

Collision-Induced Mixing in the First Excited States of Sodium and Potassium*

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The cross sections for the collision-induced transfer of excitation from the ${}^2P_{3/2}$ level to the ${}^2P_{1/2}$ level of the first excited states of the alkali atoms have been measured for several alkali-noble gas systems. The cross sections were determined with a conventional resonance fluorescence technique in which the radiation from a spectral source was absorbed and re-emitted by an alkali vapor at low pressure ($\sim 10^{-6}$ Torr), and the scattered light analyzed with a scanning spectrometer. Provision was made for the introduction of various noble gases at controlled pressures into the alkali vapor. The determined cross sections are (in units of 10^{-16} cm 2): Na-He, 41.1 ± 2.9 ; Na-Ne, 36.1 ± 2.5 ; Na-Ar, 64.6 ± 5.2 ; Na-Kr, 68.2 ± 5.5 ; Na-Xe, 61.8 ± 4.9 ; K-He, 52.8 ± 5.8 ; K-Ne, 14.0 ± 1.2 ; K-Ar, 34.0 ± 3.1 . The quoted errors are estimated 70% confidence intervals. The measurements are compared with other experimental results and with various estimated cross sections.

I. INTRODUCTION

MANY important modern experiments exploit the resonance fluorescence process, which is the absorption and subsequent re-emission of a photon whose energy is equal to or very close to that of an excited state of a fluorescing system. For the case of an isolated atom, the absorbed and re-emitted radiation have exactly the same energy. If, however, the atom is perturbed by some collision while it is in the excited state, a nonradiative transition to another excited state can occur, followed by radiation to the ground state of a photon of different energy. The radiant energy lost or gained will be balanced by a change in the kinetic energy of the collision partners; the transfer of excitation from one atomic state to another is termed *collision-induced mixing*.

Collision-induced mixing between the fine structure states of the alkalis is particularly feasible for study. The first excited states of these atoms are 2P levels which exhibit a fine structure splitting small compared with the excitation energy and with the separations from other excited states. In addition, the experimental situation is favorable because the resonance radiation is in the visible region, and the physical properties of most of the alkalis simplify the construction of the requisite lamps and absorption cells.

Collision-induced mixing, caused by collisions between alkali atoms and foreign gas atoms, was first observed in the early experiments of Wood and Mohler.¹ In these experiments it was observed that the ratio of the sodium D lines² emitted in a resonance fluorescence

cell changed when a few tenths of a Torr of hydrogen were introduced into the cell. Lochte-Holtgreven³ performed a series of experiments in which he measured the change in the ratio of the sodium D lines as a function of buffer gas pressure, using argon, nitrogen, hydrogen, and a helium-neon mixture as buffer gases. Collision-induced mixing has also been observed in the resonance fluorescence of mercury in mercury-nitrogen systems.⁴ Recently, Chapman and Krause have reported their careful measurements of collision-induced mixing in the potassium-argon system.⁵

Estimates of collision-induced mixing cross sections have been made by Bender⁶ and by Jordan⁷ and these results are compared with the present experimental data in Sec. IV. One of the most important features of the mixing process is that the leading term in the relevant interaction falls off as the inverse sixth power of the interatomic separation. This steep dependence makes the estimated cross sections relatively insensitive to uncertainties in the interaction constants and wave functions, and thus a meaningful comparison between the theoretical estimates and the experimental values is possible.

Collision-induced mixing processes are of considerable interest to the analysis of optical pumping experiments,⁸ since these experiments are usually performed in the presence of a noble gas. In the parlance of optical pumping, the condition which obtains if there are no collisions, and hence there is no transfer of excitation,

e.g., the $4{}^2P_{1/2}$ to $4{}^2S_{1/2}$ transition in potassium is the potassium D_1 line. In this paper, the term " D -line ratio" always refers to the ratio of the intensity of the D_2 line to that of the D_1 line.

³ W. Lochte-Holtgreven, *Z. Physik* **47**, 363 (1928). This paper does not report an actual cross section which can be compared with the results of other work. However, enough of the experimental data was reported so that we were able to derive the cross section we list in Table I, and used for discussion in Sec. IV. Our derived value is in agreement with the derived value quoted by W. Franzen and A. G. Emslie, *Phys. Rev.* **108**, 1453 (1957).

⁴ E. Gaviola, *Phys. Rev.* **34**, 1373 (1929).

⁵ G. D. Chapman and L. Krause, *Can. J. Phys.* **43**, 563 (1965).

⁶ P. Bender, Ph.D. thesis, Princeton University, 1956 (unpublished).

⁷ J. A. Jordan, Jr., Ph.D. thesis, University of Michigan, 1964 (unpublished).

⁸ H. G. Dehmelt, *Phys. Rev.* **105**, 1487 (1957).

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¹ R. W. Wood and F. L. Mohler, *Phys. Rev.* **11**, 70 (1918).

² The D lines are the resonance lines of sodium which connect the $3{}^2P_{3/2}$ level and the $3{}^2P_{1/2}$ level to the $3{}^2S_{1/2}$ ground state. The two components are designated D_2 and D_1 , respectively. This nomenclature is also used to designate the transitions from the first excited states to the ground state in the other alkalis;

is one of *no mixing*. If, however, there are so many collisions during the excited-state lifetime that the magnetic sublevels of the excited state are populated in the ratio predicted by Boltzmann statistics, one has the condition referred to as *complete mixing*. In the context of optical pumping, the transfer of excitation which is of interest is that between the hyperfine-structure magnetic sublevels.⁸ We restrict our considerations to the simpler problem of transfer of excitation between fine-structure magnetic sublevels. Complete mixing of the hyperfine sublevels in the atoms considered certainly implies complete mixing of the fine-structure sublevels, although the converse is not necessarily true. Thus the cross sections found here represent maximum cross sections for the hyperfine-structure mixing. Usually in the analysis of optical pumping experiments it has been assumed that the buffer gas concentration is sufficiently high as to ensure complete mixing. The present work serves in part as a test for this assumption, with the interesting result that higher buffer gas pressures than those previously estimated are required for a large degree of mixing.

II. THE RATE EQUATIONS

In the present experiments the intensities of the two D lines were monitored as a function of buffer gas pressure. The ratio of these intensities is equal to the ratio of the populations of the two levels, since the radiative lifetimes are identical.⁹ The relative populations are, in turn, affected by the introduction of a buffer gas. The relevant rate equations which govern the kinetics of this process are

$$dn_2/dt = I_2\sigma_2N_s - n_2\gamma + 2K\sigma n_1n_A v - \sigma n_2n_A v, \quad (1a)$$

$$dn_1/dt = I_1\sigma_1N_s - n_1\gamma + \sigma n_2n_A v - 2K\sigma n_1n_A v. \quad (1b)$$

The number densities of alkali atoms in the ${}^2P_{3/2}$ and the ${}^2P_{1/2}$ levels are denoted by n_2 and n_1 , respectively. The first terms in Eqs. (1) describe the excitation of ground-state alkali atoms, with number density N_s , into the excited states. I_2 and I_1 are the intensities of the incident D lines, and σ_2 and σ_1 are the absorption cross sections for the two lines. (Consideration of statistical weights show that $\sigma_2 = 2\sigma_1$.) The second terms describe the radiative decay from the two excited states where γ is the transition rate for spontaneous decay. The atoms which enter and leave the excited states because of mixing collisions are described by the third and fourth terms respectively. In these terms, n_A is the number density of the buffer gas atoms and v is the relative velocity of the collision pair. σ is the cross section for a mixing transition from any of the ${}^2P_{3/2}$ magnetic sublevels to either of the ${}^2P_{1/2}$ magnetic sublevels. The cross section for a mixing transition from

either of the ${}^2P_{1/2}$ sublevels to any of the four ${}^2P_{3/2}$ sublevels is $2K\sigma$, where K is the Boltzmann factor.¹⁰

Equations (1) can be solved for the steady-state solution $dn_1/dt = dn_2/dt = 0$, and yield for the population ratio n_2/n_1 the following expression:

$$\frac{n_2}{n_1} = \frac{R\gamma + (R+1)(2K\sigma n_A v)}{\gamma + (R+1)(\sigma n_A v)}. \quad (2)$$

Here R is the excitation ratio $I_2\sigma_2/I_1\sigma_1$.

Equation (2) permits the determination of the collision-induced mixing cross section σ from measurements of n_2/n_1 as a function of buffer gas pressure. If there is no buffer gas, the emitted ratio is equal to that absorbed. As the buffer gas pressure is increased, the emitted ratio tends monotonically to the ratio $2K$, predicted by Boltzmann statistics.

Inherent in the derivation and proper use of Eq. (2) are several assumptions:

(1) The cross sections for mixing out of the $m_J = \pm\frac{3}{2}$ sublevels and out of the $m_J = \pm\frac{1}{2}$ sublevels of the ${}^2P_{3/2}$ level are assumed to be the same, which assumption has no *a priori* validity. However, theoretical arguments⁷ indicate that the two cross sections are probably equal to within 10%. Furthermore, the experimental data were as well fitted by the one cross section as they were by a set of rate equations which explicitly took into account this small difference.

(2) The value of the excitation ratio R is assumed to be independent of the buffer gas pressure.

(3) Quenching collisions are ignored, which is equivalent to assuming that the spontaneous decay transition rate γ is independent of pressure.

(4) Only alkali-noble gas collisions are assumed to contribute to the mixing process.¹¹

(5) It is assumed that the alkali vapor pressure is low enough so that multiple scattering will not affect the observed ratio of the D lines.

The appropriateness of these assumptions is reviewed in Secs. III and IV, and a more detailed discussion is available in Ref. 7.

¹⁰ In other words, if there were no fine-structure splitting, $\sigma/2$ would be the cross section for any transition from *one* magnetic sublevel to another. In such a case, the cross section for a transition from a certain ${}^2P_{3/2}$ sublevel to the two ${}^2P_{1/2}$ sublevels would be σ , but that for a transition from a certain ${}^2P_{1/2}$ sublevel to the four ${}^2P_{3/2}$ sublevels would be 2σ . In actuality, the fine-structure splitting exists and the latter cross section must be reduced by the Boltzmann factor $e^{-\hbar\omega/kT}$, where $\hbar\omega$ is the energy of the splitting, k is the Boltzmann constant, and T the absolute temperature.

¹¹ Mixing collisions can also occur, of course, between excited alkali atoms and ground-state alkali atoms. Earlier work on this problem [see, e.g., R. Seiwert, *Ann. Physik* **13**, 54 (1956)] indicated that these cross sections were on the order of 2×10^{-14} cm², and thus the effects would be negligible. More recently, however, Chapman, Krause, and Brockman, *Can. J. Phys.* **42**, 535 (1964), have measured the cross section for potassium-potassium collisions and find it to be 6.6×10^{-12} cm². For the present experiments, even this large a potassium-potassium interaction would induce somewhat less than 1% of the observed mixing.

⁹ G. Stephenson, *Proc. Phys. Soc. (London)* **A64**, 458 (1951).

III. THE EXPERIMENTS

The mixing cross sections were determined for five sodium-noble gas systems, and for three potassium-noble gas systems. The apparatus is schematically indicated in Fig. 1. The spectral sources were Osram lamps excited by 1.1 A at 60 cps. After considerable aging, the sodium lamp was found to yield a ratio $R = I_{2\sigma_2}/I_{1\sigma_1}$ of the D lines absorbed in the cell of about 1.35, and the potassium lamp yielded a ratio which was somewhat less than 1.0. An attempt was made in the sodium experiments to further suppress the D_2 line by using an interference filter. Although it was possible to obtain a ratio of 0.16, this could be achieved only by suppressing the D_1 line by a factor of 100. The resultant signal-to-noise ratio was intolerable. In potassium, where the doublet separation is 34 Å, it is more feasible to use interference filters, and a ratio R of 20 could easily be obtained. The ratio of the emitted D lines was found to be dependent upon the current through the lamp and care was taken to ensure that the current remained constant throughout the experiments.¹²

The resonance fluorescence cells were of a classical Cario-Lochte-Holtgreven design,¹³ 3.5 cm in diameter and 10 cm long. The incident light was focused 1 cm behind the entrance window and about 1 cm from the side of the cell which was used as the exit window. The cells were prepared using Baker reagent grade alkali metal which had been doubly distilled before the final deposition of a thin layer onto the back of the vessels. Efforts were made to ensure that no alkali metal was deposited toward the front, and the cells were inspected periodically during the experiments to ensure that no deposits were developed on the entrance or exit windows. The cell was placed in an oven capable of maintaining a temperature constant to within $\pm 1^\circ\text{C}$.

The gas handling system could maintain a vacuum of 5×10^{-6} Torr. The buffer gas pressure was varied by leaking Linde MSC noble gases into the system and by subsequent partial evacuation. A McLeod gauge was used to measure pressures in the range from 10^{-2} to 15 Torr; for pressures above 15 Torr, a manometer was employed.

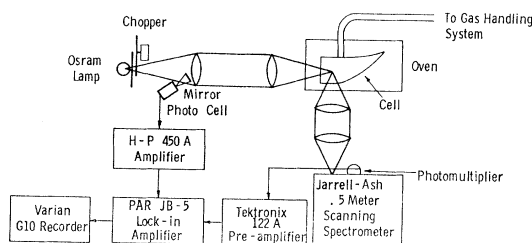


Fig. 1. Schematic diagram of the apparatus.

¹² Details of the dependence of R upon the lamp excitation current, as well as the dependence of line shape on current, may be found in Ref. 7.

¹³ A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1961).

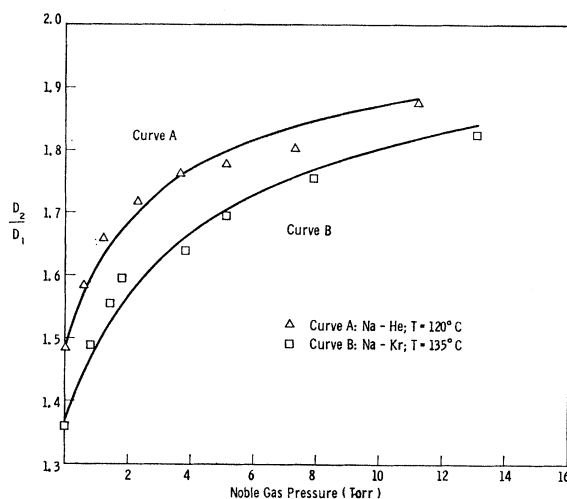


Fig. 2. Representative reduced data for the sodium-helium and sodium-krypton systems. The solid lines were generated from Eq. (2), in which the excitation ratio R for each system was fixed by the zero-pressure data. The mixing cross section was then varied to obtain the best fit.

The light scattered by the alkali vapor at 90° was focused on the slits of a Jarrell-Ash 0.5-m scanning spectrometer. For the sodium experiments, a 931-A photomultiplier was used as a detector, and a liquid-nitrogen-cooled Dumont K2276 photomultiplier was used in the potassium work. The electronic apparatus was traditional⁷ and the linearity was verified to within 2%.

The sodium data were taken by setting the slits of the spectrometer so that the D lines were comfortably resolved. It was found that a one-second response time of the electronics was needed to develop a signal-to-noise ratio greater than 20; this response permitted the spectrum to be scanned at 5 Å/min. The experimental procedure was to admit some 10 to 30 Torr of noble gas into the resonance fluorescence cell, and obtain ten scans of the spectrum at that pressure. After a small amount of the noble gas was pumped out, the scanning procedure was repeated in order to achieve another datum point. It was found to be most convenient to proceed from higher to lower pressures in the course of a run. However, some points were occasionally taken by increasing the noble-gas pressure in order to verify that there was no systematic effect associated with the direction of the pressure change. During any given run, care was taken to ensure that the sum of the intensities of the D lines was constant from scan to scan within 10%. This was done to verify that there were no major variations of alkali vapor pressure. The total lamp intensity was also monitored and the variations were found to be less than 5%.

The ratio of the scattered intensities of the two components is the same as the ratio of the areas under the spectral curves generated in each scan. It was found in practice that the ratio of these areas was the same

as the ratio of the peak intensities, which fact greatly diminished the tedium of data reduction. Two examples of sodium runs are exhibited in Fig. 2, in which a least-squares-fit to Eq. (2) is also shown. It is to be emphasized that each fit has been achieved by varying the mixing cross section only, since the other parameters of Eq. (2) are fixed by the experimental conditions.

A similar experimental procedure was attempted for the potassium systems, but severe signal-to-noise problems were encountered. The potassium experiments required the use of a photomultiplier with an S-1 photocathode, which is inherently less sensitive and more noisy than the S-4 photocathode appropriate to the sodium work. Although the photomultiplier was cooled to liquid-nitrogen temperatures, the signal-to-noise ratio was so poor that the techniques of the sodium experiment had to be modified. Fortunately, the potassium fine structure separation of 34 Å is sufficiently large that the entrance and exit slits of the spectrometer could be opened to 400 and 1000 μ, respectively, and the two lines could still be completely resolved. The resultant trace for each component was a trapezoid, since the bandpass of the spectrometer was now much greater than the width of the spectral lines and the exit slit was larger than the entrance slit. Data could be taken by alternately sitting on the top of each trapezoid for several minutes. It was possible to locate these positions consistently because the very wide slits minimized the effects of backlash in the scanning mechanism. The time constant of the electronics was 15 sec; thus the values of the intensity taken 15 sec apart were relatively uncorrelated. Thirty to fifty values were used to determine the intensity of the lines at each pressure. Reduced data for some of the potas-

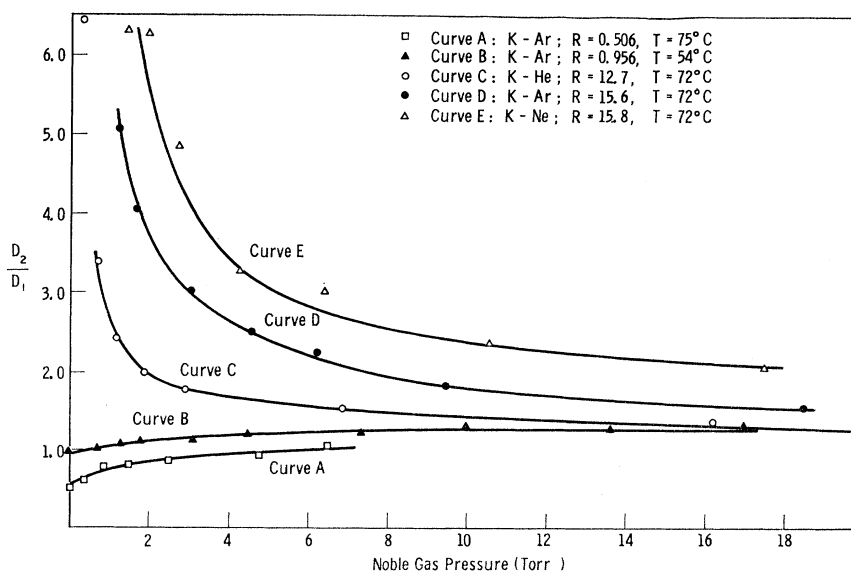
sium runs are shown in Fig. 3. (In principle, this same experimental technique could have been used in the acquisition of the sodium data. However, the smaller fine structure makes the resolution requirements so much more severe that it would have been virtually impossible to find the tops of the trapezoids repeatedly with our spectrometer.)

Care was taken to ensure that the experimental conditions were such that Eq. (2) did indeed apply. An extensive examination of line-shape effects in potassium resonance fluorescence⁷ indicated that pressure broadening and pressure shifts would be negligible in the pressure regime of these experiments. Our findings are further substantiated by Jarrett's investigations¹⁴ of sodium resonance fluorescence.

The presence of multiple scattering in these experiments would mar the integrity of the data. In order to eliminate the multiple scattering problem, the *D*-line ratio was first studied as a function of temperature at some fixed pressure. As the temperature was lowered, the *D*-line ratio rose to some asymptotic limit. (That this was always a rising approach simply reflects the fact that the absorption cross section is larger for *D*₂ than for *D*₁ radiation.) The actual experiments were performed at temperatures for which the *D*-line ratio was very nearly at its asymptotic value. These temperatures ranged from 120 to 140°C for the sodium experiments and 50 to 75°C in the potassium work. It is estimated that at these temperatures the mean free path of a photon in the vapor was in excess of 10 cm, whereas the distance from the entrance and exit windows to the observed sample was on the order of 1 cm.

The alkali vapor pressures implied by the tempera-

FIG. 3. Representative reduced data for the potassium-helium, potassium-neon, and potassium-argon systems. The solid lines were generated from Eq. (2), in which the excitation ratio *R* for each system was fixed by the zero-pressure data. The mixing cross section was then varied to obtain the best fit.



¹⁴S. M. Jarrett, Ph.D. thesis, University of Michigan, 1962 (unpublished).

TABLE I. Comparison of experimentally derived and calculated noble gas induced mixing cross sections for the transition from any ${}^2P_{3/2}$ magnetic sublevel to the ${}^2P_{1/2}$ set, in the first excited states of sodium and potassium. Units are 10^{-16} cm 2 .

Collision partners	Experimental cross sections		Calculated cross sections ^a
	Previous work	Present work	
Na-He		41.1±2.9	35.2± 8.4
Na-Ne		36.1±2.5	46.0±11.0
Na-Ar	60.0±15.0 ^b	64.6±5.2	69.9±16.8
Na-Kr		68.2±5.5	74.0±17.8
Na-Xe		61.8±4.9	82.6±19.8
K-He		52.8±5.8	36.2± 9.0
K-Ne		14.0±1.2	40.5±10.0
K-Ar	42.0±1.0 ^c	34.0±3.1	91.0±40.0

^a J. A. Jordan, Jr., Ph.D. thesis, University of Michigan, 1964 (unpublished). The large uncertainty in the K-Ar value is a consequence of the breakdown of the classical path approximation.

^b Derived by the authors from the data given by W. Lochte-Holtgreven, *Z. Physik* **47**, 363 (1928).

^c G. D. Chapman and L. Krause, *Can. J. Phys.* **43**, 563 (1965). This value is appropriate to the pressure region 0.3 to 2.5 Torr.

tures used in these experiments are on the order of 10^{-6} Torr. The noble-gas pressures used were on the order of several Torr. Thus, even though the alkali-alkali mixing cross section is reported¹¹ to be larger than the alkali-noble gas cross section by a factor of 10^3 , the observed mixing was predominantly induced by the noble gas.

A few examples of the reduced data are shown in Figs. 2 and 3 of the present paper, which have been abstracted from the complete presentation of Ref. 7. The cross sections which have been derived from these data by the application of Eq. (2) are tabulated in Table I, and the quoted uncertainties are the estimated 70% confidence intervals. It is estimated that the McLeod gauge could be read accurately to within 5%.¹⁵ The lifetime of the sodium excited state is known to about 3%; that of potassium to about 4%. The statistical uncertainty of the least squares fit of the data points to the cross section ranged from 8% in the K-He system to 3% in the Na-He and Na-Ne systems. Other uncertainties such as those introduced by temperature variations, and those introduced by contamination effects, are estimated to be no larger than 1%.

IV. DISCUSSION OF RESULTS

The experimental cross sections of the present work, the results of the previous experiments by Lochte-Holtgreven³ and by Chapman and Krause,⁵ and the cross sections calculated by Jordan⁷ are listed for comparison in Table I. The sodium-argon cross-section

¹⁵ After the work reported here was completed, we learned of the work of K. Nakayama and H. Ishii, *Transactions of the Eighth National Vacuum Symposium* (Pergamon Press, Inc., New York, 1962), Vol. I, p. 519. This is a study of errors in McLeod gauge readings due to the streaming of mercury vapor toward cold traps in the vacuum system. The resultant pressure corrections can be quite large for pressures on the order of 10^{-3} Torr. [See, e.g., B. L. Schram *et al.*, *Physica* **31**, 94 (1965).] The lowest pressures used in our work were on the order of 0.5 Torr, which pressure is well above that region in which mercury streaming would have a significant effect.

of the present experiment is in good agreement with that we derived from the data published by Lochte-Holtgreven.³ Our potassium-argon result is also in reasonable agreement with that quoted by Chapman and Krause⁵ for the pressure range 0.3 to 2.5 Torr.¹⁶

We have a nagging reluctance to accept the potassium-neon cross section we report here. Only one run was taken in this system and, although it is highly self-consistent, the cross section implied by the data is exceedingly small. Even though theoretical reasons can be advanced to account for a somewhat smaller cross section than estimated by Jordan,⁷ we find it very hard to reconcile the almost minute experimental value with our present understanding of the mixing process.^{16a}

The agreements between the experimental and theoretical cross sections for the sodium systems (Table I) are quite satisfying. In addition, Bender's calculations⁶ yield a cross section for the sodium-argon system of 85×10^{-16} cm 2 which is reasonably consistent with the experimental value. It is interesting to note that even though the mixing collision involves very complicated processes, the interaction falls off at least as fast as the inverse sixth power of the interatomic distance. It is this very steep dependence which permits a relatively accurate evaluation of the cross sections despite the poverty of quantitative information about the interaction.

The compatibility of theory and experiment in the potassium systems is not as satisfactory as the comparison for the sodium work. As discussed above, we have some *a priori* question about the validity of our potassium-neon experimental value, but we view the two other potassium cross sections with as much confidence as we hold in the sodium work. It should be noted that the potassium calculations⁷ are inherently more vulnerable to criticism than the sodium estimates owing to the increased tendency of the potassium systems to violate the classical path approximation. In addition, the larger fine structure of potassium makes a proper description of the kinetics of the process more difficult.

Moskowitz and Thorson¹⁷ have also analyzed the mixing process. However, they believe that their numerical results are not too meaningful because of

¹⁶ Chapman and Krause actually report cross sections for three pressure ranges. $(72 \pm 5) \times 10^{-16}$ cm 2 pertains to the low-pressure region (0–0.06 Torr); $(42 \pm 1) \times 10^{-16}$ cm 2 is appropriate to the intermediate-pressure region (0.3–2.5 Torr); and $(11 \pm 0.2) \times 10^{-16}$ cm 2 is listed for the high-pressure region (50–160 Torr). Our cross section is derived from data taken in the pressure region 0.5 to 20 Torr and thus is comparable most directly with the cross section found in Chapman and Krause's intermediate-pressure regime.

^{16a} Footnote added in proof. Since the completion of our work, we have learned that Chapman *et al.* have also observed a very small experimental value for the potassium-neon cross section. [G. D. Chapman *et al.*, *Proceedings of the IVth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters Inc., Hastings-on-Hudson, New York, 1965), p. 55.]

¹⁷ J. W. Moskowitz and W. R. Thorson, *J. Chem. Phys.* **38**, 1848 (1963).

TABLE II. Noble gas pressures needed to ensure various degrees of mixing. The degree of mixing is defined as the fraction of the high-pressure limit of the D_2/D_1 ratio observed at a given buffer gas pressure, and under conditions of pure D_1 excitation.

Collision partners	Noble gas pressures (in Torr) needed to ensure 65, 80, and 95% mixing		
	65%	80%	95%
Na-He	7	16	75
Na-Ne	15	32	152
Na-Ar	10	21	99
Na-Kr	10	23	107
Na-Xe	12	26	125
K-He	4	8	32
K-Ne	24	51	215
K-Ar	12	26	108

their particular need for accurate wave functions of the alkali-noble gas quasimolecule.¹⁸

The present data can be used to predict an upper

¹⁸ W. R. Thorson (private communication).

limit to the degree of mixing between hyperfine structure magnetic sublevels in those optical pumping experiments⁸ in which an alkali vapor is exposed to resonance radiation while immersed in a noble gas. We elect to define the "degree of mixing" as the fraction of the high-pressure limit of the D_2/D_1 ratio observed at a given buffer gas pressure, and under conditions of pure D_1 excitation. The high-pressure limit is just twice the Boltzmann factor and appears as $2K$ in Eq. (2). Table II lists the buffer gas pressure required for various degrees of mixing. The fact that relatively high pressures are required to achieve 95% mixing simply reflects the algebraic rather than exponential nature of Eq. (2).

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Intensity-Correlation Spectroscopy*

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A survey is given of techniques for spectroscopic analysis using intensity fluctuations. Particular attention is given to counting times, the role of macroscopic sources and detectors, and the electronic constraints placed on the observations.

I. INTRODUCTION

VARIOUS techniques have been suggested in the past few years for applying the study of intensity fluctuations to spectroscopic analysis. An excellent review of these has been given by Wolf and by Glauber.¹ We have recently provided a quantum-mechanical description² of intensity correlations in connection with

a method for measuring the phase of a scattering amplitude in x-ray scattering. We shall here apply this quantum-mechanical analysis to several of the proposed spectroscopic techniques. We have in mind particularly the observation of the shape and width of a single spectral line. Although the relevant machinery was completely discussed in Ref. 2, we shall utilize some notational simplifications which have been developed in some later work.^{3,4}

We shall consider measurements of intensity fluctuations and time correlations in detectors at separate space points. The classical theory of these is described

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¹ E. Wolf, Proceedings of the I.C.O. Conference on Photographic and Spectroscopic Optics, Tokyo, Japan, 1964, J. Appl. Phys. (Japan) (to be published); R. J. Glauber, in *Quantum Optics and Electronics*, edited by C. DeWitt *et al.* (Gordon and Breach Science Publishers, Inc., New York, 1965).

² M. L. Goldberger, H. W. Lewis, and K. M. Watson, Phys. Rev. **132**, 2764 (1963). This paper will be referred to as I.

³ M. L. Goldberger and K. M. Watson, Phys. Rev. **137**, B1396 (1965). This paper will be referred to as II.

⁴ M. L. Goldberger and K. M. Watson, Phys. Rev. **140**, B500 (1965). This paper will be referred to as III.