by the light in the discrete region of its atomic spectrum. This ionization has been known[2,3] to take place by absorption of the light at the principal series of cesium (6S→*n*P). Their observation suggested that the mechanism of the ionization processes was

$$Cs + h\nu \rightarrow Cs^*(nP) \qquad n \geq 8 \qquad (1)$$

$$Cs^* \rightarrow Cs + h\nu \qquad (2)$$

$$Cs^* + Cs \rightarrow Cs_2^+ + e \qquad (3)$$

From the measurement of the mobility of the ions Lee and Mahan[4] showed that another process

$$Cs^* + Cs \rightarrow Cs^+ + Cs^- \qquad (4)$$

can not be excluded for the state above 12P. On the basis of the energetic relation the old[2,5] and recent[4,6] data have indicated that the one-electron bond in such ions as Cs_2^+ is stronger than the two-electron bond in Cs_2. Another paper[7] of Mohler and Boeker showed the effects of the foreign gases on the photoionization of cesium at line absorption. They obtained the value of σ (collision radius) between 1.4 and 4×10^{-8} cm for foreign gases, N_2, H_2, He, and Ar, while the value for Cs-Cs collision was about ten times larger. Recent work[8] by Williams has shown the effect of Cs using a Kingdom Cage or space-charge ion collector. The addition of ammonia has altered the photoionization at the principal series lines of cesium by attenuating the wavelength peaks longer than 3440 Å and intensifying the shorter wavelength peaks. They suggested the two processes, one is quenching and the other is ionization.

$$Cs^* + NH_3 \rightarrow Cs + NH_3 \qquad (5)$$

$$Cs^* + NH_3 \rightarrow Cs(NH_3)^+ + e \qquad (6)$$

The latter is similar to the molecular ion formation by collisions between Cs* and normal Cs. The present authors have reported the mass spectrometric identification of Cs_2^+ ion produced by line absorption at 3888 Å.[9] In this paper we report detailed measurements for the chemi-ionization of Cs at 3888 Å and the effects of foregin gas atoms on the chemi-ionization.

Experimental

Reaction System. In the static system, the cesium vapor was irradiated with the 3888 Å light from a microwave discharge He lamp. Figure 1 illustrates the reaction system used in this work. The quartz cell contained platinum parallel-plate electodes of 1.5×4 cm dimension separated by 2 cm. The cell with a window for light irradiation, a small tube for cesium supply and a side-arm to a vacuum system through two grease-free valves was placed in a constant temperature oven. Another small oven around the Cs tube was heated independently in order to control the Cs vapor pressure. Light from the He lamp passed through a chopper, a filter, a collimating lens, a slit, and the photoionization cell. Care was was taken to prevent scattered light or photoexcited atoms from striking the electrodes. The helium discharge lamp emitted the two intense lines at 3888 and 3188 Å in the region between 3000 and 4000 Å. The longer wavelength lines than 4000 Å could not be absorbed by Cs and the shorter ones than 3000 Å could not be through a pyrex window. The 3188 Å line was re-

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[1] E. O. Lawrence and N. Edlefsen, *Phys. Rev.*, **34**, 233 (1929). K. Freudenberg, *Z. Physik*, **67**, 417 (1931).

[2] F. Mohler and C. Boecker, *J. Res. Natl. Bur. Std.*, **5**, 51 (1930).

[3] F. Mohler, P. Foote and R. Chenault, *Phys. Rev.*, **27**, 37 (1926).

[4] Y. T. Lee and B. H. Mahan, *J. Chem. Phys.*, **42**, 2893 (1965).

[5] H. M. James, *ibid.*, **3**, 9 (1935).

[6] R. F. Barrow, N. Travis and C. V. Wright, *Nature*, **187**, 141 (1960).

[7] F. L. Mohler and C. Boeker, *J. Res. Natl. Bur. Std.*, **5**, 399 (1930).

[8] R. A. Williams and S. Naiditch, *J. Chem. Phys.*, **41**, 343 (1967).

[9] Y. Ono, I. Koyano and I. Tanaka, *ibid.*, **52**, 5969, (1970).

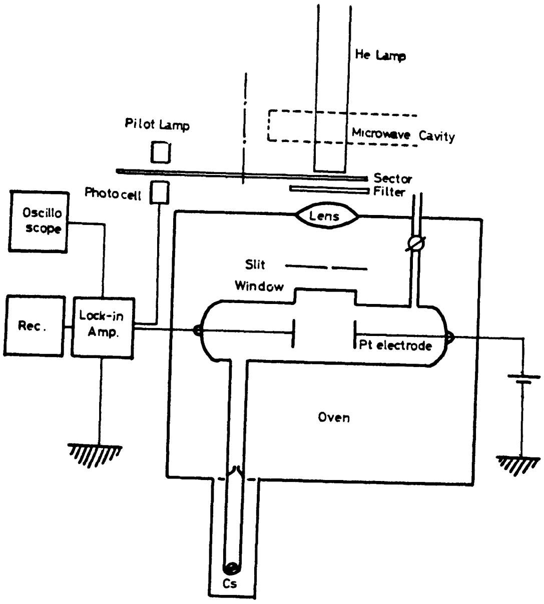

Fig. 1. Schematic diagram of reaction system.

moved by a filter and the essentially monochromatic 3888 Å light was then modulated by a chopper to form the 20 Hz square-wave. The total ions arriving to the cathode were detected by a lock-in amplifier tuned to 20 Hz. Dc voltage from mercury dry cells was applied between the electrodes.

Materials. An ampule of Cs metal from Merck Ltd. was opened in an evacuated tube and the metal was distilled into the tube with a break-off seal and the tube was sealed off. The rare gases such as He, Ne, Ar, Kr, and Xe, inorganic gases such as NH_3, H_2 and N_2, saturated hydrocarbons such as CH_4, C_2H_6, C_3H_8 and n-C_4H_{10} and unsaturated hydrocarbons such as C_2H_4, C_3H_6, *cis*-2-butene, and 2-pentene were supplied from Takachiho Co., Ltd.

Procedure. Before the experiment, the reaction cell was heated at 400°C and evacuated to less than 10^{-6} Torr for at least a few days. The metal vapor was introduced into the cell through the break seal from the Cs tube, and the foreign gas was introduced through a tube containing Cs getter to remove a trace of impurities in the gas after the gas pressure was measured by an oil manometer. During the experiments the vapor pressure of Cs was controlled by the temperature of the Cs supply tube. The temperature of the reaction cell was maintained about 350°C in order to avoid the condensation of Cs in the reaction cell.

Since the electrodes were always covered by adsorbed Cs metal, a current due to surface ionization followed by detachment from the surface by electric field was detected. In a new cell this ion current was 10^{-9} amp/cm^2 at 350°C with 1.3 V collecting potential and became larger as the cell aged. Since this ion current was always much larger than the expected photoionization current, the latter could only be detected by chopping the incident light beam and using a lock-in amplifier. By using this technique the limit of detection for photoionization current was 10^{-13} A, and 10^{-14} A with a narrow-band preamplifier. In most runs the collecting voltage was fixed at 1.3 V dc for the reason which will be described later. The sector was so designed that the light was irradiated during 1/120 sec by a hysteresis motor of 10 Hz.

At first the photoionization for Cs vapor without foreign gases was measured, and then the variation of the ion current by the addition of foreign gases was measured. The pressure of foreign gas introduced was measured by an oil manometer through a tube of getter of Cs to remove a trace of impurities. Since the pressure effect of the absorption lines of Cs atoms due to foreign gases can not be ignored, a correction was made as described in the appendix.

Results

i) Collecting Efficiency of Chemi-ionization Current. In order to confirm the saturation of the ion collecting efficiency by the electrodes the ion current was examined by changing the collecting voltage. The plots of the ion current *versus* the voltage were shown in Fig. 2. Curve 1 shows the variation of the ion current for Cs vapor only, curve 2 that for the addition of N_2 gas at 4 Torr, and curve 3 that for the addition of Xe gas at 6 Torr. All curves indicated that the collecting voltage of about 1.3 V was suitable for measuring the ion current. The output of the lock-in amplifier used depends on the input signal form, therefore the values of ion currents measured by the lock-in amplifier must be corrected by a suitable method. In our experiments this correction was made by the use of dc amplifier.

ii) Chemi-ionization of Cs*(8 $^2P_{1/2}$) with Cesium Atom. The vapor pressure of cesium was calculated from the relation given by Langmuir and Kingdon.[10] In order to interpret these experimental results, the reaction mechanisms can be assumed as follows:

$$\mathrm{Cs(6S)} + h\nu(3888\,\text{Å}) \rightarrow \mathrm{Cs^*(8^2P_{1/2})} \qquad (7)\quad I_{\mathrm{abs}}$$

$$\mathrm{Cs^*(8^2P_{1/2})} \rightarrow \mathrm{Cs'(7S,\ 6S,}\ etc.) + h\nu' \qquad (8)\quad 1/\tau$$

$$\mathrm{Cs^*(8^2P_{1/2})} + \mathrm{Cs(6S)} \rightarrow \mathrm{Cs_2{}^+} + \mathrm{e} \qquad (9)\quad k_i$$

$$\mathrm{Cs^*(8^2P_{1/2})} + \mathrm{Cs(6S)} \rightarrow \mathrm{Cs_2\ or\ Cs + Cs} \qquad (10)\quad k_g$$

where I_{abs}, the light intensity absorbed by Cs(6S), is nearly equal to $\varepsilon l I_0$[Cs], ε is the absorption coefficient of Cs at 3888 Å He line which was determined to be 1.4×10^{-19} cm^2/molecule as described in the appendix, l is the absorption path length, 15 mm, I_0 is the intensity of the incident light which was measured to be 1×10^{15} photons/sec, τ is the radiative life time of Cs*(8 $^2P_{1/2}$), k_i and k_q are the rate constants of the collisional ionization with Cs and of the quenching process by Cs, respectively. The possibility of the ion pair formation was neglected because the electron affinity of Cs is about 0.19 eV[4] whose energy is insufficient to produce Cs^+ ion and also the ion except $Cs_2{}^+$ was not detec-

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[10] I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.*, **107A**, 61 (1925).

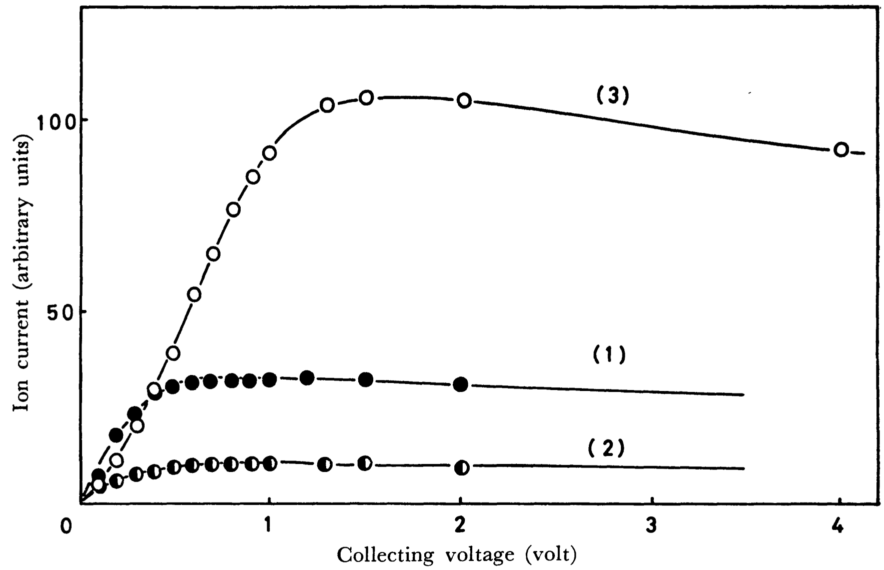

Fig. 2. Ion-current *versus* collecting voltage.
curve (1): ● Cs vapor (10^{-2} Torr)
curve (2): ◐ Cs vapor (10^{-2} Torr) + N_2(4 Torr)
curve (3): ○ Cs vapor (10^{-2} Torr) + Xe(6 Torr)

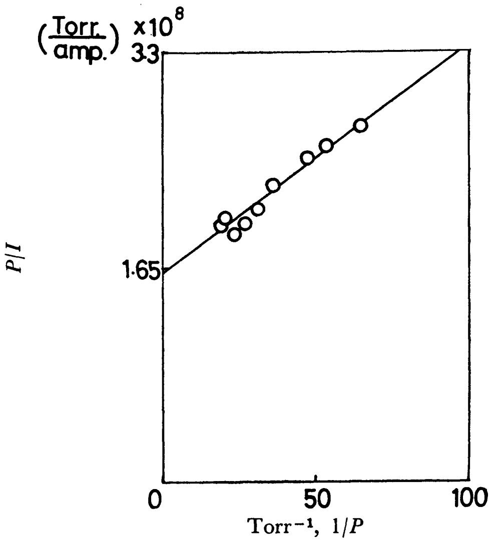

Fig. 3. Plot of the ratio of the pressure of Cs to the chemi-ionization current against the reciprocal value of the pressure according to Eq. (15) for cesium.

ted by the mass spectrometer as has been described in the previous paper.[9] The rate equation for the concentration of $Cs^*(8\ ^2P_{1/2})$ is

$$\frac{d[Cs^*]}{dt} = \varepsilon l I_0[Cs] - \frac{1}{\tau}[Cs^*] - (k_i + k_q)[Cs^*][Cs] \tag{11}$$

Since the apparent life time of Cs* is much shorter than the duration of irradiation pulse, *i.e.*, 1/120 sec, the stationary concentration would be maintained during the irradiation. In this case the concentration of Cs* is obtained as follows:

$$[Cs^*] = \frac{\varepsilon l I_0[Cs]}{1/\tau + (k_i + k_q)[Cs]} \tag{12}$$

Now the equation for the ion current of Cs_2^+ ion is

$$I = k_i[Cs][Cs^*] \tag{13}$$

Substituting Eq. (12) into Eq. (13) we obtain

$$I = \frac{\varepsilon l I_0 k_i [Cs]^2}{1/\tau + (k_i + k_q)[Cs]} \tag{14}$$

and

$$\frac{[Cs]}{I} = \frac{1}{\varepsilon l I_0}\left\{\frac{1}{\tau k_i}\cdot\frac{1}{[Cs]} + \frac{k_i + k_q}{k_i}\right\} \tag{15}$$

The values of P/I were plotted against $1/P$ and then a straight line was obtained as shown in Fig. 3. These experimental results indicated that the reaction mechanisms (7)—(10) were reasonable, and the values of τk_i and τk_q were determined from the intercept and the slope of these linear plots. τk_i was calculated to be $1.3\times10^{-15}\ \text{mol}^{-1}\ \text{cm}^3$ and τk_q was $1.6\times10^{-15}\ \text{mol}^{-1}\ \text{cm}^3$. Using the following relation between the reaction rate k and the cross section σ^2, $k = \sigma^2(8\pi RT/\mu)^{1/2}$, the products of the life-time τ of Cs* and the cross sections for photo-ionization σ_i^2, and quenching, σ_q^2, have been calculated to be

$$\tau\sigma_i^2 = 9.5\times10^{-21}\ \text{cm}^2\cdot\text{sec}$$

and

$$\tau\sigma_q^2 = 1.17\times10^{-20}\ \text{cm}^2\cdot\text{sec}$$

respectively.

iii) Chemi-ionization of $Cs^*(8^2P_{1/2})$ with Foreign Gas. The gases used were a) rare gases such as He, Ne, Ar, Kr, and Xe, b) simple inorganic gases NH_3, H_2, and N_2, c) saturated hydrocarbons CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} and d) unsaturated hydrocarbons C_2H_4, C_3H_6, *cis*-2-butene, and 2-pentene. The results were described qualitatively as follows. The addition of rare gas except He increased the ion current, while the He gas decreased it. The H_2, NH_3, and N_2 gases decreased the ion current. The saturated hydrocarbon increased the ion current but the unsaturated hydrocarbons C_2H_4, C_3H_6, and 2-pentene except *cis*-2-butene decreased it.

From these qualitative results, the following processes should be added to the previous four processes (7)—(10).

$$Cs^*(8^2P_{1/2}) + M \rightarrow CsM^+ + e \qquad (16)\ k_i'$$

$$Cs^*(8^2P_{1/2}) + M \rightarrow Cs + M \qquad (17)\ k_q'$$

where k_i' and k_q' are the rate constants of the collisional ionization between Cs* and a foreign gas M, and of the collisional quenching process by M, respectively. Since the electron affinities of atoms and molecules used in this experiment are considered to be less than 0.7 eV, the ion pair formation ($Cs^*+M \rightarrow Cs^+ + M^-$) seems to be impossible so that the ion pair formation can be excluded. Therefore the rate equation for the excited Cs* atom is

$$\begin{aligned} d[Cs^*]/dt &= \varepsilon I I_0[Cs] - (1/\tau)[Cs] \\ &- (k_i + k_q)[Cs^*][Cs] - (k_i' + k_q')[Cs^*][M] \end{aligned} \qquad (18)$$

The stationary state treatment leads to the following equation for the concentration of the Cs*,

$$[Cs^*] = \frac{\varepsilon I I_0[Cs]}{1/\tau + (k_i + k_q)[Cs] + (k_i' + k_q')[M]} \qquad (19)$$

The ion current for the total ionic species is

$$I' = k_i[Cs^*][Cs] + k_i'[Cs^*][M] \qquad (20)$$

Substituting Eq. (19) into Eq. (20), the following equation is derived,

$$I' = \frac{\varepsilon I I_0\{k_i[Cs] + k_i'[M]\}[Cs]}{1/\tau + (k_i + k_q)[Cs] + (k_i' + k_q')[M]} \qquad (21)$$

The ratio of the ion current in the presence of a foreign gas to that in the absence of foreign gas is

$$\frac{I'}{I} = \frac{k_i[Cs] + k_i'[M]}{1/\tau + (k_i + k_q)[Cs] + (k_i' + k_q')[M]} \cdot \frac{1/\tau + (k_i + k_q)[Cs]}{k_i[Cs]} \qquad (22)$$

Changing this equation to the suitable form to analyse the data, the following equation can be derived,

$$\frac{[M]}{Y-1} = \frac{(k_i' + k_q')[M]}{k_i'(\beta-\alpha) - k_q'\alpha} + \frac{\alpha\beta}{\{k_i'(\beta-\alpha) - k_q'\alpha\}\tau} \qquad (23)$$

where $Y = I'/I$,

$$\alpha = \tau k_i[Cs],$$

and

$$\beta = \tau(k_i + k_q)[Cs] + 1.$$

Since for a series of measurements the vapor pressure of cesium was kept constant, α and β have the constant values. The plots of $[M]/(Y\text{-}1)$ *versus* [M] gave straight lines as shown in Figs. 4—7. These results suggested that the mechanisms considered for chemi-ionization and quenching of cesium with M should be reasonable. From the slopes and the intercepts of these lines the values of $\tau k_i'$ and $\tau k_q'$ could be determined. Utilizing the values of $\tau k_i'$ and $\tau k_q'$, the values of $\tau\sigma'^2_i$ and $\tau\sigma'^2_q$ could be obtained. The values of $\tau\sigma'^2_t = \tau(\sigma'^2_i + \sigma'^2_q)$, $\tau\sigma'^2_i$ and $\tau\sigma'^2_q$ were summarized in Table 1. The value of collisional cross

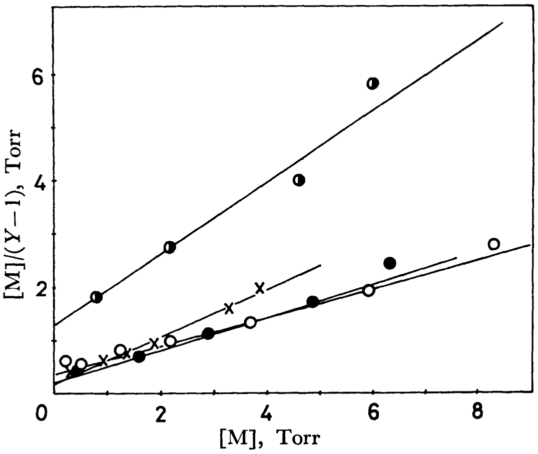

Fig. 4. Plot of $[M]/(Y-1)$ against [M] according to Eq. (23).
◑ Neon, ● Krypton, ○ Argon, × Xenon

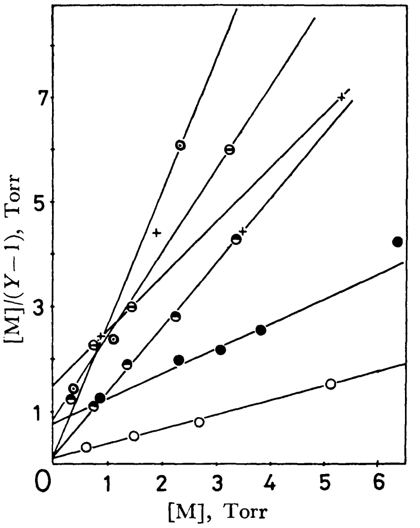

Fig. 5. Plot of $[M]/(Y-1)$ against [M] according to Eq. (23).
⊖ CH_4, + C_2H_6, ○ C_3H_8, ⊙: cyclo-C_3H_6, ◓ n-C_4H_{10}, ● *cis*-2-butene

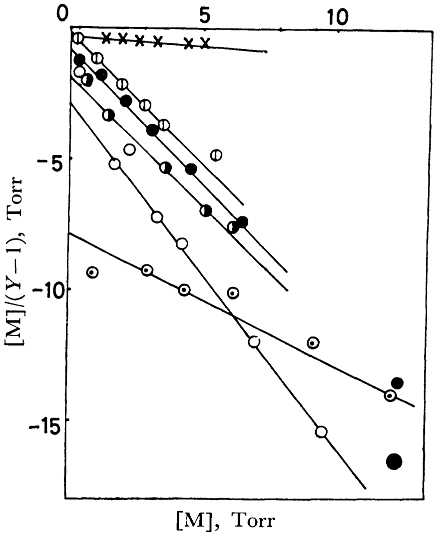

Fig. 6. Plot of [M]/($Y-1$) against [M] according to Eq. (23).
○ C_3H_6, ◑ He, ⊙ C_2H_4, ● N_2, ⦶ H_2, × NH_3

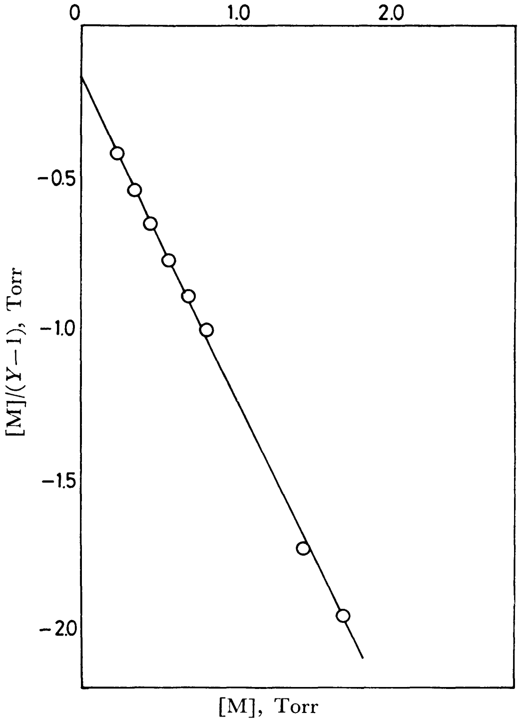

Fig. 7. Plot of [M]/($Y-1$) against [M] according to Eq. (23).
○: 2-pentene

section was nearly equal to $2.2\times10^{-20}/\tau$ cm^2/sec obtained by Mohler using the space charge method. This coincidence is surprising, considering the two quite different experimental techniques. If the life time of $Cs^*(8^2P_{1/2})$ is assumed to be the order of 10^{-6} sec, the value of collisional radius is estimated to be 1—3×10^{-7} cm for Cs–Cs collision. This value remarkably large compared with the kinetic radius obtained from the viscosity data. The collisional cross sections for excited cesium with foreign gases, are reduced by two or three orders. The radii for collisions with foreign gases agree in magnitude with the kinetic radii. For the Cs-Cs collision, the ionization and the quenching cross sections are almost equal.

Discussion

Figure 8 shows the schematic potential energy curves for Cs–M system relevent to the ionization quenching processes from the system $Cs^*(8^2P_{1/2})+M$. It is to be seen in Fig. 8 that Cs^++M^- and Cs^++M+e curves both interact with the curve for the $Cs^*(8^2P_{1/2})+M$, and also the repulsive curves (Π state) of the lower excited states of Cs with M (for example, $Cs^{**}(7^2P_{1/2})+M$) cross the curve of Cs^*+M in the $\sum$ state. The quenching of $Cs^*(8^2P_{1/2})$ by M can be interpreted by cross over from Cs^*+M to $Cs^{**}+M$. The chemi-ionization of $Cs^*(8^2P_{1/2})$ with M can be interpreted by transfer from the Cs^*+M curve to the CsM^++e curve.

As predicted in the theories of inelastic collisions[11] between alkali and rare gas atoms concerning the spin-orbit relaxation of alkali atoms, cross section should depend on the attractive force between the atoms, and increase monotonically with the polarizabilities of rare gas atoms from helium to xenon. The total cross section equal to the sum of the quenching and ionization cross sections should follow exactly the predicted sequence. The plots of $\tau\sigma_t{}^2/r_0{}^2$ *versus* $\alpha\mu^{1/2}$ gave a straight

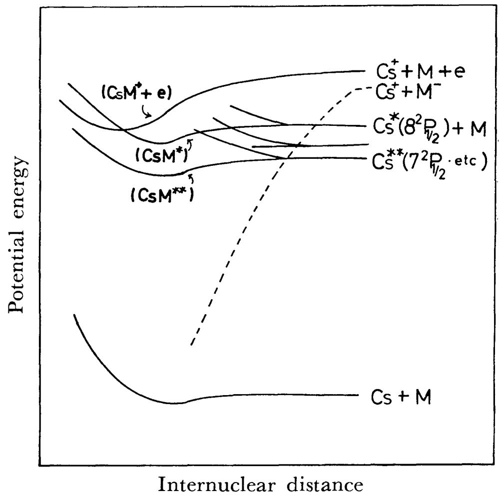

Fig. 8. The schematic potential energy curves for Cs-M system.

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[11] L. Krause, *Applied Optics*, **5**, 1375 (1966).

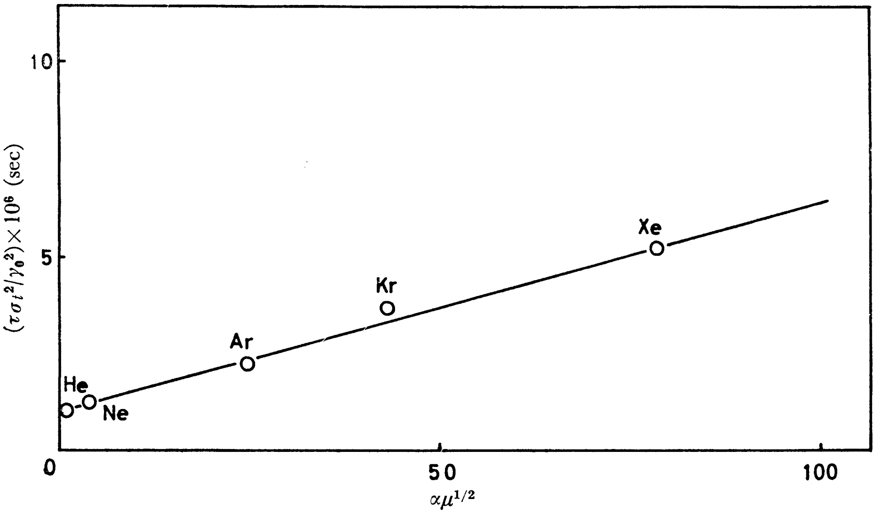

Fig. 9. Correlation the ratio of the total cross section to the kinetic collision cross section *versus* $\alpha\mu^{1/2}$.

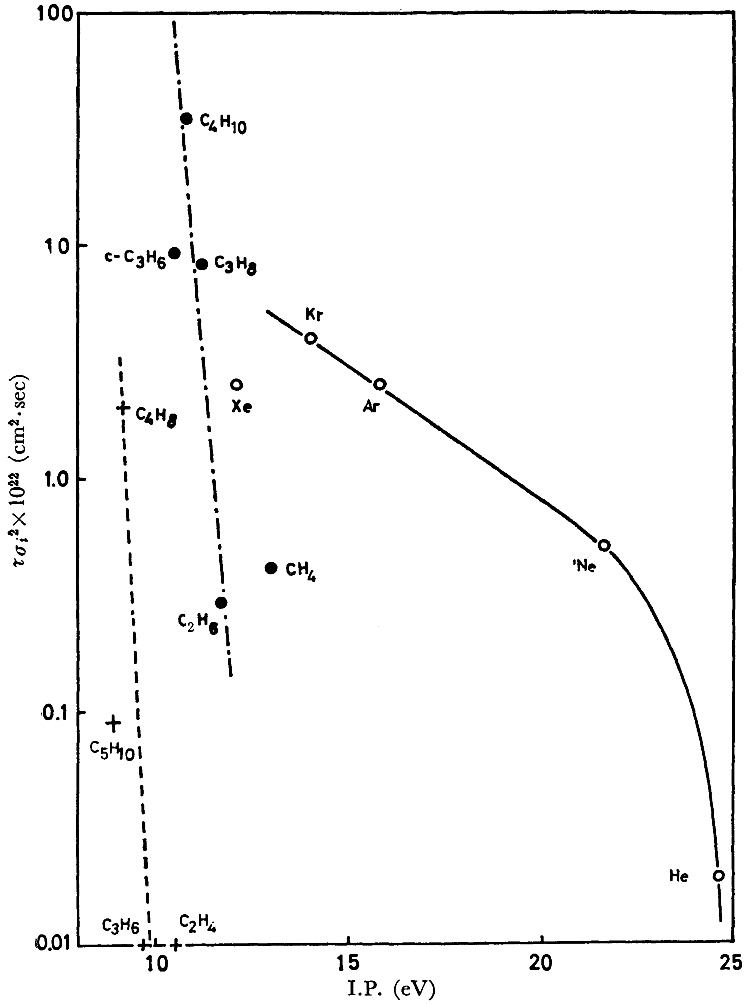

Fig. 10. Correlation $\tau\sigma_i^2$ *versus* the ionization potential.

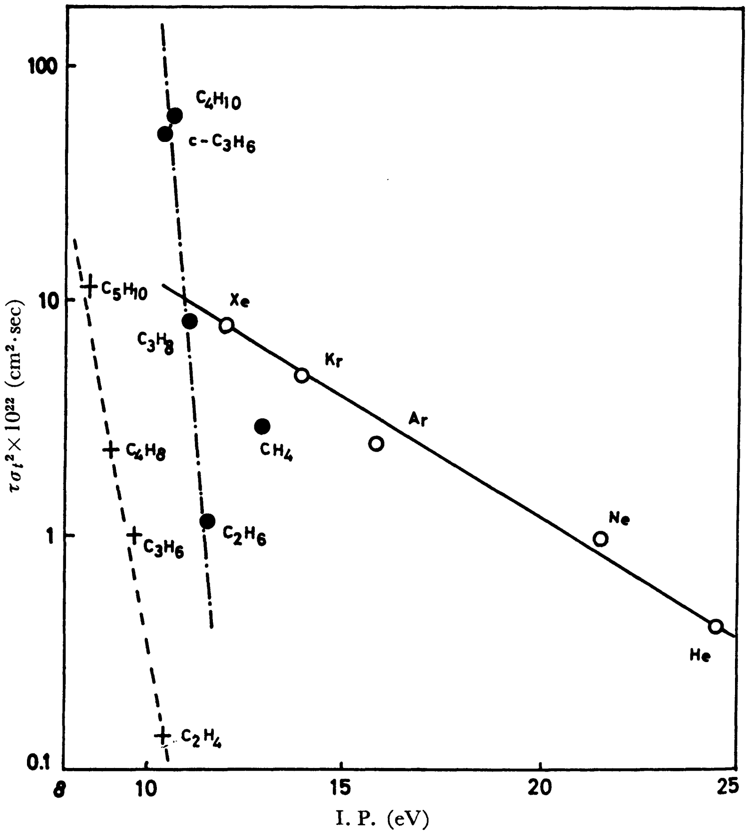

Fig. 11. Correlation $\tau\sigma_t^2$ *versus* the ionization potential.

line as shown in Fig. 9, where r_0 is the kinetic collision diameter between the Cs atom and the rare gas atoms, α is the polarizability of each rare gas atom, and μ is the reduced mass of cesium and each rare gas atom. This relation indicated that the total cross section ($\sigma_t'^2$) divided by kinetic cross section (πr_0^2) corresponding to the easiness of making collision complex should be related with the $\alpha\mu^{1/2}$ which means the effective intermolecular attractive force. H_2, N_2 and NH_3 have larger cross sections than rare gases, and H_2 has the largest one. In the case of hydrocarbons, the cross section decreases from CH_4 to C_2H_6 and then shows a rather steep rise to n-C_4H_{10}. The cross sections of unsaturated hydrocarbons have smaller values than those of rare gases and those of corresponding saturated hydrocarbons. This tendency seems to be reverse to that for the physical quenching cross sections of Na*(3^2P) by hydrocarbons.[12] This difference may be caused by the different processes from excited states of atoms.

Since we can exclude the ion pair formation in the reaction of Cs*($8^2P_{1/2}$) with the foreign gases as described before, the increase of ion current by the foreign gases should be explained by the occurrence of chemi-ionization reaction

$$Cs^* + M \rightarrow CsM^+ + e$$

Herman and Cermak[13] confirmed the presence of ions $CsAr^+$ and $CsKr^+$ in the reactions

$$Ar^* + Cs \rightarrow ArCs^+ + e$$

and

$$Kr^* + Cs \rightarrow KrCs^+ + e$$

A recent work by Williams and Naiditch[8] suggested the molecular ion $Cs(NH_3)^+$, from the reaction

$$Cs(nP) + NH_3 \rightarrow CsNH_3^+ + e \quad (n \geq 12)$$

On the energetic basis for the possibility of the chemi-ionization reaction between Cs*($8^2P_{1/2}$) and M, the value of bond energy of molecular ion CsM^+ should be greater than 0.7 eV. The bond energy of CsM^+ strongly depends on the polarizability and/or ionization potential of foreign gases. If the ionization potential of M is lower, the energy of the molecular ion becomes lower. It is expected that the ionization cross section with M may be correlated with the ionization of M. This correlation is found in the series of foreign gases such as rare gases and saturated hydrocarbons

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[12] R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc.*, **A176**, 295 (1940).

[13] V. Cermak and Z. Herman, *Collect. Czech. Chem. Commum.*, **30**, 169 (1965).

TABLE 1. THE VALUES OF $\tau\sigma_t'^2$, $\tau\sigma_i'^2$, $\tau\sigma_q'^2$ AND RELATIVE IONIZATION EFFICIENCY η FOR INERT GASES AND SIMPLE MOLECULES WITH CESIUM ATOM
(Prime of collisional radius is removed in this Table)

Gas M	Cross section			Relative ionization efficiency
	$\tau\sigma_t^2$ ($\times 10^{22}$)	$\tau\sigma_i^2$ ($\times 10^{22}$)	$\tau\sigma_q^2$ ($\times 10^{22}$)	$\eta = \frac{\sigma_i^2}{\sigma_t^2}$
He	0.41	0.019	0.39	0.046
Ne	0.98	0.51	0.47	0.52
Ar	2.5	2.5	0	1.00
Kr	4.8	3.9	0.90	0.81
Xe	7.8	2.5	5.3	0.33
H_2	6.5	0.060	6.4	0.0093
N_2	3.3	0.026	3.3	0.008
NH_3	2.7	0	2.7	0
CH_4	2.9	0.41	2.5	0.14
C_2H_5	1.2	0.29	0.88	0.25
C_3H_8	8.2	8.2	0	1.00
C_4H_{10}	62	35	27	0.56
c-C_3H_6	51	9.1	42	0.18
C_2H_4	0.14	0	0.14	0
C_3H_6	1.0	0	1.0	0
C_4H_8	2.3	2.0	0.32	0.86
C_5H_{10}	12.6	0.06	12.5	0.007
Cs	212	95	117	0.18

except for Xe and CH_4 as shown in Fig. 10. Compared with the ionization cross section, $\tau\sigma_i^2$, it is interesting to note that the plots of $\log \tau\sigma_t^2$ *versus* the ionization potential give three straight lines for three groups of foreign gases; rare gases, saturated hydrocarbons, and unsaturated hydrocarbons as shown in Fig. 11.

In Fig. 12 the quenching cross sections listed in Table 1 are plotted against atomic weight in cesium-rare gas system. The plots show a minimum at argon. Similar behavior of the cross sections was observed in the cases of the collisional spin-orbit relaxation of $Cs(6^2P_{1/2}\rightarrow 6^2P_{3/2})$ by rare gases.[11] It was demonstrated that there was a good correlation between the spin-orbit relaxation cross sections for $Cs(6^2P_{1/2})$-rare gas collisions and the elastic scattering cross sections of electrons by the rare gases with the electron velocity assumed as equal to that of the valence electron of cesium. However the complete theoretical interpretation of this behavior of rare gases has not been given.

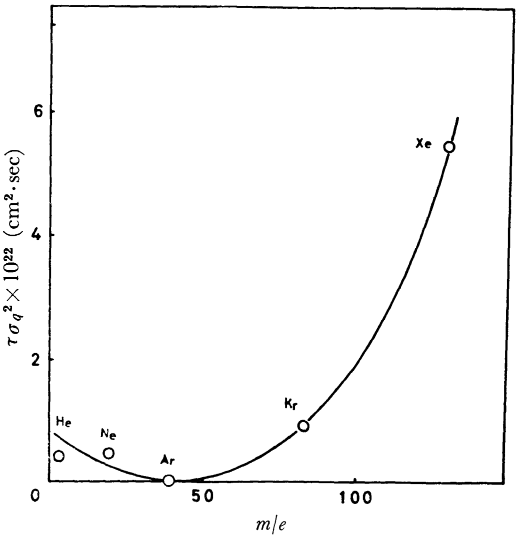

Fig. 12. Correlation $\tau\sigma_q^2$ *versus* atomic weight.

Figure 13 shows that the plots of $\eta(\sigma_i^2/\sigma_t^2 = \sigma_i^2/(\sigma_i^2+\sigma_q^2))$, relative ionization efficiency, *versus* the mass weight gave the same configuration for each group of gases. For rare gases they have a maximum at arogn, and the saturated hydrocarbons at C_3H_8 and the unsaturated at C_4H_8. The increases in η from He to Ar, CH_4 to C_3H_8 and C_2H_4 to C_4H_8, can then be ascribed to the increase in the ionization probability owing to the decrease in ionization potential of M which lowers the $CsM^+ + e$ curve. The decrease from Ar to Xe for rare gases can be interpreted by the rapid increase in the quenching probability owing to the increasing spin-orbit interaction which will be evidenced from the experimental results shown in Fig. 12. However, for the saturated and unsaturated hydrocarbons, the increase in the number of potential curves which cross the CsM* curve to dissipate the electronic energy to various vibrational energies may play an important role for the decreases in η from C_3H_8 to n-C_4H_{10} and from

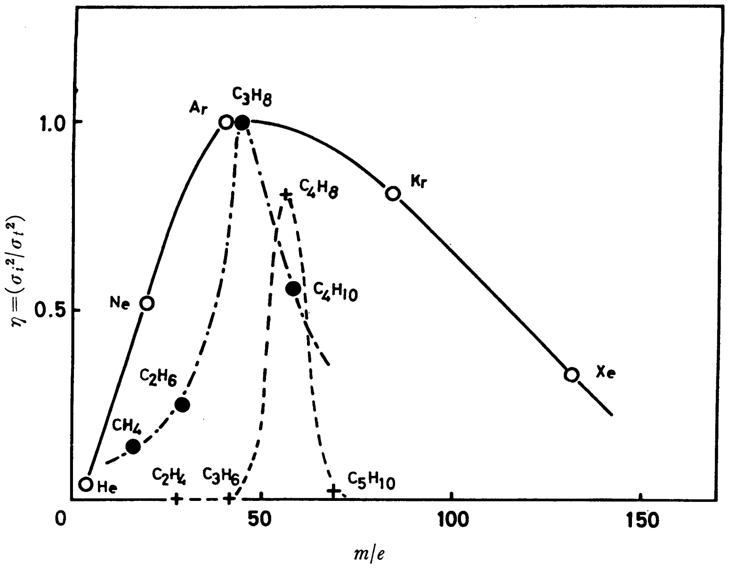

Fig. 13. Correlation ionization efficiency of chemi-ionization for Cs–M system *versus* atomic and molecular weight.

C_4H_8 to C_5H_{10}.

Appendix

Effects of Foreign Gases on the Line Absorption of Cs. The modification of the spectral lines of emitting or absorbing atom due to collisions with other atoms and molecules is exhibited by broadening, shift and symmetry of lines and the occasional appearance of a certain diffuse band. The emission line 3888 Å from the He lamp used is substantially broader than the absorption line of cesium, and also the peak of He line does not coincide with that of cesium line. Since the added gas pressure was varied up to about 10 Torr in this experiment, the pressure effect on the absorption of the light at 3888 Å could not be neglected for the quantitative discussion.

The absorption cell consists of 150 cm length and 1.5 cm diameter pyrex tube with pyrex windows at both ends, a small tube for supply of Cs vapor and a tube connected with a gas inlet system through the two grease-free valves. The cell was mounted in a constant temperature oven. Before measurement the cell was evacuated to less than 10^{-6} Torr by heating at 400°C for a few days, and kept at 350°C during the measurement. In the experiment the slit width of the monochrometer 0.1 mm was enough to cover the whole emission line at 3888 Å line. After the absorption of the light by Cs vapor only was measured, a foreign gas purified by a getter was introduced into the cell and the variation of the intensity by adding a foreign gas was measured.

The Apparent Absorption Coefficient. The logarithmic plots of the transmitted light intensity, I, *versus* the cesium pressure can give the apparent absorption coefficient. The value of the apparent absorption coefficient calculated from Fig. 14 was 1.4×10^{-19} cm²/molecule.

Pressure effects of foreign gases on the absorption line of Cs. Relative measurements of the

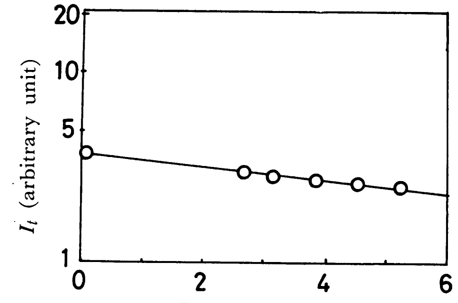

Fig. 14. Plot of the transmitted light against the vapor pressure of Cs.

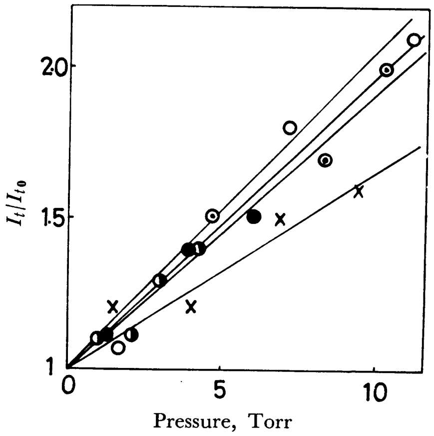

Fig. 15. Pressure effects of foreign gases on the absorption line of Cs.

⊙ He, × Ne, ● Ar, ○ Kr, ◑ Xe

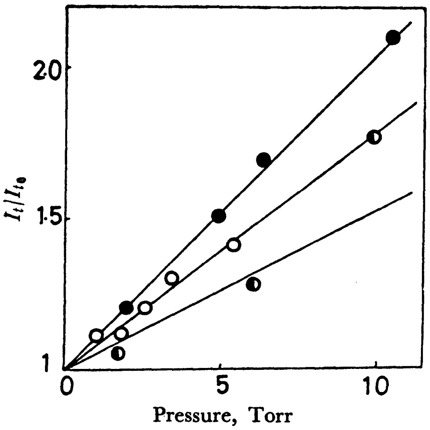

Fig. 16. Pressure effects of foreign gases on the absorption line of Cs.
● H_2, ○ NH_3, ◐ N_2

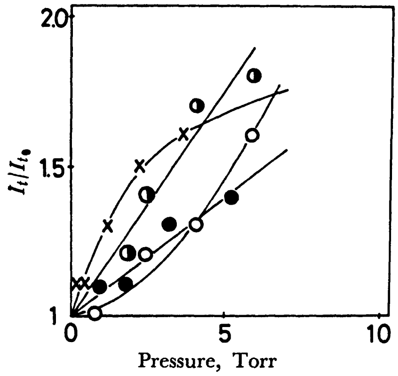

Fig. 17. Pressure effects of foreign gases on the absorption line of Cs.

absorption of the line at 3888 Å from He lamp with and without foreign gases were made to correct the effects of gases on the chemi-ionization of Cs. The effects of rare gas atoms in the pressure region, 0 to 10 Torr were shown in Fig. 15. The results for simple inorganic gases such as H_2, N_2, and NH_3 were shown in Fig. 16, the results for CH_4, C_2H_4, C_2H_6, and cyclo-C_3H_6, for C_3H_6, C_3H_8, and n-C_4H_{10}, and for C_5H_{10} are shown in Fig. 17, 18, and 19, respectively. For each foreign gas plots of the relative absorption *versus* the pressure of gas yield almost a straight line. In order to evaluate the pressure effect of the foreign gas on the chemi-ionization of Cs, the ion current of chemi-ionization is corrected by multiplying the factor I_{t0}/I_t at each foreign gas pressure, where I_t and I_{t0} are the transmitted light intensities with and without foreign gases, respectively.

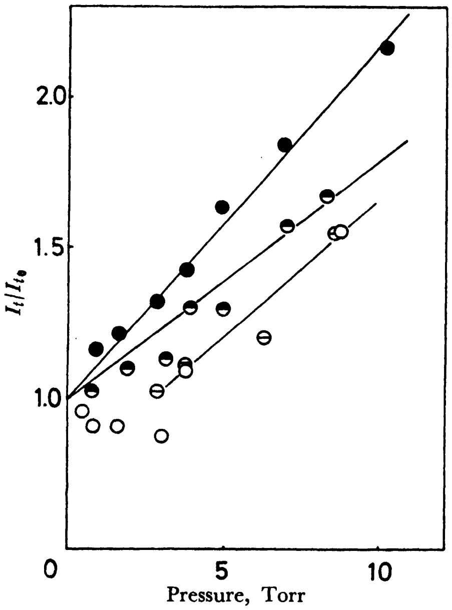

Fig. 18. Pressure effects of foreign gases on the absorption line of Cs.
● n-C_4H_{10}, ◓ C_3H_8, ○ C_4H_8, ⊖ C_3H_6

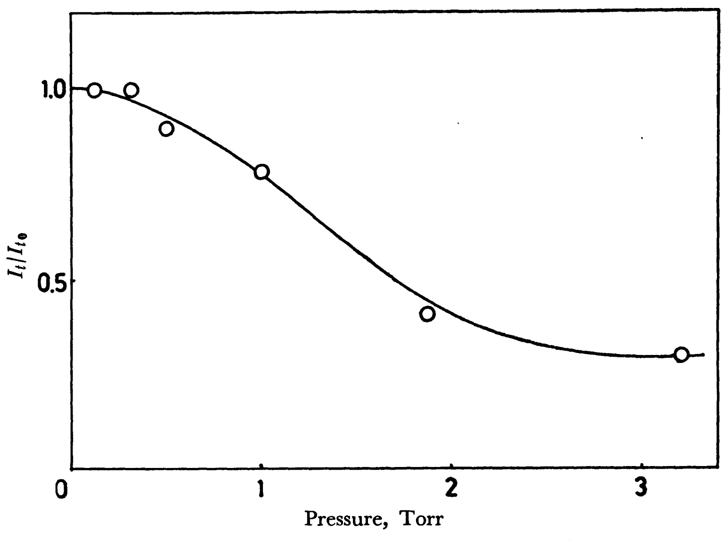

Fig. 19. Pressure effects of 2-pentene on the absorption line of Cs.