Collisional depopulation of excited Na s states by He, Ar, and Xe

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The authors have measured the collisional depopulation cross sections of Na s states from $n = 6$ to 11. The maximum cross sections observed for He, Ar, and Xe, respectively, are ~ 20, 20, and 100 Å^2. The cross sections rise from ~ 0.1 Å^2 at $n \sim 6$ to a plateau at $n \sim 10$. The small size of the cross sections suggests that the process proceeds via the interaction of the Na^+ core with the rare-gas atom. Specifically, this short-range interaction produces a transient dipole on the rare-gas atom which efficiently couples Na states of different n. This is an entirely different mechanism than that responsible for the collisional l mixing previously reported.

I. INTRODUCTION

Recently, experimental investigations of many facets of collisions of Rydberg atoms have been reported. For example, Gounand *et al.*[1] have investigated the collisional depopulation of the Rb p states in the range $12 \leq n \leq 22$. For collisions with rare gases they found cross sections of ~20–60 Å^2. Our experiments with Na d states[2] have shown that collisions with rare-gas atoms produce mixing with the nearly degenerate higher Na l states of the same n. The cross sections for this process are approximately equal to the geometric size of the Rydberg atom for $n \leq 10$ and are ~1000 Å^2 for $n > 10$. Recently, Kocher and Smith[3] have reported deflections of an atomic beam of highly excited Li atoms by collisions with rare-gas atoms, and their results indicate that the cross sections for deflection, without depopulation, are ~100 Å^2. The last type of investigation recently reported is the study of collisional dephasing of transitions involving Rydberg atoms both by photon echo[4] and radio frequency spectroscopy.[5]

Theoretical interest in the general problem of collisions of Rydberg atoms with rare-gas atoms stems from the apparent simplicity of the problem and the possibility of tying the experimental results to low-energy electron scattering results. This was first done very elegantly by Fermi[6] to explain the pressure shifts of highly excited alkali p states by the rare gases.[7] The theory has been extended by Alekseev and Sobel'man[8] to cover pressure broadening as well as pressure shifts of high-lying atomic levels. Recently, much theoretical progress along the same lines has been made by Olson,[9] Hickman,[10] and Omont.[11]

The most satisfying theoretical results are the calculations[9,10] of the cross sections for collisional mixing of the Na nd states with the nearly degenerate $l \geq 2$ states of the same n. The more general problem of collisional depopulation is as yet poorly understood.

The cross sections for collisional depopulation of the lowest excited states of Na by rare gases are known to be exceedingly small,[12] and those for high n states of Rb are constant (~30 Å^2) independent of n. To gain further insight we have investigated the process in the intermediate regime. Here we report measurements of the collisional depopulation of Na ns states from $n = 5$ to $n = 11$ by He, Ar, and Xe. Over this range of n the cross section increases from ~0.1 to >10 Å^2. To explain the observed cross sections for collisional depopulation we present a simple physical model based on the Na^+–rare-gas interaction and its effect on the Na Rydberg electron.

II. EXPERIMENTAL APPROACH

The experiments were done using a time-resolved laser-induced fluorescence approach which we shall only briefly outline here since it is described in detail elsewhere.[13] Na atoms at a temperature of 425 °K are contained in a Pyrex cell to which we add rare gas. The rare-gas pressure is measured with a Baratron at pressures less than 1 Torr or with an oil manometer for pressures up to 20 Torr.

We use two-step laser pumping, that is, one laser at 5890 Å to pump the $3s_{1/2} \rightarrow 3p_{3/2}$ transition, followed by a second laser at 5200–4200 Å to pump the $3p_{3/2} \rightarrow ns_{1/2}$ transition. The second laser is delayed by $4ns$ from the first to insure complete population of the $3p_{3/2}$ state. The laser pulses are $4ns$ full width at half-maximum and are thus much faster than any of the radiative lifetimes of the states under study.

We observe the time-resolved $ns \rightarrow 3p$ fluorescence emanating from the ns state under study. By observing the decay rate as a function of rare-gas pressure we are able to determine the collisional depopulation cross sections. We use a small monochromator of ~50-Å resolution to insure that

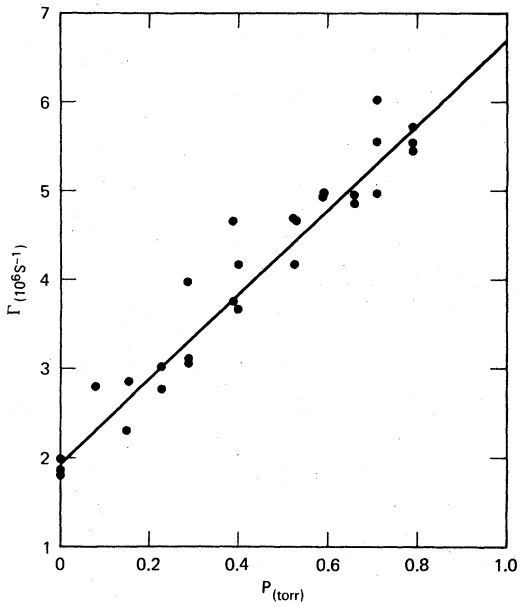

FIG. 1. Decay rate Γ of the Na 8s state vs Xe pressure.

we are only observing fluorescence from the state of interest. The decay curves are recorded using an analog boxcar averager for the lower states ($n \leq 9$) and a digital boxcar averager for $n = 10$ and 11 and are stored in a laboratory computer for analysis.

III. OBSERVATIONS

The data we accumulate are typified by Fig. 1, which is a plot of the decay rate Γ of the Na 8s state versus Xe pressure. From the slope of the line fit to the data we calculate the cross section σ using the simple relation $\Gamma = n\sigma v$, where n is the number density of the rare-gas atoms, and v is the collision velocity $(8\,kT/\pi\mu)^{1/2}$. Here k is the Boltzmann constant, T is the temperature, and μ is the reduced mass of collision partners.

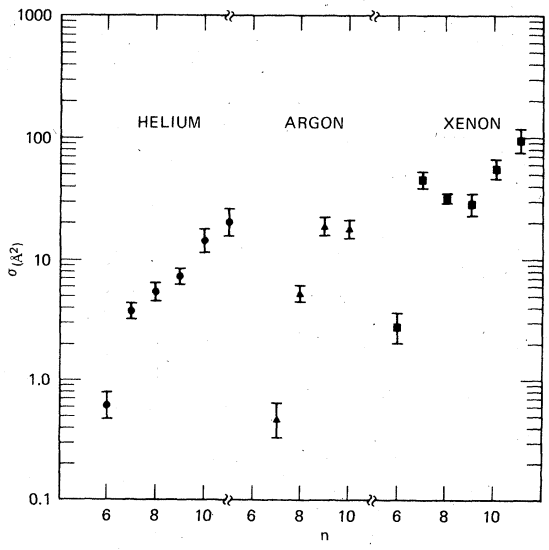

FIG. 2. Plot of the Nans depopulation cross section vs n for He (●), Ar (▲), and Xe (■).

TABLE I. Depopulation cross sections for Na(ns) with He, Ar, and Xe.

State	He (Å^2)	Ar (Å^2)	Xe (Å^2)
6s	0.62(15)	<0.12	2.8(8)
7s	3.8(6)	0.48(15)	46(7)
8s	5.5(9)	5.3(8)	32(3)
9s	7.3(10)	18.9(30)	29(6)
10s	14.4(30)	18.1(30)	56(9)
11s	21(5)		97(20)

In Table I we give the measured cross sections for He, Ar, and Xe and in Fig. 2, the cross sections are presented graphically. An interesting feature of the experiments is apparent in Fig. 2. There is a noticeable step in the He and Xe cross sections at 10s. In fact, when we pump the 9s or lower s states we only observe fluorescence from s and d states below the s-state populated. (The ultraviolet fluorescence from the p states does not pass through the Pyrex cell.) However, for $n = 10$ and 11, we observe fluorescence from the states above the one populated by the laser as well. As indicated by Fig. 3, an energy level diagram for Na near $n = 9$, collisional excitation to higher states becomes important when the process becomes thermally accessible; that is, when the energy separation is less than kT. As shown by Fig. 3, the 8s-7d energy separation is only slightly less than kT so that in only a small fraction of the collisions will the atoms have enough energy to induce the collisional transfer 8$s \rightarrow$ 7d. In Ar we are able to observe fluorescence even from the 7d state when we pump the 8s state, although the same is not true of the 7s and 6d states. Since in Ar the cross section only becomes appreciable for $n = 8$, the step is not apparent.

IV. DISCUSSION

The small size of the measured cross sections suggest either of two general types of interactions might be responsible for the collisional depopulation: a low probability event at large impact parameter (comparable to the size of the Rydberg atom's orbit) or a high probability event at small impact parameter.

Let us consider for a moment the case of a low-probability event at large impact parameter. The

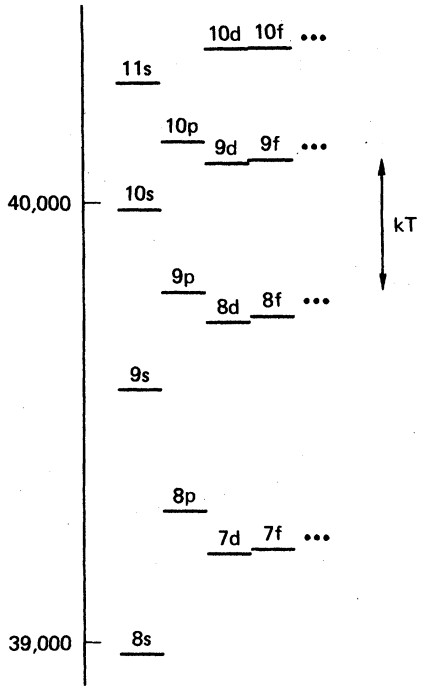

FIG. 3. Na energy levels near $n=9$, with an indication of thermal energy kT.

only such interaction is the short-range interaction between the Rydberg electron and the rare-gas atom. We do not consider this to be responsible for n changing collisions for two reasons.

First, the coupling between states is weak compared to the level spacing for all nearly degenerate levels such as the Na $l \geq 2$ levels. From the work of Hickman[9] we estimate the coupling matrix element to be LP/n,[5] where L is the scattering length of the rare-gas atom (typically ~1 a_0), and P is an overlap factor ≤ 1. Even in the case of complete overlap such a matrix element is not sufficient to couple states differing in n^* by 0.1 for $n^* > 3$. Only in rare cases (such as the high l states) will the energy difference be small and the overlap substantial.

Second, we would expect that if the collisional depopulation such as that reported here and by Gounand *et al.*[1] were due to an interaction occurring at large impact parameter at high n, *some* dependence on the radius of the Rydberg electrons orbit and hence on n would be observed. Rather, the cross sections for collisional depopulation of Rb p states measured by Gounard *et al.* are constant from $n=12$ to 22. This is in marked contrast to the very evident n dependence of the collisional mixing of the Na d states, which is attributed to the electron–rare-gas interaction occurring at large impact parameters. Both the experimental results and the theoretical calculations show a marked n dependence for high n states.

We suggest that the collisional effects reported here can be understood qualitatively on the basis of the short-range Na^+–rare-gas interaction and its effect on the Na Rydberg electron. Specifically, in the short-range collision of the Na^+ core with the rare-gas atom, a transient electric multipole moment is formed which couples adjacent n states of the Rydberg electron, and thereby induces the collisional transition. The attribution of collisional properties of Rydberg atoms to the ion-atom interaction is not new; Kocher and Smith[3]

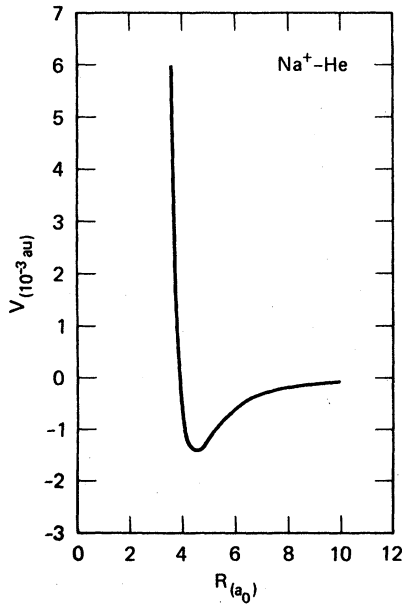

FIG. 4. Na^+-He potential vs internuclear separation R, from Ref. 14.

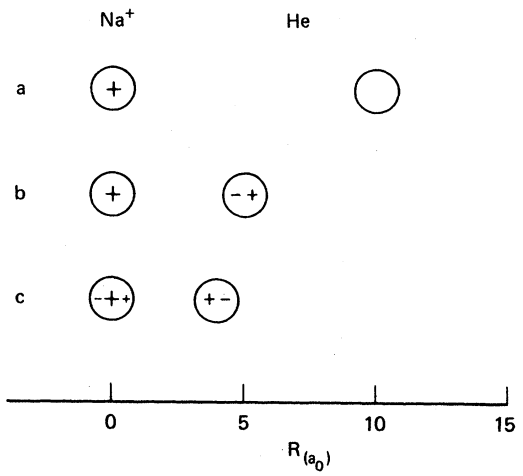

FIG. 5. Charge distributions of the Na^+ ion and He atom for (a) $R=10\,a_0$, (b) $R=5\,a_0$, in the polarizability regime, and (c) $3\,a_0$, in the electron overlap regime.

attributed their observed deflections of Li Rydberg atoms to Li^+–rare-gas-atom scattering.

Before we consider such a model in any detail let us consider for a moment what happens when a rare-gas atom comes close to the Na^+ core. For concreteness we shall specialize the discussion to He. In Fig. 4 we show the Na^+-He potential V as a function of internuclear separation R as calculated by Kim and Gordon.[14] The Na^+-Ar potential is also given in Ref. 14. The Na^+-Xe potential may be derived to adequate accuracy for our purposes from the work of Pascale and Vandeplanque.[15] The main components of the potential V are the polarization of the He atom by the Na^+ and the overlap of the Na^+ electrons with the He electrons. As shown by Fig. 4, for $R>4.5\ a_0$ the potential is mainly attractive due to the interactions of the positive charge of the Na^+ ion with the polarizability of the He atom. For $R<4\ a_0$ the potential is repulsive, reflecting the fact that at very small R the electron clouds of Na^+ and He overlap, leading to a strong Coulomb repulsion. Explicitly, we may write $V=V_0+V_p$, where V_0 is the repulsive potential due to electron overlap, and V_p is the attractive polarization potential $-\alpha/2R^4$. In Fig. 5 we show schematically the charge distributions of the Na^+ ion and the He atom at $R=10$, 5, and 3 a_0. At $R=10\ a_0$ the charge distribution of the He atom is essentially spherical. As R is reduced to 5 a_0, where the polarizability effects are important, the charge of the Na^+ induces a dipole moment in the He. At $R=3\ a_0$, in the electron overlap region, the dipole moment of the He is in fact reversed and a small dipole is also produced in the Na^+ ion.

Now let us examine the effect of the He dipole on the Rydberg electron. The presence of the dipole moment on the He atom means that there exists a series of multipole moments about the center of charge (roughly the center of the Na^+). These multipole moments have a significant effect on the valence electron because they break the spherical symmetry of potential it experiences.

For the moment let us ignore the higher-than-dipole moments for simplicity. This is by no means a good approximation since these moments can be comparable in effect to the dipole moment, but it serves to convey the essence of our collision model. The dipole moment $\bar{\mu}$ about the center of charge is equal to the dipole moment induced on the He atom and couples states differing in l by 1 through the matrix elements of $\bar{\mu}\cdot\bar{r}/r^3$, where $\bar{r}$ is the radial position of the Rydberg electron relative to the center of charge (the Na^+). From the known expressions[16] for $\langle 1/r^2\rangle$ it appears that a reasonable estimate for the radial matrix element between nl and $nl+1$ states is $n^{-3}(l+1)^{-1}$. Angular factors are ~1. Note in particular that the matrix element scales as $\sim 1/n^3$, that is, in the same manner as the energy separation between n states. Thus a constant dipole moment is equally effective in mixing high and low n states. Since the He dipole couples states differing in l by 1, its effect is similar to the Stark effect, which for large fields leads to energy shifts comparable to the term separations. Similarly, the He dipole moment produces shifts of $\cong\mu/n^3$ for the most strongly shifted states. Accordingly, for $\mu\sim\frac{1}{2}$ the highest and lowest states of the n and $n+1$ levels, respectively, are shifted into degeneracy, independent of n. Actually, there is not really a degeneracy but an avoided crossing of the energy levels as a function of μ. The magnitude of the splitting is determined by the quantum defects[17] and fine-structure intervals[18,19] of the atom under consideration. Littmann *et al.*[17] have mapped the energy levels of Na, the case of interest, in an electric field. Their Stark map may be viewed as indicative of the dependence of the energy levels on μ, the interaction of the Stark manifolds of n and $n+1$ states occurring at $\mu=\frac{1}{2}$. For values of $\mu>\frac{1}{2}$, the atomic levels become a maze of avoided level crossings.

Having considered the effect of the transient He dipole on the states of the excited Na atom, the mechanism for the collisional change of state is now apparent. During the collision μ changes from 0 to 1 to 0. As μ becomes $\geq\frac{1}{2}$ the energy levels of adjacent Na n states are shifted into the regime where diabatic transitions between levels can occur at the narrowly avoided level crossings. Then as μ returns to 0, the Na atom can exit in a different level from the one on which it entered. It is worth noting that this process is similar to pulsed electric field ionization, the most notable difference being that the times of the collisions are considerably shorter than the times required to apply a macroscopic field. For this process to be efficient in coupling states of n differing by one, two criteria must be met. First, the He atom must come close enough to the Na^+ ion to induce a dipole moment of $\frac{1}{2}$; second, the dipole must be formed quickly enough that the process not be adiabatic.

First we must estimate the size of the dipole produced by the polarization of the He atom by the Na^+ ion and by the electron overlap effect. The He dipole, from the polarizability interaction, is given by $\mu=\alpha/R^2$. For He, Ar, and Xe the polarizabilities α are 1.38, 11.1, and 27.3 a_0^3, respectively.[20] In the repulsive electron overlap region, μ is calculated using the harmonic-oscillator model developed by Drude[21] and used by Kim and Gordon.[14] It is a straightforward matter to show that, to a good approximation, $\mu=(2\alpha V_0)^{1/2}$. (There is an additional, considerably smaller, dipole induced in the Na^+, which we shall ignore.) In Table

TABLE II. Values of R for which $\mu = \frac{1}{2}$ due to the polarizability and electron overlap interactions, the predicted cross sections for high n πR_0^2, and the experimental values of the cross section σ.

	R (polarizability) (a_0^3)	R (electron overlap) (a_0)	πR_0^2 (Å^2)	Γ_{obs} (Å^2)
He	1.6	2.8	7	21
Ar	4.7	4.5	19	18
Xe	7.3	5.0	48	97

II we tabulate the values of R for which the polarizability and electron overlap interactions lead to values of $\mu = \frac{1}{2}$. As an estimate of the cross section we use πR_0^2, where we take the larger value for R_0. Note that in this model the requisite value $\mu = \frac{1}{2}$ is only reached in the energetically inaccessible electron overlap region for He, in the accessible electron overlap region for Ar, and in the polarization region for Xe. The model thus suggests that quenching by He should not occur, but it obviously does. We attribute this discrepancy to the fact that we have ignored the higher multipole moments, which, as we pointed out earlier, are comparable in magnitude to the dipole moment. Since $\langle r^{-k} \rangle$ varies as n^{-3} for $k \geq 2$, the higher multipole interactions have the same n^{-3} dependence as the dipole interaction. The presence of these added higher multipole interactions allows the Stark level crossing to occur at lower values of μ and hence at larger values of R, which are in the energetically allowed region for He.

The results obtained for the quenching cross sections are clearly dependent on the calculated potential curves of the Na^+–rare-gas pairs. For example, if we use the Na^+-He potential curves of Krauss *et al.*[22] we find a slightly smaller value of $R_0 \sim 2.2\ a_0$, leading to a predicted cross section of 4.3 Å^2, a value 40% lower than that given in Table II.

In any event, the values of πR_0^2 given in Table II can be viewed as reasonable lower limits to the quenching cross sections in the asymptotic limit of high n. When viewed in that light they are in reasonable agreement with the measured quenching cross sections as shown by Table II.

Thus far we have assumed that the collision happens fast enough that the level crossings are traversed diabatically with the result that the n state of the Rydberg atom is changed. As noted above, our model suggests that the internuclear distance R at which the interaction becomes important is independent of n, and thus the characteristic time is also independent of n. However, all the energy spacings between levels scale as $1/n^3$. Thus we may use the characteristic time of the interaction to estimate the n threshold for collisional n changing by this mechanism. Explicitly, we require that the collision time τ must be comparable to the smallest energy spacing Δ/n^3 (the magnitude of the avoided level crossings which occur for $\mu \geq \frac{1}{2}$) between the states during the collision. Here τ is the time required to traverse the avoided level crossing.

Thus the threshold value of n for collisional depopulation n_T is given by $\Delta/n_T^3 = 1/\tau$. The most rapidly changing part of the Na^+–rare-gas potential, the repulsive electron overlap region, is most effective in producing collisional transitions. Using the value of $\Delta \sim 0.1$ from the work of Littman *et al.*,[17] the potentials of Refs. 14 and 15, and typical thermal collision velocities we estimate that the collision times are ~2000 (a.u.). This implies that $n_T \sim 6$, in good agreement with our observations.

As mentioned earlier, for Xe it appears that a dipole of $\mu = \frac{1}{2}$ is produced in the polarization region at $R = 7.3\ a_0$. The n threshold for collisions by this effect is of course higher due to the longer range of the interaction and longer collision time. We estimate the threshold to be $n_T \sim 10$. This may be the cause of the obvious structure in the plot of the Xe cross sections versus n.

V. CONCLUSION

The measured cross sections for n changing collisions are orders of magnitude smaller than the geometric cross sections of the Rydberg atoms. These results are consistent with a simple model of the collision based on the short-range interaction of the Na^+ ion with the rare-gas atom. The n state of the Rydberg electron is changed by the transient dipole moment induced in the rare-gas atom during the Na^+–rare-gas collision. It is important to note that this is an entirely different mechanism than that believed to be responsible for collisional l mixing of the nearly degenerate $l \geq 2$ states of Na. The l mixing is attributed to the direct interaction of the Rydberg electron with the rare-gas atom, an interaction which depends critically upon the spatial overlap of the Rydberg state wave functions and on the energy separations of the states under consideration. Because of both of these considerations we do not expect the direct interaction of the Rydberg electron with the rare-gas atom to play a major role in n changing collisions. Experiments to test this hypothesis are currently in progress.

ACKNOWLEDGMENTS

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