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Fine-Structure Mixing Within the Zn(43PJ) Multiplet by Collisions with the Noble Gases

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Fine-structure mixing within the Zn(4 ^3P_J) multiplet by collisions with the noble gases

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Measurements of rate coefficients for intramultiplet state transfer of Zn($4\,^3P_1 \rightarrow 4\,^3P_{J'}$) by collisions with the rare gases are presented. The state-to-state binary rate coefficients are derived from least-squares fittings of the time-resolved triexponential behavior of the $4\,^3P_1$ fluorescence. These rate coefficients were studied systematically over a temperature range of 690–1100 K in order to characterize the velocity dependence of the collisional coupling. The systematic behavior of the rate coefficients with varying temperature and noble gas species is qualitatively consistent with a nearly adiabatic coupling limit for noncrossing levels.

I. INTRODUCTION AND BACKGROUND

Nonadiabatic transitions which result from thermal collisions of neutral atoms are useful probes of interatomic interactions. Measurements of energy transfer within the principal ^2P doublets of alkali metals, started by Krause,[1] spurred an intensive theoretical investigation by Nikitin and coworkers to understand level coupling.[2] A consequence of this theoretical work was the realization that localized regions of nonadiabatic coupling in alkali–rare gas complexes could be treated with the semiclassical theories of "two level" recoupling of Landau, Zener, and Stueckelburg. The magnitude of nonadiabatic transitions can be estimated in terms of the (Massey) parameter $\xi = (\Delta E/\hbar)/v/\rho)$; ΔE and ρ are the adiabatic level separation and effective range of interaction where mixing occurs and v is the relative velocity of the colliding pair of atoms. The level mixing can be calculated precisely with Nikitin's molecular recoupling scheme in two limits: $\xi \ll 1$ where collisions are termed sudden and $\xi \gg 1$ which corresponds to a nearly adiabatic process. Gallagher[3] performed the seminal study of temperature dependence on nearly adiabatic fine structure mixing in Rb($5\,^2P$) and Cs($6\,^2P$) by the noble gases which verified Nikitin's semiclassical model for $\xi \gg 1$. It was shown that strong temperature and reduced-mass variations of the rate coefficients were consistent with Stueckelburg's model of nearly adiabatic mixing.[4,5] In essence, when the level separation of the coupled states remains constant for all internuclear separations R, then the cross sections for nearly adiabatic mixing scale as $\exp(-\xi)$ when $\xi \gg 1$.

The experimental studies of "one-electron" systems have led to the development of reliable model potential calculations for alkali–noble gas interactions.[6] A very complete theoretical case study of alkali–He interactions demonstrates that a broad class of experimental studies dealing with alkali–rare gas interactions can now be calculated very accurately.[7]

Attention is currently shifting to the detailed analyses of interatomic potentials between the multivalent atoms and the rare gases. The divalent group II elements are being studied intensively because their level structure is accessible to optical dye laser technology and accurate theoretical treatments of their correlated electronic behavior are also emerging. Recently, crossed beam experiments have been exploited to understand specific dynamics of collision interactions.[8] Dagdigian[9] has used crossed beam experiments to measure state-to-state mixing of the Ca($4\,^3P_J$) multiplet due to collisions with He and H_2, D_2, while Leone[10] has studied total rates for intramultiplet mixing of Ca($5\,^3P_{1-J'}$) for each of the rare gases. Crossed beam techniques have also been used to study mixing of a high spin multiplet in the transition metal Cr.[11] Fully quantum mechanical calculations now also exist for Ca($4\,^3P_J$)–He[12] and Mg($3\,^3P_J$)–He.[13]

A distinguishing feature of most crossed beam experiments done to data is the small fine-structure splitting of the excited states that were studied. This will lead to collisional mixing rates characterized by $\xi \ll 1$ and hence cross sections typically $> 10^{-16}$ cm^2 for relative translational energies > 0.03 eV. (This was confirmed by experiment for the noted cases.)

The heavier group II elements Sr, Ba, Zn, Cd, and Hg with their large fine-structure splitting, are expected to experience nearly adiabatic collisional mixing of their lowest ^3P_J multiplets.[14-16] Indeed, various early measurements of intramultiplet mixing[17] of Cd($5\,^3P_J$) and Hg($6\,^3P_J$) by rare gases yielded upper bound cross sections $< 5 \times 10^{-19}$ cm^2 at temperatures < 600 K. More recent measurements of state-to-state rate coefficients for Sr($5\,^3P_1$–$5\,^3P_{J'}$)[16] and total rate coefficients for Ba($6\,^3P$),[18] Zn($5\,^3P$),[19,20] Cd($5\,^3P$),[21,22] and Hg($6\,^3P$)[23] are all consistent with a model of nearly adiabatic level transitions.

Nikitin has emphasized that nonadiabatic coupling of levels is affected predominantly by the nature of the exchange interaction.[24] This is expected to be especially significant in complexes where large spin–orbit interactions of the optically active electron(s) can insure the noncrossing of the adiabatic levels.[16] With this in mind, we have undertaken a study of the state-to-state rate coefficients for Zn($4\,^3P_1 \rightarrow 4\,^3P_{J'}$) by collisions with noble gases. The fine-structure level splitting of the Zn($4\,^3P$) triplet is very nearly equal to that of Sr($5\,^3P$) ($< 2\%$ difference) and the principal quantum numbers for both multiplets are comparable. Thus, their level mixing rates are expected to be similar to the extent that spin–orbit and correlation effects of their active electrons are comparable.

Published semiclassical treatments of the cross sections for intramultiplet mixing of Sr($5 \, ^3P_{2 \rightarrow 1}$) and Zn($4 \, ^3P_{2 \rightarrow 1}$) by the rare gases make use of Nikitin's exponential model to handle the exchange interaction.[25] These model calculations show that the temperature dependence for the state-specific cross sections is nearly adiabatic in both cases, but the cross sections for the fine structure mixing of Zn($4 \, ^3P$) are as much as an order of magnitude larger than those for Sr($5 \, ^3P$).[25(b)]

Accurate measurements of state-to-state rate coefficients for nearly adiabatic mixing can be obtained with good signal-to-noise ratios from static cell experiments. We make use of a time-resolved study of the $^3P_1$ fluorescence to measure state-specific transitions for $^3P_1$–^3P_J.[16,26] This technique is particularly effective when the rate(s) of collisional transfer can be arranged to be comparable to the natural radiative rate Γ_N from the $^3P_1$ level; then the triexponential development of the laser excited population can be temporally resolved.

II. MEASUREMENT AND ANALYSIS

A. Measurement

The experimental setup is very similar to that reported previously for the Sr experiment,[16] but is shown in Fig. 1 for
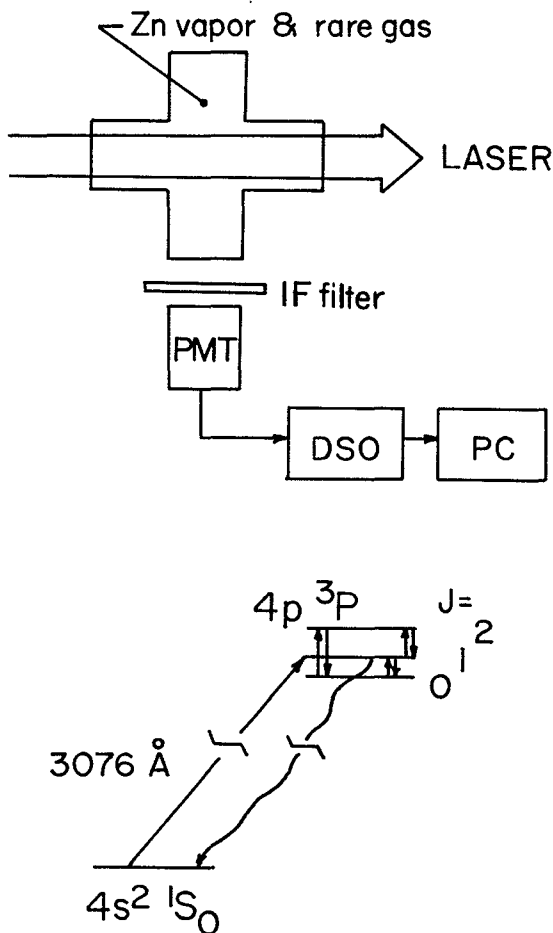

FIG. 1. A schematic diagram of the apparatus used to study collisional transfer effects on the laser-induced fluorescence of the Zn $4 \, ^3P_1$–$4 \, ^1S_0$ transition. DSO is a LeCroy 9400 digitizing-storage oscilloscope.

completeness. A heated inconel 5-way cross contains both the zinc vapor and a buffer charge of rare gas (typically $P_{RG} \sim 10$–100 Torr). The buffer gas pressures were measured with a capacitance manometer calibrated for 0–1000 Torr with $\pm 0.25\%$ accuracy. The zinc vapor is produced by separately heating a cold finger containing high purity zinc metal (metal purity $> 99.996\%$). The cold finger is maintained at temperatures < 650 K to minimize self-interactions and density effects such as optical trapping and energy pooling. (Typical ground state zinc densities in the interaction region were usually $< 10^{12}$ cm^{-3}.) An ultraviolet laser pulse at $\lambda = 307.5$ nm is used to excite $< 10\%$ of the ground state zinc atoms into the $4 \, ^3P_1$ state of zinc. Collisions between the excited zinc atoms and the rare gas atoms subsequently transfer the fine-structure $4 \, ^3P_J$ populations. The 307.5 nm fluorescence resulting from the $4 \, ^3P_1$–$4 \, ^1S_0$ transition is selected by an interference filter and detected by a photomultiplier tube (PMT) capable of sustaining high photoelectron currents with better than 1% linearity. The fluorescence signal is imaged onto the PMT's photocathode so that effects of diffusion of the excited states (transverse to the excitation axis) are minimized under the conditions studied. The signals from the PMT are digitized and averaged with a digital oscilloscope (LeCroy 9400 series) and stored in a computer for later analyses. This system provides a fluorescence record 32 K channels long with typically 10 bits of signal to noise after averaging 2000 single shot realizations.

The biggest complication with this type experiment is contamination of the rare gases by molecular species. The latter have rate coefficients for collisional transfer which are substantially larger than those expected for the rare gases. We used reagent quality rare gases with purities better than 99.9995% in all cases. Although our all metal-to-metal sealed reaction cell, with metal-to-glass windows, and ultrahigh vacuum (UHV) vacuum gas manifold were extensively baked out, some outgasing still persisted when the cell was maintained at very high temperatures. Commercial zinc contains hydrogen, which may also be a source of contamination;[20] we melted our zinc samples in conjunction with purging our cell with many charges of Ar (99.9995%) before beginning our measurements, so presumably this source of contamination is not significant.

Nevertheless, the following procedure was adopted when obtaining the time-resolved fluorescence data: the cell was pumped out below 10^{-6} Torr before any run, then after adding a rare gas, the time averaged signals were acquired so that the outgassing period was kept minimal and *constant* for all data scans. Assuming the outgassing rate is the same for different rare gas concentrations, then a linear plot of the collisional transfer rates would yield a slope independent of the molecular gas contributions. If the outgassing rate is perhaps inversely proportional to the buffer gas densities, then our derived rate coefficients would be underestimated accordingly. At a later stage of this experiment, a liquid nitrogen trap and a calcium getter pump (roasting at ~ 500 °C) were installed to further purify the buffer charges of any molecular species. No difference in the level mixing rates were observed before and after using this trap.

B. Data analysis

1. Rate equation model for intramultiplet mixing

A pulse laser, with duration ($\tau \sim 6$ ns) much shorter than any fine-structure level mixing time, is used to excite a specific level ($^3P_1$) which collisionally mixes with its neighboring levels. Complete M_j mixing occurs within the manifold of substates of each J level in a very short time compared to the J mixing. Hence, it is possible to model the total population N_j of the three ^3P_J states with coupled rate equations. The initial conditions representing the populations produced by much faster excitation with the pulse laser are taken to be $N_0 = 0$, $N_1 = N$, $N_2 = 0$. The $^3P_1$ level will lose population by fluorescing to the ground state with a natural radiative rate Γ_N and by collisional transfer to the neighboring $J = 0,2$ levels with rates R_{10} and R_{12}, respectively.[27] All three levels will mix with various collisional rates $R_{JJ'}$ so that the J-level populations will exhibit multiexponential behaviors. We can reduce the set of six unknown rates $R_{JJ'}$ to three by using the principle of detailed balance to give

$$R_{J'J}/R_{JJ'} = (g_J/g_{J'})e^{[(E_{J'} - E_J)/kT]}, \quad (1)$$

where T is the temperature of the gas and $g_J = 2J + 1$. Under the present experimental conditions, the elastic collision rates between Zn and the rare gas atoms are much higher than the J-level transfer rates, so the Zn(4 ^3P_J) atoms are in thermal equilibrium with the environment. Therefore, the temperature T is taken to be the measured cell temperature. [It should be noted that this is generally not always the case;[28] in some situations, such as self-interactions, T has to be taken as an effective temperature.] Should quenching (due to molecular species) or diffusion of the Zn (4 $^3P_1$) atoms out of the detection viewing volume be significant, then extra loss rates R^q are needed. The rate equations used to describe the population of the ^3P_J multiplet were thus taken to be

$$\dot{N}_0 = -(R_{01} + R_{02} + R^q)N_0 + R_{10}N_1 + R_{20}N_2, \quad (2a)$$

$$\dot{N}_1 = R_{01}N_0 - (R_{12} + R_{10} + \Gamma N + R^q)N_1 + R_{21}N_2, \quad (2b)$$

$$\dot{N}_2 = R_{02}N_0 + R_{12}N_2 - (R_{21} + R_{20} + R^q)N_2. \quad (2c)$$

Here the rate R^q is assumed to be the same for all three levels. This seems very plausible for diffusion[26] and should be a fair approximation for molecular gas quenching because we do not expect accidental energy degeneracies between the Zn(4 ^3P_J) levels and likely molecular quenchers. In any case, the empirical rate R^q is found to be small, typically < 5% of the natural radiative decay rate Γ_N. The latter is treated as a known constant $\Gamma_N = 20 \pm 0.2 \, \mu s$.[20,29]

The experimentally measured time-dependent fluorescence signal is proportional to the population of Zn(4 $^3P_1$) given by $N_1(t)$. Equations (2a)–(2c) are solved numerically, with the resulting $N_1(t)$ least-squares fitted to the experimentally measured signals to obtain the rates R_{01}, R_{12}, and R^q. The rate R_{02} is assumed to be zero.[30] The systematic uncertainty arising from this assumption will be discussed later. However, given the initial conditions, the fluorescence signal shape will be very insensitive to the value of R_{02} because it requires a two-step collision process to affect changes in its development. In the work performed on Sr,[16]

this was handled better by studying simultaneously the populations of the $J = 0,2$ levels using time-resolved absorption. In this work we did not have a cw source of sufficient spectral intensity to probe the time evolution of the $J = 0,2$ levels with good signal to noise.

2. Fitting data to obtain the collisional transfer rate coefficients

A typical time-resolved fluorescence signal is shown in Fig. 2. The least-square fit solution of $N_1(t)$ is also shown in Fig. 2. As mentioned previously, the rate R_{02} is assumed to be zero. This assumption seems reasonable since the earlier measurements for Sr found that R_{02} is typically < 1/5 of the smaller of R_{12} or R_{10}.[16] Furthermore, the theoretical evaluations[25] for intramultiplet mixing of Sr(5 ^3P_J) and Zn(4 ^3P_J) by the rare gases found that the velocity-averaged cross section $\langle\sigma(^3P_2 \to {}^3P_0)\rangle$ for both cases are quite small; $\langle\sigma(^3P_2 \to {}^3P_0)\rangle \sim 10^{-7}$ (Å)^2 for Sr and $\langle\sigma(^3P_2 \to {}^3P_0)\rangle \sim 10^{-5}$ (Å)^2 for Zn. By assuming $R_{02} = 1/3$ of the derived values for R_{01}, we estimated by using simulated data that the systematic errors of ignoring R_{02} were < 5%. Likewise, we have determined by using synthetic data that the systematic errors for fitting k_{01} and k_{12} are < 20% given our signal-to-noise ratios.

The collisional transfer rates $R_{JJ'}$ were determined with a variety of noble gas concentrations and for a variety of temperatures. The collisional transfer rates for a given species and temperature were studied as a function of buffer pressure to assess effects of three-body processes in the intramultiplet mixing. Harris et al. reported such processes for the intramultiplet mixing of Sr(5 ^3P_J) by the heavy rare gases.[31] A linear relationship was observed in all circumstances as shown for the case of Zn + Ar in Fig. 3. These collisional transfer rates were least-squares fit to a straight line

$$R_{JJ'} = B_{JJ'} + k_{JJ'} n, \quad (3)$$

where n is the rare gas concentration. A typical fit is shown in Fig. 3. The fit slope $k_{JJ'}$ is the collisional transfer rate coefficient and $B_{JJ'}$ represents a background contribution (presumably due to outgassed molecular species). The rate
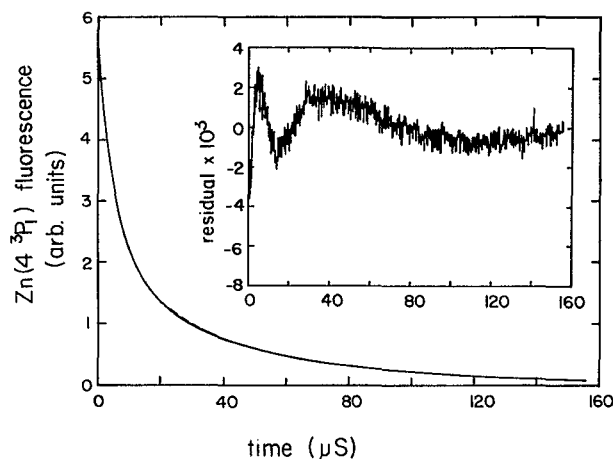

FIG. 2. A typical laser-induced fluorescence signal after averaging 2000 shots with its least-squares fit of the solution of Eq. (2). The inset shows the residual difference between the fit and data.
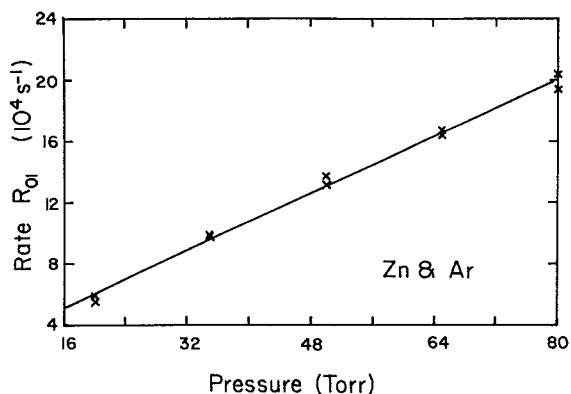
FIG. 3. The collisional transfer rate R_{01} as a function of perturber pressure and the least-squares fit of eq. (3) to the data.

coefficient $k_{JJ'}$ obtained in this way should be more reliable than any individual measurement since it is effectively the averaged value of many $R_{JJ'}$ measurements; thus, these $k_{JJ'}$ are presented as our final results.

III. RESULTS

Figures 4(a)–4(d) show the final $k_{JJ'}$ (cm³/s) obtained in this work over a temperature range 690–1100 K. The rate coefficients $k(T)$ can be fit by a power function in the measured temperature range[3]

$$k(T) = KT^m. \qquad (4)$$

The fitted values of K and m are listed in Table I and the calculated $k(T)$ are plotted in Figs. 4(a)–4(d) as solid lines. We emphasize that Eq. (4) should be considered as an empirical description of the rate coefficient $k(T)$ over this particular range. The fluctuations in the measured rate coefficients $k(T)$ are ~10% [see Figs. 4(a)–4(d) for details] around the values calculated from Eq. (4). This is assigned as the random statistical uncertainty of the measured rate coefficients $k_{JJ'}$. In addition to this, total systematic errors which might result from our fitting numerics (and assumptions) are estimated to be <30%. The largest systematic error would result for the case of Ne because values for k_{01} and k_{12} are apparently quite similar in magnitude.

IV. DISCUSSION

The electronic structure of the lowest ^3P_J multiplet of zinc and strontium are very similar; in fact, the fine-structure splittings are almost identical (<2% difference— 190:389 cm^{-1} for Zn and 187:394 for Sr). Surprisingly, however, the measured rate coefficients for transfer by each of the rare gases are grossly different for the first excited multiplet of these two elements. For strontium collisions,[16] $k_{01} < k_{12}$ for argon and neon perturbers, while $k_{01} > k_{12}$ for helium. However, for zinc collisions, with all rare gases measured, $k_{01} > k_{12}$. The absolute magnitudes of the rate coefficients are also very different; the rate coefficients k_{01} for Zn + Ar and Zn + Ne collisions are about 25 times as large as those corresponding to Sr.
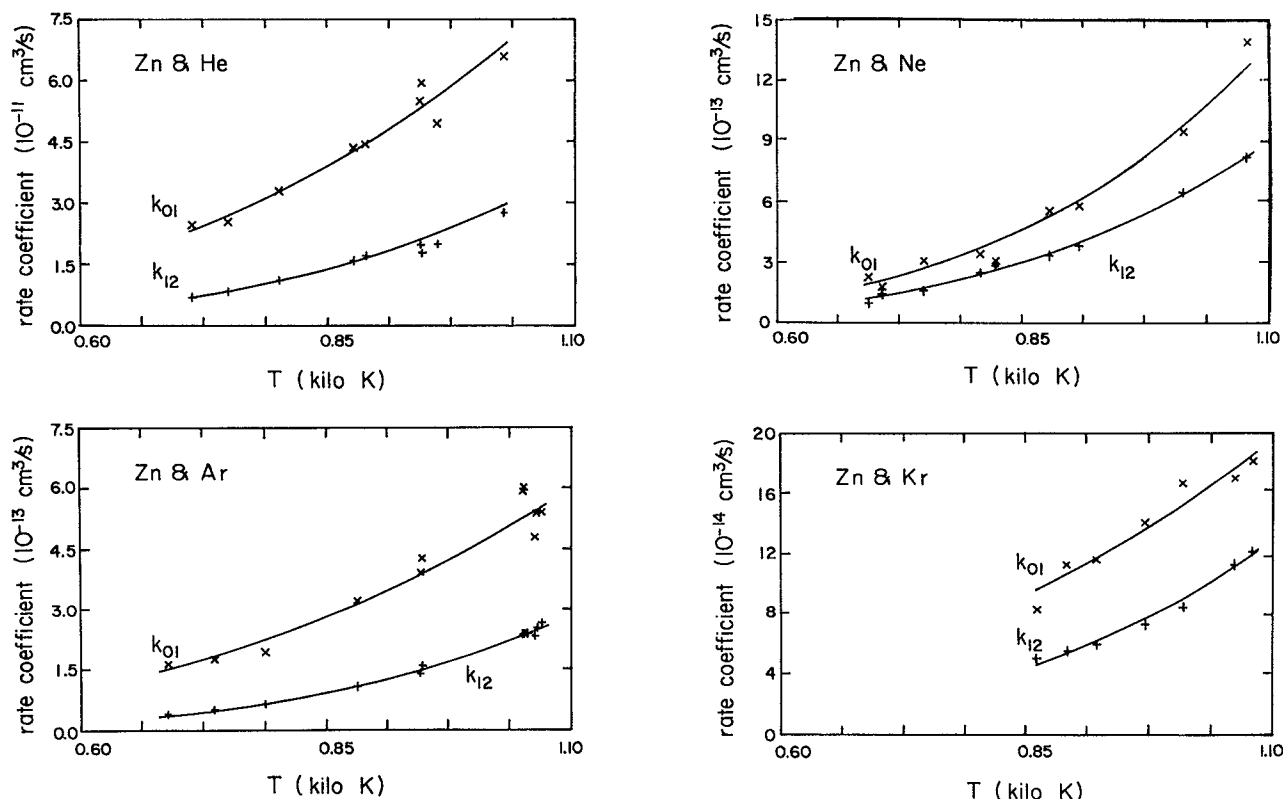
Three-body collisions, which were observed in Sr,[31]

FIG. 4. The reduced rate coefficients k_{01} (T) and k_{12} (T) with their least-squares fit power functions [Eq. (4)] for the cases: (a) Zn–He; (b) Zn–Ne; (c) Zn–Ar; and (d) Zn–Kr.

TABLE I. The rate coefficient $k(J,J') = KT^m$, with T in units of kK and $k(J,J')$ in units of cm³/s.

Noble	J	J'	K	m
He	0	1	6.31e-11	2.97
	1	2	2.64e-11	4.01
Ne	0	1	9.19e-13	4.29
	1	2	5.98e-13	4.27
Ar	0	1	4.53e-13	2.98
	1	2	1.87e-13	4.43
Kr	0	1	1.48e-13	2.94
	1	2	8.59e-14	4.27

were not observed here. This is probably due to the lower buffer gas concentrations used in this experiment and larger binary collisional transfer rates. If three-body effects exist, then they are included as an additional systematic error in the binary collisional transfer rate coefficients that we derived.

The collisional transfer rate coefficients have a systematic temperature dependence, similar to the Rb, Cs, and Sr collision data. Figure 5 shows a plot of these rate coefficients vs a reduced temperature T' given by $T' = T(K)$ (μZn–He/μZn–noble gas). This corrects for the differences between the rate coefficients that result from a different reduced mass μ in the Maxwellian velocity distribution.[3] In this manner, for the same T', all the Zn–noble gas pairs have the same velocity distribution. Thus, the differences between the rate coefficients for different Zn–noble gas pairs are attributed to differences in their interactions. From Fig. 5 one can see that the Zn–Ar and Zn–Ne rate coefficients have the right order of magnitude of extrapolation of the Zn–He rate coefficients to lower temperature regions. This indicates, as expected by Nikitin's semiclassical model of nearly adiabatic transfer, that the Zn–noble gas collision cross sections have similar strong velocity dependencies. Our results are in good quantitative agreement with an earlier measurement[20] of total rate coefficients for Zn($4\,^3P_1$–$4\,^3P_{J'}$) which were obtained at a lower cell temperature of 570 K. Table II shows a comparison of the total rate coefficients for transfer of Zn($4\,^3P_{1\rightarrow0,2}$) measured in Ref. 20 and our calculated values based upon the extrapolations of data presented in Table I. The errors listed in our calculated values correspond only to the sum of the noted random statistical uncertainty (1σ) for k_{01} and k_{12}. The theoretically derived temperature dependencies for the collisional mixing cross sections in Ref. 25 become steeper below 600 K so some of the differences in our extrapolation may in fact reflect this behavior. The apparent increase in the measured rate coefficients between Ar and Kr probably result, as noted in Ref. 20, from the marked increase in polarizability for Kr. This indicates the probable extent that dispersion interactions play in these collisions.

Our temperature dependences studies of k_{12} match the trends shown for the semiclassical calculations of $\langle\sigma(^3P_2\rightarrow^3P_1)\rangle$ that are presented in graphical form in Refs. 25(a) and 25(b). The magnitudes for their velocity-averaged cross sections also agree fairly well with our k_{12} data.
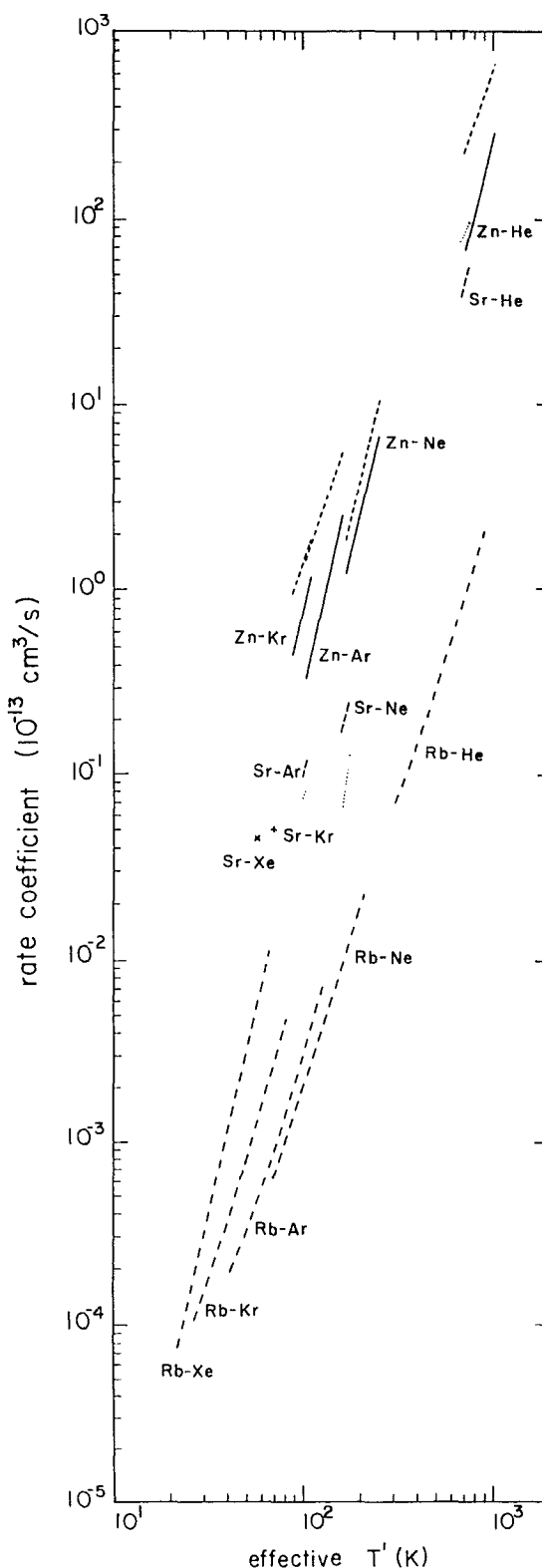

FIG. 5. A comparison of the collisional transfer rate coefficients for J mixing of Rb($5\,^2P$), Sr($5\,^3P$), and Zn($4\,^3P$) vs a reduced temperature T' (see the text for details).

[This is not necessarily a meaningful comparison, however, since Ref. 25(b) used judiciously chosen parameters for their model potentials to calculate total cross sections which match experimental results for Zn.[19] References 20 and 25(b) detail several experimental difficulties in Ref. 19,

TABLE II. Total collisional transfer rate coefficients $k_{1\rightarrow J'}$ for Zn($4\,^3P_1$–$4\,^3P_{0,2}$) in units of 10^{-14} cm^3/s. The experimental values are taken from Ref. 20 for $T = 570$ K, while the calculated values are derived from extrapolations of our empirical fits (Table I) to 570 K.

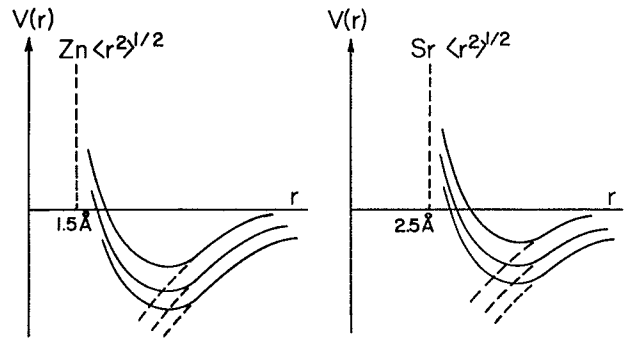| $k_{1\rightarrow J'}^{\text{Total}}$	He	Ne	Ar	Kr
$k_{1\rightarrow J'}^{\text{exp}}$ (570 K)	1140 ± 140	6.2 ± 0.6	4.2 ± 0.4	4.1 ± 0.3
$k_{1\rightarrow J'}^{\text{calc}}$ (570 K)	930 ± 200	9.9 ± 2	6.2 ± 1.2	2.3 ± 1.0

FIG. 6. A schematic comparison of a 6-12 type model potential for Zn–RG and Sr–RG. It is assumed that the electrostatic interactions are comparable.

which suggest these values are rough estimates.] For example, the calculated mixing cross section for Zn($4\,^3P_2 \rightarrow\,^3P_1$) by He is $\langle\sigma_{21}\rangle \simeq 3.9 \times 10^{-17}$ cm^2 at 1000 K, which results in a calculated value for $\sigma_{12}\bar{v} = 8.5 \times 10^{-12}$ cm^3/s. (Compare this to our $k_{12}^{\text{exp}} = 2.64 \times 10^{-11}$ cm^3/s). Gallagher[3] has noted that when $\sigma(T) \propto T^n$ then $\sigma(v) \propto v^{2n}$, so the average of $v\sigma(v)$ over a Maxwellian velocity distribution leads to a sharply peaked integrand in the average. The effect is to weight strongly a narrow range of velocities in the average of $v\sigma(v)$. In the case of Zn + He at 1000 K, if the rate coefficients $k(T) \propto T^4$, then velocities close to $2.5\bar{v}$ are strongly weighted. Agreement with the experimental rate coefficient k_{12} is improved if the cross section from Ref. 25 is multiplied by this factor of $2.5\bar{v}$ instead of $\bar{v}$. The close agreement of our results with theory for this case is somewhat fortuitous since the experimental results of Ref. 19 agree within a factor of 2 with Ref. 20 and our measurements.

Our state-specific measurements for k_{10}, in contrast, do not match the model potential calculations of Ref. 25(b) or the close coupling calculations provided by Umemoto et al.[20] Both sets of calculations show that $\langle\sigma_{10}\rangle \ll \langle\sigma_{12}\rangle$, whereas our results show that these cross sections are comparable in magnitude. In the cases of He and Ar perturbers, the former is actually somewhat larger by $\sim$30–40%. The model potential parameters chosen by Ref. 25(b) for the case of Zn + He led to a reasonably large, mostly radial coupling for $\langle\sigma_{21}\rangle \sim 2.3 \times 10^{-17}$ cm^2 (at 700 K) while producing a small, Coriolis-only contribution for $\langle\sigma_{10}^c\rangle \sim 5 \times 10^{-18}$ cm^2. It is notable that their calculations[25(b)] for intramultiplet mixing in Sr($5\,^3P_J$), which match well the state-specific measurements of k_{12} and k_{10},[16] found a partition of the mixing process due to angular and radial motions to be very similar in magnitude; the calculated $\langle\sigma(^3P_2 \rightarrow\,^3P_1)\rangle$, which consists of both contributions $\langle\sigma^r\rangle$ and $\langle\sigma^c\rangle$, is about twice as large as $\langle\sigma(^3P_1 \rightarrow\,^3P_0)\rangle$, which consists only of $\langle\sigma^c\rangle$. From our data, we infer that $\langle\sigma_{10}\rangle \gtrsim \langle\sigma_{12}\rangle$, which seems to imply that in the case of Zn($4\,^3P_J$) the Coriolis contribution is dominant and at least an order of magnitude larger than that estimated in Ref. 25(b).

Both sets of calculations find that the cross section $\langle\sigma(^3P_2 \rightarrow\,^3P_0)\rangle$ is fairly small; however, the results of Umemoto et al.[20] are surprising since they show $\langle\sigma_{20}\rangle \gtrsim \langle\sigma_{10}\rangle$. As shown in Ref. 25, the mixing between the $^3P_0$ and $^3P_2$ states is generally quite small compared to either $\langle\sigma_{10}\rangle$ and $\langle\sigma_{12}\rangle$ for both Zn($4\,^3P$) and Sr ($5\,^3P$). Our current experi-

mental technique is not particularly sensitive to the rate coefficient k_{02} (k_{20}), but the previous, more accurate study of intramultiplet mixing in Sr($5\,^3P_J$) indicates such mixing terms are $< 1/5$ of the smaller of k_{10} or k_{12}.

V. CONCLUSION

A notable general result of this study is that the less chemically reactive element Zn has much larger rate coefficients for nonadiabatic mixing of its ^3P_J multiplet by collisions with noble gases. This nonintuitive result is consistent, however, with the earlier interpretations of nearly adiabatic mixing by Nikitin and Gallagher which posit a constant level separation of the coupled states for all internuclear separations R (see Fig. 6). In the case of Sr, with its unfilled core of d states, one expects a larger turning radius r_0 to occur for its repulsive exchange interaction. Indeed, Zn with its completely filled core of d states is much more compact, e.g., Zn$\langle r^2\rangle^{1/2} \sim 1.53$ Å, while Sr$\langle r^2\rangle^{1/2} \sim 2.45$ Å. Thus, even though the electrostatic interactions of the valence electrons with noble atoms may be fairly comparable (since their effective quantum numbers are comparable), the well depths and range of interaction ρ can be expected to be greater in the case of Zn. This underscores a point first made by Nikitin that even if the electrostatic interaction were largely responsible for the level coupling, the exchange force largely dominates the shape of the adiabatic curves and, therefore, the rates for nearly adiabatic state transfer.[24]

Specifically we find that our temperature-dependence studies extrapolate well ($\sim \pm 40\%$) to the total rate measurements of Umemoto et al.[20] taken at a lower temperature (570 K). In contrast to previous calculations, our state-specific measurements for intramultiplet mixing of Zn($4\,^3P_J$) by the rare gases apparently require that the cross sections obey the inequalities $\langle\sigma(^3P_1 \rightarrow\,^3P_0)\rangle \gtrsim \langle\sigma(^3P_1 \rightarrow\,^3P_2)\rangle \gg \langle\sigma(^3P_2 \rightarrow\,^3P_0)\rangle$. The first inequality differs significantly with the analogous process in Sr($5\,^3P_J$). This illustrates again the utility of studying nearly adiabatic energy transfer to provide a stringent probe of the exchange interaction.

ACKNOWLEDGMENTS

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