Deexcitation of Rydberg states of He by He, Ne, Ar, Kr, and Xe

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The total quenching cross sections for He(n $^{1,3}S$)($2 \leq n \leq 11$) states by thermal collisions [600(+200, −100) K] with He, Ne, Ar, Kr, and Xe have been measured. The main quenching mechanism is attributed to Penning ionization for lower n, and collisional angular-momentum transfer for highly excited states. Measured cross sections are of the order of 10^{-15} to 10^{-14} cm^2. The values for higher n states are much smaller than the geometrical cross section; this is explained by a relatively large energy spread between the S state and $l \geq 1$ states.

I. INTRODUCTION

The collision process between excited atoms and neutral atoms and molecules has received considerable experimental and theoretical attention. The process is interesting because of its importance in gaseous lasers, in plasmas, in astrophysics and in radiation chemistry. The process includes Penning ionization, associative ionization,[1] the Hornbeck-Molnar process and excitation transfer, etc.

Considerable data have been accumulated on Penning ionization due to energy transfer from metastable atoms. But few experiments have been performed on collisions which involve resonance atoms[2-4] or highly excited atoms.[4-7] On the other hand, theoretical work has concentrated on resonance atoms[8-11] and metastable atoms.[12-16] No satisfactory theory exists for highly excited atoms. The Hornbeck-Molnar process has been studied by several authors[17-22] particularly for small values of the principal quantum number n.

Excitation transfer in pure helium has been studied for many years[23-32] particularly for small values of n and also these studies have been restricted mainly to $l \geq 1$. Although the experimental results are scattered, the consensus of previous workers is that the cross section is large and increases in proportion to the geometrical cross section $\sigma_g(\pi a_0^2 n^4)$.

In recent years, there has been a growing interest in collision processes of highly excited atoms and neutral atoms.[33-44] Gallagher *et al.*,[33] using a tunable dye laser, have studied angular-momentum mixing of highly excited Na(n ^2D) states by rare gases and reported that the cross sections are of the order of 10^{-13} cm^2 and increase in proportion to σ_g for $5 \leq n \leq 10$.

The process involving S states, however, because of a relatively large energy spread ΔE with respect to $l \geq 1$ states, is expected to have cross sections of considerably small value. Freund *et al.*[34] have studied $nS-nD$ transitions in helium by singlet-triplet anticrossing spectroscopy and found that they are small and are not strongly dependent on n, particularly above $n = 7$. Recently, Gallagher and Cooke[35] have measured the collisional depopulation cross sections of Na(n ^2S) states from $n = 6$ to 11. They reported that the maximum cross sections observed for He, Ar, and Xe were ~2, 2, and 10×10^{-15} cm^2, respectively. These experiments show that the process has a much smaller cross section. It is interesting then to study the effect of the energy spread on angular-momentum transfer by collisions with rare gases.

We report here the observation of quenching of He(n $^{1,3}S$) states by thermal collisions with He, Ne, Ar, Kr, and Xe. We have obtained the cross sections by observing the decay rate of helium excited states as a function of the perturbing-gas pressure. The results for higher n states will be discussed with respect to collisional angular-momentum transfer with relatively large energy spread.

II. EXPERIMENTAL METHOD

The experimental apparatus was similar to that described before.[4] The helium atoms were excited by electron impact, using a pulsed beam of electrons of variable duration and rapid time cutoff. The energy of the electrons is controlled to be as close as possible to the energy of the required excited state (threshold excitation). A time-to-amplitude converter is started by a trigger pulse from the pulse generator at the pulse cutoff time. Photons from the gas cell pass through a sapphire window and a quartz lens and are energy resolved with a $\frac{3}{4}$-meter Czerny-Turner spectrometer and are detected by a Mullard 56 TUVP photomultiplier. The photoelectron pulse from the photomultiplier stops the time-to-amplitude converter. The output from the time-to-amplitude converter is fed into the pulse height analyzer where the decay curve is accumulated. If necessary the excitation energy of the electrons can be cycled above and below the excitation threshold of the state of interest. Counts accumulated in the part of the cycle below threshold can be subtracted from those above threshold in order to remove background counts.

The ultimate vacuum obtained was about 5×10^{-9} Torr and the outgassing rate was less than 2×10^{-5} Torr per hour. Spectroscopically pure rare gases obtained from the British Oxygen Company and containing impurities of less than 10 ppm were used. Spectrum scans from 250 to 750 nm showed that a few lines from impurities were observed but their intensities were weak and did not affect the results.

Emission from $nS\rightarrow 2P$ transitions ($n\geq 3$) were monitored to obtain the pressure dependences of the decay rates for nS states. A small amount of nitrogen was introduced into the cell and the nitrogen first negative system ($B^2\Sigma_u^+\rightarrow X^2\Sigma_g^+$) was monitored to obtain the decay rate for the $2\,^3S$ state. The radiative lifetime of $N_2^+(B^2\Sigma_u^+)$ is about 60 ns (Ref. 45) and is much shorter than the decay of the observed nitrogen first negative emission which is attributed to transfer from and decay of He($2\,^3S$). The details of the quenching of the metastable atoms will be published elsewhere. The typical spectrometer bandwidth was less than 0.1 nm for $n=4$ and 0.4 nm for $n=10$. Typical helium pressures were 1 Torr for lower n and 0.15 to 0.5 Torr for higher n.

The principle of the experiment is as follows. The nS states are removed by radiative decay to lower nP states, by collisions with neutral atoms to form He_2^+, by Penning ionization if other gases whose ionization potential is lower than the excited state of helium are present, and by collisional transfer to the $l\geq 1$ states. A schematic diagram of the deexcitation of He(nS) states is shown in Fig. 1. The last process is reciprocal. When reciprocal processes are negligible, e.g., for lower n states, the decay will be single exponential after the excitation pulse has been cutoff. If two states are included in the reciprocal process, the decay will be described by two exponentials. When the pressure is low or when the decay rates of each state is not at all comparable, the two com-

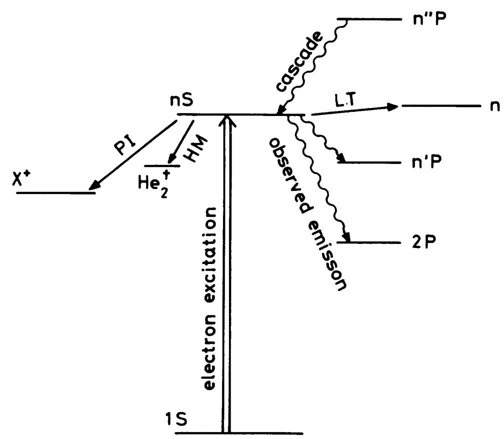

FIG. 1. Schematic diagram illustrating the deexcitation of He(nS) states. He atoms are excited by electron impact. The nS state decays by radiation and collisions which ionize the perturber X and populate higher l states. We observe the $nS\rightarrow 2P$ emissions to monitor the decay of the nS state. PI, HM, and LT stand for Penning ionization, the Hornbeck-Molnar process, and collisional angular-momentum transfer, respectively.

ponents represent the decay of each states.[18] Then the decay rate $1/\tau$ for an S state will be

$$1/\tau = 1/\tau_0 + k_c[X]\,, \tag{1}$$

where $1/\tau_0$ is the total radiative decay rate of the nS state for pure helium or the total decay rate at the constant helium partial pressure used in the gas mixture, $[X]$ (cm^{-3}) is the concentration of the atom X, and k_c ($cm^3\,sec^{-1}$) is the total quenching rate due to collisions with X. When more than two states are included in the transfer process, one will have merely increased the number of decay channels and the number of exponential terms describing the decay of each state.

The thermal velocity averaged cross section σ for an S state can be obtained from a relation

$$k_c = \sigma v\,, \tag{2}$$

where v is the average collision velocity. Then,

$$\sigma = k_c(\pi\mu/8k_BT)^{1/2}\,, \tag{3}$$

where k_B is the Boltzmann's constant, T is the temperature of atoms, and μ is the reduced mass.

III. RESULTS

The decays obtained showed practically a single exponential form for almost two orders of magnitude in photon number for $n\leq 5$ and 7 for the singlet and the triplet states, respectively. Typical decay curves are shown in Fig. 2. For the higher

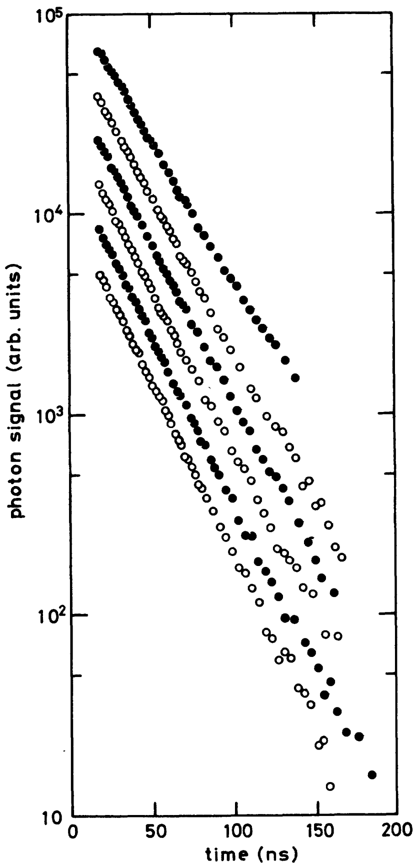

FIG. 2. Experimental decay curves obtained for the $4\,^3S$ state of helium at constant helium pressure (1 Torr) and xenon pressure of, from head to bottom, 0, 19, 39, 62, 89, and 109 mTorr, respectively.

values of n, a slow decay component appeared. The fast component represents the decay of the nS state and the slow one is due to cascade from higher n states and/or collisional transfer from $l \geq 1$ states. Decays were fitted to a functional form of single exponential and a constant term since the relative intensity of the slow component at the pulse cutoff was more than an order of magnitude smaller than that of the fast component and the decay rate was about an order of magnitude smaller than that of the fast component. The decay rates were plotted as a function of the perturbing-gas pressure (some are shown in Fig. 3). The plotted points lie reasonably well on straight lines.

The helium lifetimes obtained here agreed with theoretical values within experiment errors for $n \leq 5$ and 8 for the singlet and the triplet states, respectively. However, those for $6\,^1S$ (204 ± 6 ns), $8\,^1S$ (283 ± 40 ns), and $9\,^3S$ (390 ± 50 ns) are shorter than theoretical values[24,26] (240 ± 12, 520 ± 52,

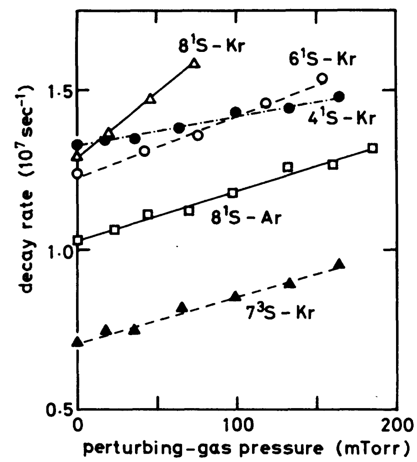

FIG. 3. Variation of He(nS) decay rates as a function of perturbing-gas pressure at constant helium pressures of 0.21, 0.31, 0.54, 0.29, and 0.31 Torr for $8\,^1S$ Ar (□), $4\,^1S$ Kr (●), $6\,^1S$ Kr (○), $8\,^1S$ Kr (△), and $7\,^3S$ Kr (▲), respectively.

and 500 ns for $6\,^1S$, $8\,^1S$, and $9\,^3S$, respectively). The value measured for $10\,^3S$ is 450 ± 100 ns. The value for 6^1S agreed with Thomson and Fowler's[24] experimental one, but that for $8\,^1S$ is shorter than

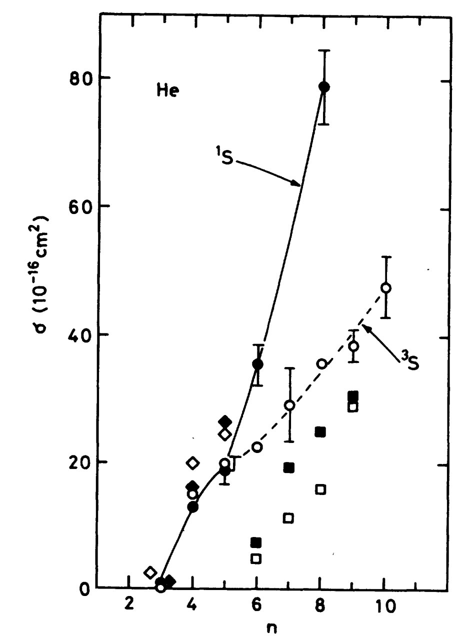

FIG. 4. Quenching cross sections measured for helium nS states (circles) by collisions with neutral helium as a function of the principal quantum number n. The error bars do not include systematic errors of (+ 15, − 8%) due to the uncertainty in the determination of the temperature; this also applies to Figs. 5–8. Diamonds show nS collision cross sections obtained by Bennett *et al.* Cross sections for $nS \rightarrow nD$ obtained by Freund *et al.* are shown by squares. Closed symbols are for the singlet and open ones for the triplet states.

TABLE I. Cross sections for quenching of He singlet nS states by collisions with He, Ne, Ar, Kr, and Xe measured at 600(+200, −100) K. All cross sections are in 10^{-16} cm^2.

n	He	Ne	Ar	Kr	Xe
3	1.26(+0.22, −0.16)	18.3(+2.9,[a] −1.7)	12.6(+2.4,[a] −1.7)	14.3(+3.8,[a] −3.3)	54.3(+10.5,[a] −7.6)
4	13.1(+2.2, −1.1)	10.0(+3.1, −2.8)		30.8(+6.2, −4.7)	73.2(+13.2, −9.3)
5	18.9(+3.6, −2.7)	11.2(+3.8, −3.5)	28.6(+4.6, −2.8)		67.1(+14.1, −11.2)
6	35.4(+6.1, −4.2)	9.4(+3.2, −3.0)		66.6(+12.4, −9.1)	96(+19, −14)
8	78.7(+13.1, −8.5)	19.3(+4.7, −4.0)	52.8(+9.5, −6.6)	134(+30, −24)	173(+29, −18)
10		38.3(+11.9, −10.8)			215(+59, −52)

[a]Reference 4; estimation of atomic velocities has yielded slightly different values, $v=(8k_BT/\pi\mu)^{1/2}$ is taken this time as described in the text.

their value (450 ± 150 ns); the reason for this disagreement is not well understood at present.

A. He-He collisions

The results for He(nS)-He collisions are shown in Fig. 4 and Tables I and II. The measured quenching cross sections are much smaller than the geometrical cross sections for larger n.

The cross sections for singlet and triplet states have similar n dependences; σ increases almost linearly with n for $n \geq 4$, although the values for singlet states are a few times those of the triplet states with the same n for $n \geq 6$. The cross sections for $n=3$ are more than one order of magnitude smaller than those of $n \geq 4$, this probably means that $n=3$ corresponds to the energy threshold for the Hornbeck-Molnar process.[47]

B. He-Ne collisions

The cross sections for He-Ne collisions have been measured for $3 \leq n \leq 10$ and $3 \leq n \leq 8$ for singlet and triplet states, respectively, and are shown in Fig. 5 and Tables I and II. The cross sections tend to decrease with n increase although those for the singlet states begin to increase at about $n=7$; these n dependences are different from those for He-Ar, -Kr, and -Xe collisions. The magnitudes of the cross sections are much smaller than those for the other rare gases for the higher values of n.

C. He-Ar, -Kr, and -Xe collisions

The quenching cross sections due to Ar, Kr, and Xe have similar n dependences as shown in Figs. 6, 7, and 8 and Tables I and II. The cross sections for singlet states for Ar and Kr increase smoothly with n, and not so rapidly as the geometrical cross section ($\propto n^4$). For Xe the singlet state value has a minimum value at $n=5$. Those for the triplet states have minima at $n=4\sim5$ and then increase with n. For $n>5$ the value for the singlet states are larger than those for the triplet states of the same n.

IV. DISCUSSION

The cross sections obtained here are the total quenching cross sections which include processes such as Penning ionization (or the Hornbeck-Molnar process for helium-helium collisions), collisional angular-momentum transfer, and n-changing collisions. The main quenching mechan-

TABLE II. Cross sections for quenching of He triplet nS states by collisions with He, Ne, Ar, Kr, and Xe measured at 600(+200, −100) K. All cross sections are in 10^{-16} cm^2.

n	He	Ne	Ar	Kr	Xe
2			9.4(+1.7, −1.3)		
3	0.12(+0.09, −0.08)	21.5(+3.4,[a] −1.9)	20.2(+4.3,[a] −3.5)	21.4(+6.1,[a] −5.4)	43.6(+8.1,[a] −5.7)
4	15.0(+2.3, −1.2)		13.1(+2.7, −2.1)	24.7(+5.1, −4.0)	83.5(+16.1, −12.1)
5	19.8(+3.1, −1.9)	10.7(+2.6, −2.3)	9.4(+2.6, −1.6)	18.2(+3.7, −2.9)	58.9(+10.5, −7.3)
6	22.4(+3.5, −2.1)	11.4(+2.2, −1.7)	16.6(+4.2, −3.6)	34.2(+6.1, −4.2)	63.7(+10.4, −6.5)
7	29.2(+7.3, −6.3)	7.3(+1.7, −1.4)	19.8(+3.9, −2.9)	48.8(+7.9, −4.9)	78.7(+13.3, −8.7)
8	35.6(+5.5, −3.1)	10.7(+3.2, −2.9)			96(+22, −18)
9	38.6(+6.3, −3.1)			66.8(+13.5, −10.5)	120(+27, −23)
10	47.7(+8.6, −6.1)			138(+26, −19)	
11			68(+23, −21)		

[a]Reference 4; estimation of atomic velocities has yielded slightly different values, $v=(8k_BT/\pi\mu)^{1/2}$ is taken this time as described in the text.

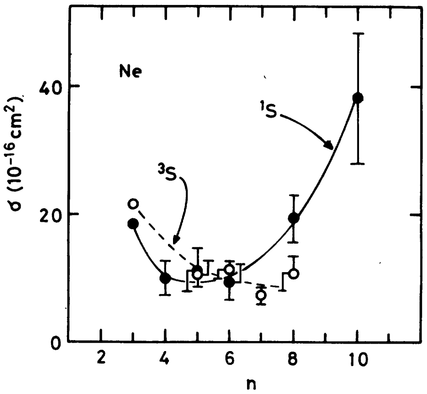

FIG. 5. Quenching cross sections measured for helium n^1S (•) and n^3S (○) by Ne against n.

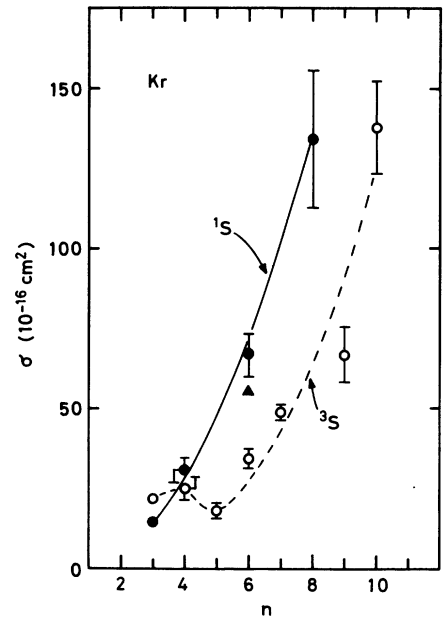

FIG. 7. Quenching cross sections measured for helium n^1S (•) and n^3S (○) by Kr against n.

ism is Penning ionization when n is small,[4] since cross sections for other processes are expected to be small because of the large energy spread.

Transitions involving $\Delta n \neq 0$ are negligible for rare-gas collisions of $n \lesssim 12$. The cross sections for the Hornbeck-Molnar process will decrease rapidly with n when n is large.[48] The Penning ionization cross section will also decrease with n when n is large. Because three particles, He^+, e^-, and the perturber X, have to interact simultaneously in Penning ionization, such a process is unlikely to occur when the electron is far from its nucleus such as in a highly excited atom.[49] Therefore, we expect that collisional angular-momentum transfer is responsible for the quench-

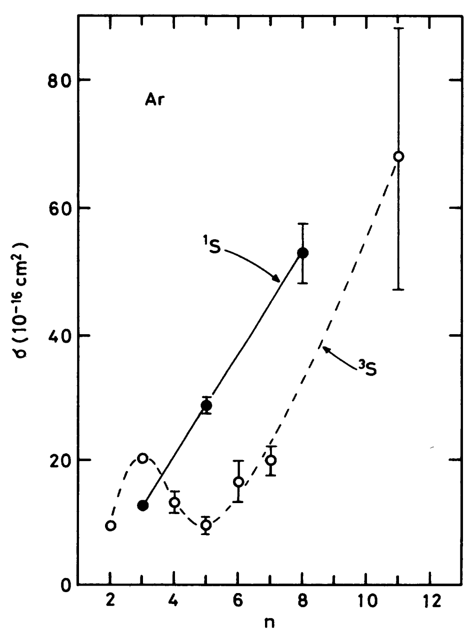

FIG. 6. Quenching cross sections measured for helium n^1S (•) and n^3S (○) by Ar against n.

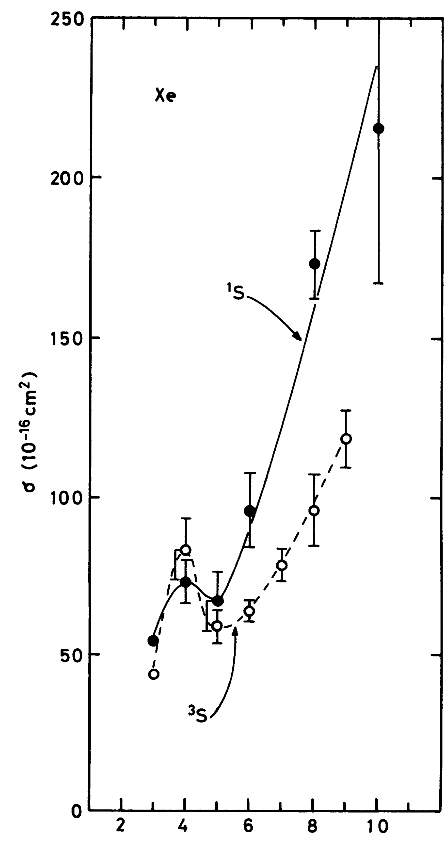

FIG. 8. Quenching cross sections measured for helium n^1S (•) and n^3S (○) by Xe against n.

ing of higher n states.

The n dependence of the experimental cross sections for He-He collisions is similar to that obtained by Bennett *et al.*[18] for $3 \leq n \leq 5$ by a similar method to the present one, although the value for $3\,^3S$ is an order of magnitude smaller than Bennett's value.

The measured cross sections for pure helium are much smaller than the values for the similar $^1P \rightarrow F$ transitions.[22-24] Relatively large energy spreads between the S and $l \geq 1$ states reduce the cross sections significantly. The results obtained by Freund *et al.*[34] for $S \rightarrow D$ transitions are consistent with present results. Cuvellier *et al.*[38] and Gounand *et al.*[39,40] have measured cross sections for transitions from P states of Rb by collisions with rare gases and have reported much smaller values than the geometrical cross sections due to large energy spread between nP and nl $(\neq nP)$ states.

The cross sections measured for the singlet states are larger than those for the triplet states of the same n $(n \geq 5)$ except for Ne. The cross sections for $n \geq 5$ increase in the same manner as the magnitude of the scattering length a of the electron,[50] i.e., $a_{Xe} > a_{Kr} > a_{Ar} > a_{Ne}$.

These results show that angular-momentum transfer should be responsible for the quenching of higher n states. As the energy spread is narrower in the singlet states, the cross sections for the singlet states are larger than those for the triplet states.

We can explain the n dependence of the quenching cross sections as follows. The main quenching mechanism is Penning ionization for lower n. The Penning ionization cross sections for He(nS) have maxima at $n=3$ or 4 and then decrease with n increase, while angular-momentum transfer becomes comparable with Penning ionization at $n=5$ or 6 and then increases with n. The minima appearing for the triplet states (Fig. 6, 7, and 8) can be explained in this way. For the singlet states, angular-momentum transfer becomes comparable before the Penning ionization cross section decreases noticeably; this buries the valley which appeared for the triplet states.

Gallagher and Cooke[35] proposed that the collisional depopulation of Na(nS) states by He, Ar, and Xe is characterized by n-changing collisions and proceeds via the interaction of the Na^+ core with the rare-gas atom. However, present experiment shows that the magnitude of the quenching cross sections correlate with the electron scattering lengths of the collision partners for higher n. This result suggests that the collisional angular-momentum transfer involving He(nS) states by rare gases proceeds mainly via the interaction of the Rydberg electron with the rare-gas atom.

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[1]Hereafter we refer to Penning ionization as including associative ionization.

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