

## Collisional angular momentum mixing of $f$ states of Na

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In Na, the energy gap  $\Delta E$  between the  $n, d$  state and the  $n, l > 2$  states is ten times larger than  $\Delta E$  between  $n, f$  and the  $n, l > 3$  states. To investigate the effect of this difference on the  $d$ - and  $f$ -state  $l$ -mixing cross sections,  $\sigma_d$  and  $\sigma_f$ , we have recently carried out experiments to measure  $\sigma_{d-f}$ , the  $l$ -mixing cross sections for a microwave-induced mixture of  $d$  and  $f$  states. Using the previously measured values of  $\sigma_d$ , we have derived values of  $\sigma_f$  which have the same  $n$  dependence as  $\sigma_d$ .  $\sigma_f$  is larger than  $\sigma_d$  for Ne, but smaller for He and Ar. In addition, we have analyzed the final states after one collision with Ar using selective field ionization of the  $17l$  states and have observed that after one collision all the  $l$  states are equally populated indicating that there are no  $\Delta l$  selection rules for the process. This confirms the earlier suggestion that  $l$  mixing is caused by a short-range interaction.

### I. INTRODUCTION

Recently, many studies of the collisional depopulation of highly excited states of alkali atoms by rare-gas atoms have been reported. For example, Gounand *et al.*<sup>1</sup> have studied the depopulation of excited  $p$  states of Rb, and we have reported the collisional depopulation of  $d$  states of Na.<sup>2</sup> In both experiments it was found that the collisions transfer the atoms to other energetically nearby states which then repopulate the initial state. In the case of the Rb  $p$  states, the other states involved are not as yet unambiguously identified. In the case of the Na  $d$  states, the other states are the higher- $l$  states of the same  $n$ , hence we have termed the process collisional  $l$  mixing. Although states of similar principal quantum number  $n$  ( $n \sim 10$ ) were used in both experiments, very different depopulation cross sections were observed. The cross section for the depopulation of the Rb  $14p$  state by Ar is  $28 \text{ \AA}^2$ , whereas for the Na  $14d$  state it is  $3800 \text{ \AA}^2$ . This enormous difference has been attributed to the difference in the energy gap  $\Delta E$  between the initially populated state and nearby levels. For the Rb  $14p$  state the nearest level,  $13d$ , is  $43 \text{ cm}^{-1}$  away,<sup>3</sup> while for the Na  $14d$  level the higher- $l$  states of the  $n = 14$  manifold are only  $1 \text{ cm}^{-1}$  away.<sup>4</sup> In both cases  $\Delta E$  is much smaller than  $kT$  which is  $\approx 300 \text{ cm}^{-1}$ .

The apparent strong dependence of the cross section on  $\Delta E$  as  $\Delta E$  is reduced from  $43$  to  $1 \text{ cm}^{-1}$  suggests that it would be interesting to see the result of reducing  $\Delta E$  by another factor of  $10$ . Intuitively, and on the basis of a classical picture of kinetic energy transfer between the rare-gas atom and the valence electron of the alkali atom, we would expect a smaller  $\Delta E$  to lead to a larger cross section. Thus we have begun collisional depopulation experiments with Na  $f$  states. The  $n = 14$   $f$ - $g$  energy gap  $\Delta E_{fg}$  is  $\sim 0.1 \text{ cm}^{-1}$ ,<sup>5</sup> a factor

of  $10$  less than  $\Delta E_{df}$ , so these experiments should show clearly the dependence of the cross section on  $\Delta E$ . Here we report the first such experiments.

In our previous measurements of the Na  $d$   $l$ -mixing cross sections, we identified the higher- $l$  states as the other states involved in the process by the radiative decay time of the mixture, which corresponded to the average lifetime of all the  $l \geq 2$  states. In the analysis of our data we assumed that the mixture of the  $l$  states was essentially statistical after the first collision (or equivalently that there were no  $\Delta l$  selection rules for the collision). This model in general implies that there should be two exponentials in the time-resolved fluorescence decay, which was consistent with our experimental observations. However, the data were not sufficiently good to definitively rule out the possibility that the decay contained more than two components. A multiexponential decay would imply that the  $l$  mixing was produced by a stepwise process, that is, that there were strong  $\Delta l$  selection rules for the collisions. Knowledge of the  $\Delta l$  selection rules is important for two reasons. First, it shows whether or not our previous analysis is correct, and second, it demonstrates clearly the range of the interaction responsible for the state changing collision. Here we report the analysis of the final-state distribution using a field ionization approach.

### II. Na $f$ - $l$ -MIXING CROSS SECTIONS

The basic idea of this experiment is to produce a mixture of Na  $d$  and  $f$  states by the use of a resonant microwave field and to study the collisional properties of this  $d$ - $f$  mixture. We know the fraction of  $d$  and  $f$  states in the mixture and the  $d$   $l$ -mixing cross sections  $\sigma_d$  so that we should be able to derive the  $f$ -state cross sections  $\sigma_f$  from the  $d$ - $f$ -mixture cross sections  $\sigma_{d-f}$ .

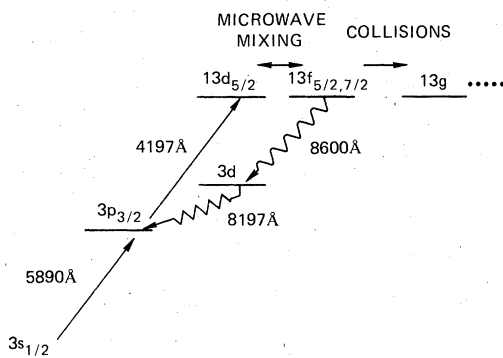


FIG. 1. Levels involved in the  $n=13$  experiment. The straight arrows pointed up indicate the laser pumping steps and the wavy arrows pointed down indicate the observed infrared fluorescence. The double-ended arrows indicate the microwave mixing of the  $d_{5/2}$  and  $f_{7/2}$  states. The collisions are indicated by the horizontal arrow.

The experimental approach is to observe the time-resolved fluorescence from Na atoms in a vapor cell. The approach of the experiment for  $n=13$  is shown in Fig. 1. Two pulsed dye lasers are used to pump Na atoms first from  $3s_{1/2} \rightarrow 3p_{3/2}$  and then from  $3p_{3/2} \rightarrow 13d_{5/2}$ . A resonant microwave field is used to drive the  $d_{5/2} \rightarrow f_{5/2}$  and  $d_{5/2} \rightarrow f_{7/2}$  transitions. The linewidth of the microwave resonance is  $\sim 25$  MHz. This ensures that both  $f_{5/2}$  and  $f_{7/2}$  states are populated, but that the  $d_{3/2} \rightarrow f_{5/2}$  transition is not driven (it is 50 MHz away). The 25-MHz linewidth ensures that the microwave transition rate,  $\approx 25$  MHz, is much faster than the 2–3-MHz collision rates so that the  $d$ - $f$  mixture is a valid concept. The microwaves are plane polarized so that  $\Delta m=0$  transitions are induced. Since the microwave radiation couples the  $d_{5/2}$ ,  $f_{5/2}$ , and  $f_{7/2}$  states, in equilibrium (which we shall assume to be the case) the mixture contains equal parts of each, i.e., the mixture is  $\frac{1}{3}d$  and  $\frac{2}{3}f$ . This is of course particularly advantageous for the measurement of  $f$ -state properties.

Although we could equally well observe the fluorescence from the  $d$  state or the  $f$  state, we observe the time-resolved infrared fluorescence from the  $f$  state as shown in Fig. 1. This ensures that we are observing only atoms which are mixed by the microwaves. It has the additional benefit of eliminating the problem of scattered laser light. By measuring the decay rate of the fluorescence as a function of added rare-gas pressure, we are able to determine the  $l$ -mixing cross section  $\sigma_{d-f}$ . The experimental apparatus and techniques used in this experiment are described fully elsewhere,<sup>2,4</sup> so we shall not describe them here.

With no added gas in the cell, we are able to make a crude measurement of the radiative lifetime of the  $f$  states. We observe the mixed state lifetimes, which are slightly too fast due to diffusion of the excited atoms out of the viewing region. From our previous measurements of  $d$ -state lifetimes we determined empirically that the diffusion rate was 0.03 MHz.<sup>2</sup> The observed lifetimes of the  $d$ - $f$  mixture,  $\tau_{d-f}^{\text{obs}}$ , and the corrected value,  $\tau_{d-f}$ , are given in Table I. The  $d$ -state lifetimes from Ref. 2 are also given and the  $f$  lifetimes are given by

$$1/\tau_d = 1/3\tau_d + 2/3\tau_f. \quad (1)$$

The  $f$  lifetimes calculated from Eq. (1) and the values extrapolated from the calculations of Tsekeris and Happer<sup>6</sup> are given for comparison. The results are in good agreement. Fortunately, the  $f$  and  $d$  lifetimes are roughly comparable. If the  $f$  lifetimes were much longer than the  $d$  lifetimes, it would be virtually hopeless to use this technique to determine the  $f$  state lifetimes.

In the discussion of the composition of the  $d$ - $f$  mixture, we have excluded the  $d_{3/2}$  state because it is not coupled by the microwaves. However, when we try to measure the  $l$ -mixing cross sections it is certainly possible that fine-structure-changing collisions would couple the  $d_{3/2}$  state to the  $d$ - $f$  mixture with a rate comparable to or greater than the  $l$ -mixing rate, resulting in a mixture other than  $\frac{1}{3}d$  and  $\frac{2}{3}f$ . To investigate this we populated the  $13d_{5/2}$  state with the lasers and scanned the microwave frequency through all three allowed  $d \rightarrow f$  transitions, with particular attention given to the frequency of the  $d_{3/2} \rightarrow f_{5/2}$  resonance. As we raised the rare-gas pressures we were unable to see any trace of a  $d_{3/2} \rightarrow f_{5/2}$  resonance even at rare-gas pressures high enough that the  $d_{5/2} \rightarrow f_{5/2}$  resonance was just barely observable (due to the  $l$  mixing's destroying the  $d$ -state population). Thus, we were led to conclude that the cross sections for fine-structure-changing collisions were at least an order of magnitude smaller than the  $l$ -mixing cross sections, and that our model of the  $d$ - $f$  mixture was not endangered.

In the  $l$ -mixing experiments with the  $d$ - $f$  mixture

TABLE I. Radiative lifetimes of Na  $d$  and  $f$  states.

$n$	$\tau_{d-f}^{\text{obs}}$ ( $\mu\text{s}$ )	$\tau_{d-f}$ ( $\mu\text{s}$ )	$\tau_d^a$ ( $\mu\text{s}$ )	$\tau_f$ ( $\mu\text{s}$ )	$\tau_f^{\text{calc } b}$ ( $\mu\text{s}$ )
13	2.04(30)	2.18(30)	2.12	2.27(40)	2.37
14	2.42(35)	2.56(35)	2.64	2.64(45)	2.94
15	3.05(40)	3.33(40)	3.24	3.54(50)	3.62

<sup>a</sup>Reference 2.

<sup>b</sup>Reference 6.

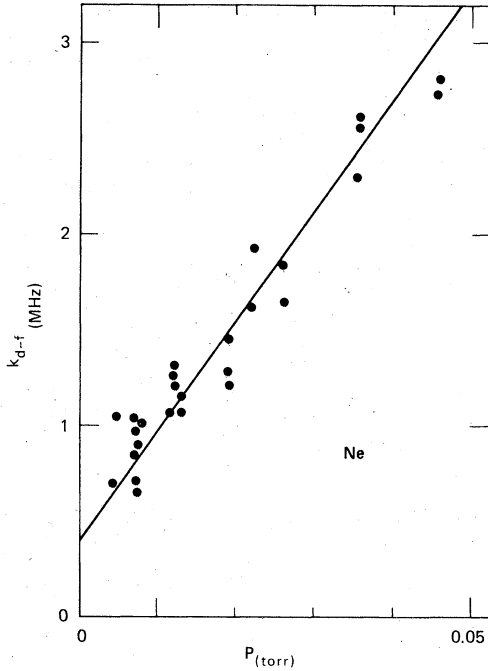


FIG. 2. Decay rate of the  $n=15$   $d-f$  mixture,  $k_{d-f}$ , vs Ne pressure.

the results were qualitatively the same as the results with the  $d$  states. When we added rare gas we observed a two-exponential decay in the time-resolved fluorescence. The initial fast component was pressure dependent and reflected the depopulation of the  $d-f$  mixture. The second slow component reflected the average radiative lifetime of all the  $l \geq 2$  states. From the pressure dependence of the initial fast decay, we can derive the  $\sigma_{d-f}$  cross sections. For example, the dependence of the fast decay rate of the  $n=15$   $d-f$  mixture on Ne pressure is shown in Fig. 2. The cross sections derived from the experiments are given in Table II.

From the data of Table II it is obvious that  $\sigma_f$  is not much, if any, larger than  $\sigma_d$ , for in that case  $\sigma_{d-f}$  would have to be much larger than  $\sigma_d$  for any reasonable model of the  $d-f$  mixture. The fact that  $\sigma_f$  is not much larger than  $\sigma_d$  implies first that the smaller energy gap does not lead to dramatically larger cross sections. This means that in the

TABLE II. Observed cross sections  $\sigma_{d-f}$  ( $10^3 \text{ \AA}^2$ ).

$n$	Ne	He	Ar
13	0.440(60)	1.36(20)	2.44(40)
14	0.354(50)	1.18(12)	2.23(40)
15	0.262(30)	1.07(15)	2.49(30)

TABLE III. Cross sections obtained for  $\sigma_d, \sigma_f$  ( $10^3 \text{ \AA}^2$ ).

$n$	Ne		He		Ar	
	$\sigma_d$	$\sigma_f$	$\sigma_d$	$\sigma_f$	$\sigma_d$	$\sigma_f$
13	0.350	0.500(80)	1.58	1.30(24)	3.94	1.50(40)
14	0.270	0.410(67)	1.46	1.08(16)	3.86	1.50(40)
15	0.210	0.298(40)	1.34	0.98(20)	3.80	1.92(45)

$l$  mixing of the  $d$  states the first step from  $d \rightarrow l'$ , where  $l'$  is some  $l$  value  $> 2$ , is not a rate-limiting step in the process.

To make a quantitative analysis of the data we must use our model of the  $d-f$  mixture. Let us first define the cross sections more explicitly.

$$\sigma_d: d \rightarrow l > 2,$$

$$\sigma_f: f \rightarrow d, l > 3,$$

$$\sigma_{d-f}: d, f \rightarrow l > 3, d', f'.$$

Here  $d'$  and  $f'$  are the parts of the  $d$  and  $f$  states not coupled by the microwave field, the  $d_{3/2}$  states and the  $f_{7/2}, |m_f| = \frac{7}{2}$  states. Next, let us assume that there are no  $\Delta l$  selection rules for the collision process, an assumption which is shown to be valid in Sec. III. Then we can express  $\sigma_{d-f}$  as

$$\sigma_{d-f} = \frac{1}{3}\sigma_d \left( \frac{n^2 - 15}{n^2 - 9} \right) + \frac{2}{3}\sigma_f \left( \frac{n^2 - 14}{n^2 - 11} \right). \quad (2)$$

The factors  $\frac{1}{3}$  and  $\frac{2}{3}$  reflect the proportions of  $d$  and  $f$  in the  $d-f$  mixture, and the factors in the parentheses reflect the fact that some of the final states for the  $\sigma_d$  and  $\sigma_f$  processes are removed in  $\sigma_{d-f}$  because the microwave field makes most  $d-f$  and  $f \rightarrow d$  collisional processes unobservable. Using Eq. (2) we may derive values for  $\sigma_f$  from the known values of  $\sigma_d$ .<sup>2</sup> Rather than use the  $\sigma_d$  values

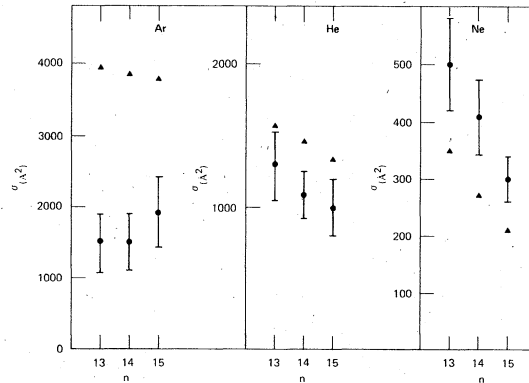


FIG. 3. Values of  $\sigma_d$  ( $\blacktriangle$ ) obtained by smoothing the data of Ref. 2 and the values of  $\sigma_f$  ( $\bullet$ ) obtained from these measurements.

of Ref. 2, we have drawn a smooth curve for  $\sigma_d$  vs  $n$  and used these smoothed values which are listed in Table III. The  $\sigma_f$  values thus obtained are given in Table III and plotted in Fig. 3. As shown in Fig. 3 all the  $f$  cross sections have the same  $n$  dependence as the  $d$  cross sections. Also note that for Ne  $\sigma_f$  is slightly larger than  $\sigma_d$ , and for He  $\sigma_f$  is slightly smaller than  $\sigma_d$ , but for Ar  $\sigma_f$  is a factor of 3 smaller than  $\sigma_d$ . Recall that for  $\sigma_d$  all the processes  $d \rightarrow l > 2$  have  $\Delta E \sim 1$  cm, whereas for  $\sigma_f$  all the processes  $f \rightarrow l > 3$  have  $\Delta E \sim 0.1$  cm $^{-1}$  and only  $f \rightarrow d_{3/2}$  has  $\Delta E \sim 1$  cm $^{-1}$ .

Intuitively we expect that the smaller  $\Delta E$  for  $\sigma_f$  would lead to a larger cross section than  $\sigma_d$ , and in fact for Ne  $\sigma_f$  is larger than  $\sigma_d$ . Why  $\sigma_f$  is smaller than  $\sigma_d$  for Ar and He is not yet understood.

### III. FINAL-STATE DISTRIBUTIONS

The basic aim of this experiment is to determine the  $\Delta l$  selection rules for the  $l$ -mixing process. In this experiment we populate the Na  $17d$  state, allow a single collision with Ar to occur, and analyze the final-state distribution using electric-field-ionization techniques.

The experimental method is a straightforward application of the field-ionization technique,<sup>7,8</sup> the details of which may be found elsewhere.<sup>9</sup> We excite the Na  $17d$  state in an atomic beam using pulsed dye lasers with 4-ns pulsewidths. A low pressure ( $\sim 10^{-4}$  torr) of Ar is added to the apparatus to induce the  $l$ -mixing collisions. The pressure is adjusted so that about 10% of the atoms in the  $17d$  state are removed by collisions, in order that we may observe the result of only a single collision. 4  $\mu$ s after the laser pulses we apply a pulsed electric field to ionize the excited atoms and collect all the ions formed. We sweep the amplitude of the ionizing pulse and measure the ion signal as a function of the amplitude of the pulse. Since each  $l, m$  state has a well-defined threshold field  $E_i$  at which it is field ionized,<sup>9</sup> the dependence of the ion signal on the amplitude of the ionizing pulse  $E$  gives us information about the final-state distribution after one collision.

This experiment rests on the premise that we do indeed have single-collision conditions. Under the conditions of the experiment, where 10% of the  $d$  state is collisionally depopulated, we would not have single-collision conditions if, for example, the process  $d \rightarrow f$  had a much smaller cross section than the process  $f \rightarrow l > 3$ . However, the experiment described in Sec. II shows that this is not the case for the  $f$  states, and it seems reasonable to assume that it is true for  $l > 3$  as well. So we are confident that we do indeed have single-collision conditions.

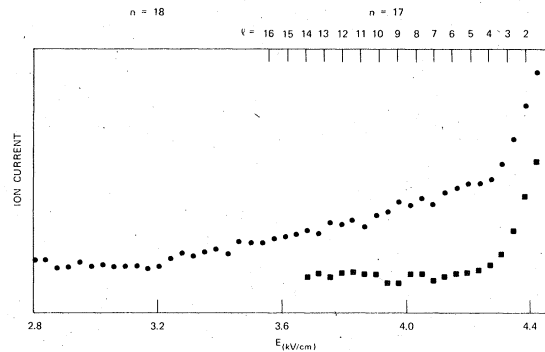


FIG. 4. Traces of ion current vs the amplitude of the field ionizing pulse when the Na  $17d$  state is excited in a vacuum, and under conditions of a single collision with Ar. At the top of the figure are indicated the ionization thresholds for the  $n=17$ ,  $l \geq 2$  states. The lower trace, taken with no added gas ( $\blacksquare$ ), shows the  $17d$  field ionization threshold at 4.36 kV/cm and current from direct photoionization at fields less than 4.36 kV/cm. The upper trace, taken with  $4 \times 10^{-5}$  torr of argon, shows the  $17d$  threshold at 4.36 kV/cm, a smoothly increasing signal from 3.50 to 4.36 kV/cm, and a constant signal below 3.50 kV/cm, due to direct photoionization. The smoothly increasing signal from 3.50 to 4.36 kV/cm indicates that all the  $n=17$ ,  $l > 2$  states are equally likely to be populated by the collision.

Typical data from these experiments are shown in Fig. 4. The locations of the lowest ( $|m|=0$ ) thresholds of the  $n=17$ ,  $l \geq 2$  states are indicated at the top of Fig. 4. As noted in Ref. 9, the  $|m|=1$  thresholds are 3% higher, the  $|m|=2$  thresholds are 19% higher, and states of  $|m| \geq 3$  require yet higher ionizing fields than those of the  $|m|=2$  states of the same  $l$ . Thus in Fig. 4, significant contributions from only  $|m|=0$  and 1 states are observed. While states of higher  $m$  are undoubtedly populated, we are unable to observe their ionization thresholds since they are masked by the much larger signal from ionization of the  $17d$  state. With no added Ar, we observed the lower trace of Fig. 4. The  $17d$  threshold at  $E = 4.36$  kV/cm is quite evident. At fields  $< 4.36$  kV/cm there is a constant, nonzero signal which is due not to field ionization but to laser photoionization of the  $17d$  state. The upper trace was taken with  $4 \times 10^{-5}$  torr of Ar in the system. The  $17d$  threshold at 4.36 kV/cm is still evident. From  $E = 3.50$  kV/cm to  $E = 4.36$  kV/cm there is a roughly linear increase in the ion signal which is due to the higher- $l$  states of the  $n=17$  manifold which are populated by collisions. Below  $E = 3.50$  kV/cm there is a constant photoionization signal. To interpret the signal we must recall that the ion signal is an integrated signal in the sense that the signal at field  $E_0$  represents the photoions plus the ions from

all the states which ionize at fields  $E \leq E_0$ . Thus, the roughly linear increase in signal from  $E = 3.50$  kV/cm to  $E = 4.36$  kV/cm represents a more or less flat population distribution over the higher- $l$  states for  $m = 0$  and 1.

Let us consider what Fig. 4 would look like if, for example, only the  $f$  and  $g$  states were populated by the first collision. In this case there would only be a photoionization signal for fields below 4.24 kV/cm, then two thresholds corresponding to the  $f$  and  $g$  states at 4.24 kV/cm and 4.30 kV/cm due to  $l$  mixing, and finally the  $d$ -state threshold at 4.36 kV/cm. Since we are unable to detect transitions to higher  $m$  states, we were unable to determine the  $\Delta m$  selection rules for the collision process. Two observations suggest that there are no  $\Delta m$  selection rules. First is the lack of  $\Delta l$  selection rules, implying no restriction to dipole processes. Second, in our previous cell experiments the observation of only two exponentials suggested that a statistical mixture of all the  $m$  states was found after, at most, a few collisions. In any event, the observation of no  $\Delta l$  selection rules supports our original interpretation of our data, and, more fundamentally, shows that the interaction responsible for the  $l$  mixing is short range.

#### IV. CONCLUSION

The microwave experiments described here have shown that reducing the energy gap  $\Delta E$  below  $1 \text{ cm}^{-1}$

by a factor of 10 does not dramatically increase the  $l$ -mixing cross sections, and in fact, even lowers the cross sections for the strongly interacting Ar. In addition, the field-ionization experiments show that there are no  $\Delta l$  selection rules for the process, confirming the suggestion that a short-range interaction of the target gas atom with the Rydberg electron is responsible for the  $l$  mixing. We hope to extend these investigations to heavier rare gases, Xe in particular, to see the effects of more strongly interacting collision partners. It will be particularly interesting to see if Xe exhibits an even larger discrepancy between  $\sigma_d$  and  $\sigma_f$  than Ar. We also plan to refine the field-ionization technique in several ways to improve the quality of the data. However, these initial experiments demonstrate the power of the technique, enabling us to explicitly determine the final-state distribution of the Na17d-Ar collision process, which we could not do by optical means.

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