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Collisional Angular Momentum Mixing in Rydberg States of Sodium*

T. F. Gallagher, S. A. Edelstein, and R. M. Hill
Stanford Research Institute, Menlo Park, California 94025

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Collisions with rare-gas atoms are observed to produce a lengthening of the lifetime of the highly excited ($n = 5$–10) d states of Na. The effect is interpreted as collisional angular momentum mixing of the d state with $l > 2$ states; thus the average lifetime of all states for which $l \geq 2$ is observed. The cross section for the process appears to increase as the geometrical cross section of the excited atom.

In a program to investigate the properties of highly excited or Rydberg atoms we first measured the radiative lifetimes of the Na s and d states for $n = 5$–13.[1] We have recently studied the effects of collisions of rare-gas atoms with sodium atoms in these high-lying s and d states. We chose to use the rare gases as collision partners to begin with since they are chemically inert, cannot absorb energy internally from the sodium atoms, and might be a good buffer gas for future experiments. In the experiments described here, when a rare gas was added to the sodium cell, we observed a lengthening of the fluorescent decay times of the nd levels of sodium. This effect is interpreted as a collisional mixing of the initially excited nd level with the higher angular momentum substates of the same n.

The experiment was done by a laser-fluorescence technique using the apparatus described in Ref. 1. The only change is the addition of a Baratron pressure gauge to measure the rare-gas pressure. An N_2 laser pumps two dye lasers which are tuned to the $3s \to 3p$ and $3p \to ns, nd$ transitions of sodium. The two laser beams are merged in a Pyrex cell containing Na vapor and the rare gas. We observe the time-resolved fluorescence, usually back to the $3p$ state, emitted as the population in the ns or nd state decays.

The behavior of the $8d$ state typifies the qualitative features of our observations with the excited Na d states. At argon pressures up to 1 mTorr, the $8d$ fluorescent decay time was not observed to be faster than the measured radiative or "vacuum" value, 502 nsec. In the 1–10-mTorr range, two easily distinguishable components were observed in the decay. The fast component was faster than the radiative decay rate, and the slow component was considerably slower than the radiative decay rate. As an example, the pressure dependence of the fast decay rate of the $10d$ state is shown in Fig. 1. At argon pressures from 10 mTorr to 1 Torr, the fast decay was too fast for us to observe; we only observed a single exponential with a pressure-independent decay time τ_{eff} considerably longer than the radiative decay time. Neon and helium showed similar behavior. The s states showed no rare-gas-pressure effects except for $n = 10$ which showed the onset of a longer decay at 1 Torr of argon.

These observations suggest that collisions with the rare-gas atoms transfer the sodium atoms in the excited d states into all the higher angular momentum states of the same n. Thus, the fast decay reflects the d-state population decaying at a rate equal to the sum of the collisional and radiative rates. The initial d-state population is then distributed over all the angular momentum states for which $l \geq 2$. Similarly, subsequent col-

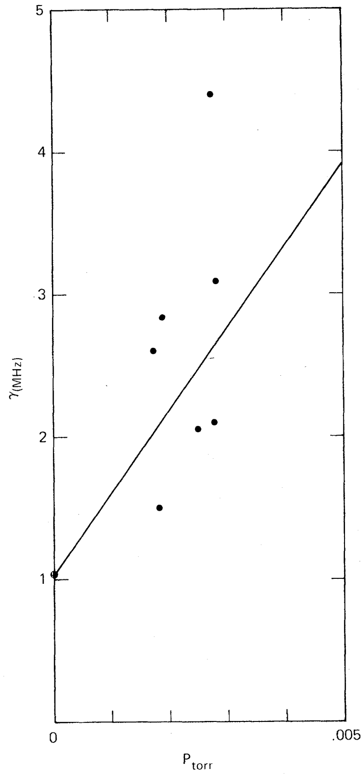

FIG. 1. Fast-decay rate γ of the 10d state versus argon pressure. The zero-pressure point is the 10d radiative decay rate. The scatter of the points is indicative of the accuracy of the measurements.

TABLE I. Radiative d-state lifetimes τ_d and the measured slow decay time $\tau_{\rm eff}$.

Sodium n state	τ_d[a] (μsec)	Argon $\tau_{\rm eff}$ (μsec)	Neon $\tau_{\rm eff}$ (μsec)	Helium $\tau_{\rm eff}$ (μsec)
5	0.120(14)	0.203(12)		
6	0.206(24)	0.391(24)	0.403(17)	0.441(77)
7	0.324(32)	0.796(58)		
8	0.502(39)	1.39(3)		
9	0.720(67)	2.54(17)	2.29(22)	
10	0.971(35)	3.68(27)	3.60(28)	3.74(21)

[a] See Ref. 1.

lisions of atoms in the higher l states repopulate the d state, allowing us to observe the nd-$3p$ fluorescence. Only the $l \geq 2$ states are involved, since they are energetically separated by much less than thermal energies, so that the $d \to l > 2$ collisions are essentially elastic. The s and p states have large quantum defects and are energetically far away from the d state of the same n. States of different n are also energetically far removed. Consequently an inelastic collision is required to transfer the sodium atom in a d state into an s or p state or any l state of different n. That these processes have much lower cross sections is supported by our observation that the radiative lifetimes of the s states up to $n=9$ show no pressure dependence due to collisions with the rare gases. The observation of a slight pressure dependence of the 10s decay time suggests that for higher n values n transitions may become important. At sufficiently high rare-gas pressures, the l-mixing time is short compared to the radiative lifetime of any of the l states. The angular momentum states are then in equilibrium with one another so that the slow, pressure-independent lifetime which we observe is the statistically averaged livetime of all the accessible angular momentum states. This lifetime $\tau_{\rm eff}$ is given explicitly by

$$\tau_{\rm eff}=\frac{1}{n^2-4}\left(\sum_{l=2}^{l=n-1}\frac{2l+1}{\tau_{nl}}\right)^{-1}, \tag{1}$$

where τ_{nl} is the radiative lifetime of the nl state. In Table I, we list the values of $\tau_{\rm eff}$ which we observed and the radiative lifetimes of the d states. It is interesting to compare the dependence of $\tau_{\rm eff}$ on n with the prediction of Bethe and Salpeter.[2] As they have pointed out, for hydrogen the average lifetime $\tau_{\rm av}$ of all the l states of a given n should increase approximately as $n^{4.5}$. Explicitly,

$$\tau_{\rm av}=\frac{1}{n^2}\left(\sum_{l=0}^{l=n-1}\frac{2l+1}{\tau_{nl}}\right)^{-1}. \tag{2}$$

Although the sodium d states are essentially hydrogenic, the s and p states definitely are not. In particular, the sodium s-, p-, and d-state theoretical radiative lifetimes are in the approximate ratio of 1:5:1.[3] Thus to compare our results with the $n^{4.5}$ relation of Bethe and Salpeter, we have assumed that the s, p, and d lifetimes are in the hydrogenic ratio of 15:1:3. Using this ratio and the measured d-state lifetimes listed in Table I, we derived s and p lifetimes which were combined with $\tau_{\rm eff}$ according to Eq. (2), yielding $\tau_{\rm av}$. Figure 2 is a plot of $\tau_{\rm av}$ obtained from the argon data versus n. A slope found from a linear least-squares fit implies that $\tau_{\rm av}$ varies as $n^{4.43(7)}$, in excellent agreement with the approximate relation of Bethe and Salpeter.

To determine the rates and cross sections for the collisional mixing, we have carried out an analysis in terms of the d state and a reservoir state R consisting of all angular momentum states

TABLE II. Observed rate constants k and cross sections σ for collisional mixing as well as geometrical cross sections $\pi n^4 a_0^2$. The rate constants are in units of 10^{-8} cm^{-3} sec^{-1} and the cross sections are in Å^2.

Sodium	Argon		Helium		Neon		
n state	k	σ	k	σ	k	σ	$\pi n^4 a_0^2$
5	0.23(9)	290					551
6	0.41(14)	510	0.70(48)	420	0.53(13)	540	1143
7	1.20(29)	1500					2118
8	2.0(8)	2500					3614
9	1.9(9)	2400			0.93(40)	1010	5789
10	3.0(15)	3700	3.7(13)	2200	2.9(13)	3080	8824

for which $l > 2$. Both have radiative decay rates which are easily determined from the vacuum and high-rare-gas-pressure limits. With the assumption that the collision-rate constants for the processes $d \rightarrow R$ and $R \rightarrow d$ are inversely proportional to the degeneracies of d and R, it can be shown that the time dependences of the populations of the d and R states are given, respectively, by the sum and difference of two decaying exponential functions. When the data from the pressure regime exhibiting two exponential decays are fitted by this model, we find the collision-rate constants $k_{d \rightarrow R}$ given in Table II. The rates are also expressed in terms of cross sections σ using $k_{d \rightarrow R} = \sigma v$, where $v = (8kT/\pi\mu)^{1/2}$. The quantity μ is the reduced mass of the collision partners, k is the Boltzmann constant, and the typical cell temperature is 430°K. In addition, values of

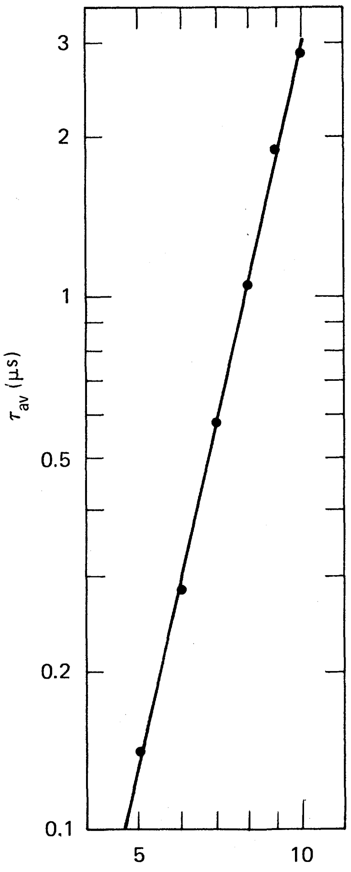

FIG. 2. Plot of τ_{av}, the average radiative lifetime for all l of given n, versus n. The data were obtained with argon in the sodium cell. The straight line is the least-squares fit yielding a slope of 4.43(7).

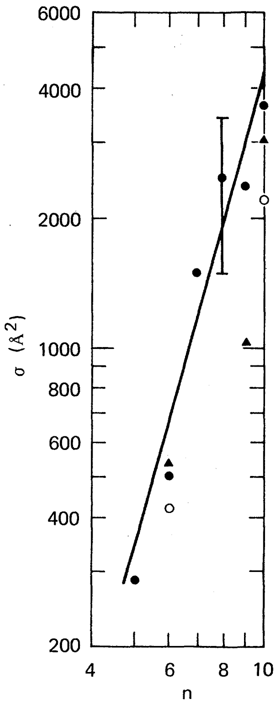

FIG. 3. Plot of σ, the collisional mixing cross section, versus n for Ar (●), Ne (▲), and He (○). For clarity, the error bars are drawn on only one typical point. The straight line is a least-squares fit to the argon points of slope 3.8(5).

$\pi n^4 a_0^2$, the geometrical cross section of an excited atom, are given. In Fig. 3 the experimental cross sections are plotted versus n. Fitting the argon points by a straight line implies that σ is proportional to $n^{3.8(5)}$.

The interaction responsible for the angular momentum mixing is probably the interaction of the sodium valence electron with the strong short-range potential of the rare-gas atom while it is within the region of the valence-electron wave function. This interaction is orders of magnitude stronger than the energy differences between the sodium $l \geqslant 2$ states, and as a result these l states are completely mixed by the presence of the rare-gas atom. Furthermore, since the interaction is so strong, it is insensitive to minor differences in the potentials of the rare-gas atoms. Consequently the cross sections for collisional angular momentum mixing should simply reflect the geometrical cross section of the excited sodium atoms for any atomic or nonpolar-molecular collision partner. This hypothesis is in agreement with our observations in that the observed cross section does increase as n^4 as does the geometrical cross section of the excited sodium atom and seems to be independent of the rare gas in spite of the fact that the polarizabilities of argon and neon differ by a factor of 5.

Here we have directed our attention mainly to collisions in which l but not n is changed. The fact that the effective decay times τ_{eff} were not noticeably changed by pressures of up to 1 Torr suggests that the radiationless quenching cross sections are < 1 Å^2.

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Infrared–X-Ray Double-Resonance Study of $2P_{3/2}$-$2S_{1/2}$ Splitting in Hydrogenic Fluorine

H. W. Kugel
Rutgers, The State University,[*] *New Brunswick, New Jersey 07102*

and

M. Leventhal, D. E. Murnick,[†] C. K. N. Patel, and O. R. Wood, II
Bell Telephone Laboratories, Murray Hill, New Jersey 07974, and Bell Telephone Laboratories,
Holmdel, New Jersey 07733

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Hydrogenic fluorine atoms in the $2S_{1/2}$ metastable state were produced at 64 MeV by use of a tandem electrostatic accelerator and suitable combinations of stripper and adder carbon foils. A pulsed HBr laser centered at 2382.52 cm^{-1} was Doppler-shift tuned through the $2S_{1/2}$-$2P_{3/2}$ energy separation to yield a resonance in Lyman-α x rays at 826 eV. This technique yields a value for the Lamb-shift splitting ($2S_{1/2}$-$2P_{1/2}$) equal to 3339 ± 35 GHz which is presently in agreement with several quantum electrodynamic calculations.

We have observed Lyman-α radiation at 826 eV induced via resonant absorption of infrared radiation (2328.52 cm^{-1}) produced by a pulsed HBr laser incident upon a high-energy beam of $^{19}\text{F}^{8+}$ in the metastable $2S_{1/2}$ state. The fixed-frequency laser was tuned through the $2S_{1/2}$-$2P_{3/2}$ resonance ($\Delta E - \mathcal{S}$, where ΔE is the fine-structure splitting and $\mathcal{S}$ the Lamb shift) by use of the Doppler shift in the frame of the particle beam ($v/c = 0.085$). This measurement for the splitting $\Delta E - \mathcal{S}$ can be used to obtain a value for the Lamb shift ($2S_{1/2}$-$2P_{1/2}$) of 3339 ± 35 GHz which can be compared with quantum electrodynamic (QED) calculations[1-3] in a strong Coulomb field. The error quoted represents 1 standard deviation; possible systematic effects are still under investigation. As this new technique is refined, an order-of-magnitude improvement in precision is