$4\,^2D \rightarrow 4\,^2F$ excitation transfer in Li induced by collisions with Li, He, and Ar ground-state atoms
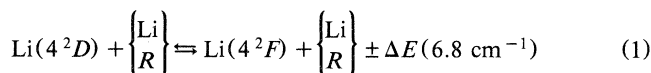
B. Dubreuil and C. Chaleard

Groupe de Recherche sur l'Energétique des Milieux Ionisés, Equipe de Recherche No. 907 associée
au Centre National de la Recherche Scientifique, Université d'Orléans,
F-45046 Orleans Cédex, France

(Received 8 July 1983)

Excitation transfers between the $4\,^2D$ and $4\,^2F$ states of lithium are studied in a temperature-controlled heat-pipe oven. These transfers are induced by collisions with Li, He, and Ar ground-state atoms. Quenching cross section and radiative rates are also measured. For the excitation transfer process, the thermally averaged cross sections are, respectively, $\sigma^{\text{Li}} = 400$ Å^2, $\sigma^{\text{He}} = 120$ Å^2, and $\sigma^{\text{Ar}} = 190$ Å^2. These values agree with the experimental results of Gallagher in Na and the calculations of Gersten. Finally, the behavior of the $4\,^2D$-$4\,^2F$ two-level system in the l-mixing regime is investigated in the case of Ar collisions.

I. INTRODUCTION

Recently we reported on an experimental study of the quenching and excitation transfers in the ^2P and ^2D, $n = 3$ lithium sublevels. These transfers were induced by collisions of the lithium excited states with ground-state parent atoms and rare gases.[1] A three-step excitation process involving the $4\,^2S$ state was used to populate the $3\,^2P$ level. In the present experiment a two-step laser excitation scheme populates the $4\,^2D$ state and allows us to study the $4\,^2D$-$4\,^2F$ population transfers

$$\text{Li}(4\,^2D) + \begin{Bmatrix} \text{Li} \\ R \end{Bmatrix} \rightleftharpoons \text{Li}(4\,^2F) + \begin{Bmatrix} \text{Li} \\ R \end{Bmatrix} \pm \Delta E (6.8 \text{ cm}^{-1}) \qquad (1)$$

and the collisional quenching.

II. EXPERIMENT

The experimental setup described in Ref. 1 is the following: The lithium vapor is produced inside a four-arm temperature-controlled heat-pipe oven working in pure lithium vapor or in a lithium rare-gas mixture (He and Ar in the present experiment). The $4\,^2D$ state is populated from the ground state using the 6708-Å line of a c.w. dye laser for the first step and the 4603-Å line of a pulsed dye laser for the last step as depicted in Fig. 1. The cell is heated in the 850–930-K temperature range giving an atomic Li vapor density $n_{\text{Li}}(\text{cm}^{-3}) = 3.5 \times 10^{14} - 2.2 \times 10^{15}$. The rare-gas pressures are varied in the ranges $0 < P_{\text{He}}(\text{Torr}) \leq 1.5$ and $0 < P_{\text{Ar}}(\text{Torr}) \leq 1.5$. The resonance and collision-induced fluorescence lights are detected with a grating spectrometer and a fast photomultiplier connected to a 2-ns resolution boxcar averager and a minicomputer.

The time dependence of the $4\,^2D$-state population $N_{4\,^2D}(t)$ is deduced from the 4603-Å resonance fluorescence light, but the population transferred by collisions on the $4\,^2F$ state, $N_{4\,^2F}$, cannot be deduced from the $4\,^2F \rightarrow 3\,^2D$ radiative transition at 1.87 μm (Fig. 1). However, $N_{4\,^2F}(t)$ can be measured from the fluorescence starting from the $3\,^2D$ level (6104 Å) which is mainly populated by the radiative cascade

$4\,^2F \rightarrow 3\,^2D$ with a rate $\alpha_{32} = 1.38 \times 10^7$ s^{-1}:

$$N_{4\,^2F}(t_i) = \frac{1}{\alpha_{32}} \left[\left[\frac{dN_{3\,^2D}}{dt} \right]_{t=t_i} - a_{33} N_{3\,^2D}(t_i) \right] .$$

The quenching coefficient of the $3\,^2D$ level a_{33} was previously measured[1,2] and can be expressed as

$$a_{33}(\text{s}^{-1}) = - \left[6.96 \times 10^{-7} + 1.1 \times 10^{-9} n_{\text{Li}}(\text{cm}^{-3}) \right.$$
$$\left. + \begin{Bmatrix} 0.18 \times 10^{-9} n_{\text{He}}(\text{cm}^{-3}) \\ 0.05 \times 10^{-9} n_{\text{Ar}}(\text{cm}^{-3}) \end{Bmatrix} \right] .$$

Contribution of the $4\,^2P \rightarrow 3\,^2D$ radiative cascade is neglected, first because as shown later the population on the $4\,^2P$ state induced by collisions from the $4\,^2D$ state remains negli-
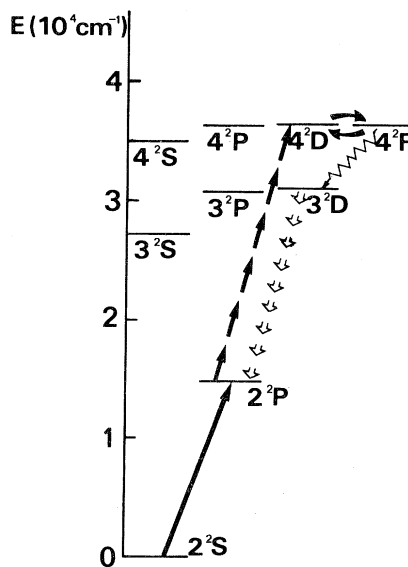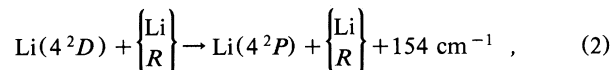

FIG. 1. Partial energy diagram of Li atom involved in the laser excitation of the $4\,^2D$ state.

gible in the pressure ranges investigated, and secondly because the radiative rate of this cascade is $\alpha_{4^2P \to 3^2D}$ $= 5.5 \times 10^5 \text{s}^{-1}$.

In fact, in the course of this experiment it was not possible to detect excitation transfers from the $4\,^2D$ state to the $4\,^2P$ state:

$$\text{Li}(4\,^2D) + \left\{\begin{matrix} \text{Li} \\ R \end{matrix}\right\} \to \text{Li}(4\,^2P) + \left\{\begin{matrix} \text{Li} \\ R \end{matrix}\right\} + 154 \text{ cm}^{-1} \ , \quad (2)$$

because the $4\,^2P \to 2\,^2S$ and $4\,^2P \to 3\,^2S$ transitions lie out of the range of the spectrometer. But as long as the collisional process (1) is not saturated (complete l mixing is not achieved), one can expect process (1) to be prominent with respect to reaction (2) because (1) is a near-resonant process. This assumption, supported by recent experiments on l-changing collisions[3] and n-changing collisions[4] in lithium, is valid in the relatively low-pressure ranges investigated.

For the same reasons, the $4\,^2D \to 4\,^2S$ excitation transfer, which is a nonresonant process ($\Delta E = 1611 \text{ cm}^{-1}$), can be neglected. Indeed, no significant signal was detected on the $4\,^2S \to 2\,^2P$ transition. An estimate of the rate coefficient for the process

$$\text{Li}(4\,^2S) + \text{Li} \to \text{Li}(4\,^2D) + \text{Li} - 1611 \text{ cm}^{-1}$$
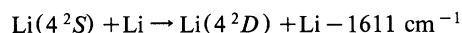
deduced from a $4\,^2S$ laser pumping experiment[1,2] is $k_{4^2S - 4^2D} = 4 \times 10^{-11} \text{ s}^{-1} \text{ cm}^3$.

On the basis of the above qualitative analysis of the experiment, the measured populations $N_{4^2D}(t)$ and $N_{3^2D}(t)$ are at the end of the laser pulse solutions of the two-level rate equations where the transfer or quenching coefficients

a_{ij} including radiative (α_{ij}) and collisional (β_{ij}) processes are expressed as

$$a_{ij} = \alpha_{ij} + \beta_{ij}^R n_R + \beta_{ij}^{\text{Li}} n_{\text{Li}} \ . \quad (3)$$

n_R and n_{Li} are, respectively, the rare-gas and lithium atom densities.

As developed in our laboratory[5] the optimization algorithm named "identification method" allows us to determine the a_{ij}'s so as to minimize the difference between the experimental $N_i(t)$ values and those calculated from the model equations. The procedure used in connection with the present experiment is similar to the one developed to extract the excitation transfer rate coefficients in the $n = 3$ and $n = 4$ sublevels of helium in a gas discharge[6,7] and the n-changing rate coefficients in lithium.[4] The experimental curves $N_{4^2D}(t)$ and $N_{4^2F}(t)$ have been identified in this manner for different temperatures of the cell (different n_{Li} values) and for different rare-gas pressure values. The radiative coefficients and the temperature-averaged collisional rate coefficients obtained by this method are grouped in Table I.

III. DISCUSSION

The radiative coefficients α_{4^2D} and α_{4^2F} are compared to the values of Wiese[8] and to the experimental results of Heldt and Leuchs[9] and Hansen.[10] The $4\,^2D \to 4\,^2F$ collisional transfer cross sections are compared to the l-mixing cross sections for the low-n values measured by Gallagher, Edelstein, and Hill in Na.[11]

TABLE I. Collisional quenching and excitation transfer rate coefficients β, thermally averaged cross sections $\bar{\sigma}$, and radiative coefficients α measured in the present experiment.

	Li (900 K)	He (875 K)	Ar (900 K)
α_{4^2D} (10^7 s^{-1})	3.0 ±0.1		
	3.22 ±0.10[a]		
	3.05 ±0.11[b]		
	2.98[c]		
β_{4^2D} $(10^{-9} \text{ s}^{-1}\text{cm}^3)$	12.2 ±1.3	3.6 ±0.5	3.6 ±0.9
$\bar{\sigma}_{4^2D}$ (Å^2)	520 ±120	134 ±25	200 ±50
$\beta_{4^2D \to 4^2F}$ $(10^{-9} \text{ s}^{-1}\text{cm}^3)$	9.5 ±2.1	3.2 ±0.4	3.4 ±0.8
$\bar{\sigma}_{4^2D \to 4^2F}$ (Å^2)	400 ±130	120 ±25	190 ±50
		380 $(n=6)$[d]	290 $(n=5)$[d]
		140[e]	510 $(n=6)$[d]
			170[e]
α_{4^2F} (10^7 s^{-1})	1.4 ±0.1		
	1.38[a]		
β_{4^2F} $(10^{-9} \text{ s}^{-1}\text{cm}^3)$	5.2 ±1.5	2.0 ±0.3	2.5 ±0.6
$\bar{\sigma}_{4^2F}$ (Å^2)	225 ±75	75 ±19	140 ±35
$\beta_{4^2F \to 4^2D}$ $(10^{-9} \text{ s}^{-1}\text{cm}^3)$	5.2 ±0.6	1.9 ±0.2	2.3 ±0.5
$\bar{\sigma}_{4^2F \to 4^2D}$ (Å^2)	225 ±50	70 ±15	130 ±35

[a]Reference 9. [d]Reference 11.
[b]Reference 10. [e]Reference 12.
[c]Reference 8.

The *l*-mixing processes investigated by these authors,

$$Na(n^2D) + R \leftrightarrows Na(n^2L \geq 3) + R, \quad \text{for } n \geq 5 \quad,$$
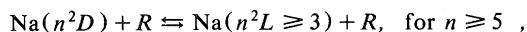
are indeed similar to the $4\,^2D \rightarrow 4\,^2F$ transfers we have studied in lithium. The same order of magnitude is obtained for Ar and He collisions, but the values for Na $n = 6$ are larger than the values obtained for Li $n = 4$. This could be predicted on the basis of the work of Gallagher et al.[11] who showed that the *l*-mixing rate coefficients are in Na a growing function of n for $n < 10$ and because the statistical weight of the $L \geq 3$ sublevels is larger for $n = 6$ than for $n = 4$.

As a supplementary test of the values obtained in lithium, it can be readily shown that the rate coefficients for the $4\,^2D \rightarrow 4\,^2F$ transfer and for the $4\,^2F \rightarrow 4\,^2D$ reverse process follow the microreversibility principle within 25%. From a theoretical point of view, many calculations have been done on the *l*-mixing and *l*-changing processes in rare-gas–Rydberg alkali atom systems (for a recent review see Ref. 13), but relatively few results are available in the case of low Rydberg states such as those studied in this paper. Gersten,[12] Olson,[14] and Hickman[15] have developed different theoretical approaches stimulated by the experimental work of Gallagher et al. in sodium. The results obtained by these authors are in good agreement with experiment for $n = 5$–18. Gersten applied the perturbation approach to the coupled-state calculation involving the degenerate (hydrogenic) manifold $l > 1$. Using a Breit-Fermi pseudopotential and hydrogen atom wave functions, he found a cross section depending on the parameter L/v, where L is the Rydberg electron rare-gas scattering length and v is the relative velocity in the collision. This calculation can be applied to the present $n = 4$ experiment in lithium. Using the curve σ as a function of L/v given by Gersten for $n = 4$ ($4\,^2D \rightarrow 4\,^2F$ transfer) with $L(\text{He}) = 1.19a_0$, $L(\text{Ar}) = -1.70a_0$ and $\bar{v}_{\text{Li-He}} = 2.73 \times 10^5$ cm s^{-1}, $\bar{v}_{\text{Li-Ar}} = 1.70 \times 10^5$ cm s^{-1} we obtain $\sigma_{4D \rightarrow 4F}^{\text{He}} \sim 140$ Å^2 and $\sigma_{4D \rightarrow 4F}^{\text{Ar}} \sim 170$ Å^2, which compare well with our experimental results.

Further comments can be made on these collisional data. Particularly, as seen in Table I, the quenching coefficients $\beta_{ii}^{\text{Li},R}$ are roughly equal to the $\beta_{ij}^{\text{Li},R}$ transfer coefficients within the error bars. This means that the $4\,^2D \rightarrow 4\,^2F$ and $4\,^2F \rightarrow 4\,^2D$ transfers are mainly responsible for the $4\,^2D$ and $4\,^2F$ collisional quenching, respectively.

All these results are deduced from the measurements performed in the relatively low rare-gas pressure and low-temperature ranges: $P_R \lesssim 1.5$ Torr, $T < 930$ K. However, we have extended this study to higher pressures. For instance, in the case of Ar, we obtain the a_{ij} coefficients for P_{Ar} up to 8 Torr.

These coefficients shown in Fig. 2 behave in an unexpected way. Whereas they are an increasing function of P_{Ar} for $P_{\text{Ar}} < 1.5$ Torr as expected from reaction (1) and Eq. (3), they decrease for the larger pressures. The quenching coefficients $a_{11} = a_{4^2D}$, $a_{22} = a_{4^2F}$ tend to become nearly equal and the transfer coefficients are found very small. This behavior is typical of the collisional *l*-mixing phenomena already described by Gallagher, Edelstein, and Hill[11,16] in Na and by Dubreuil in Li.[3,4] When the pressure is high enough to ensure that the largest collisional transfer rate is greater than the laser pumping rate, then after cessation of the laser pulse the populations N_{4^2D} and N_{4^2F} relax with the same
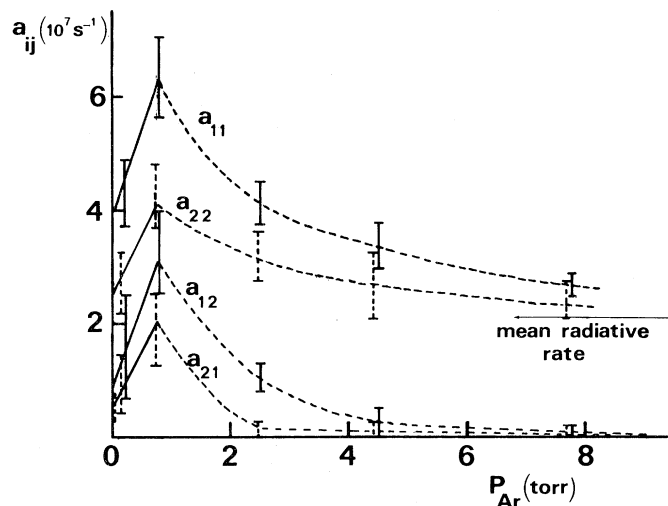

FIG. 2. Coefficients a_{ij} as a function of the argon pressures P_{Ar} for $T = 875$ K in the *l*-mixing regime.

apparent rate and are roughly in the statistical ratio. In this regime, these populations are mixed by inelastic collisions and behave on a nanosecond time scale as a single level population undergoing radiative processes towards other levels. In this case, identification of the a_{ii} coefficients from the coupled rate equations gives the apparent relaxation time of the two levels which tends in the present study to the mean radiative rate

$$\bar{\tau} = \frac{5\alpha_{4^2D} + 7\alpha_{4^2F}}{12} \cong 2.1 \times 10^7 \text{ s}^{-1} \quad .$$

But, one finds a_{ij} transfer coefficients which are nearly null since at each time the solutions of the rate equations verify

$$\frac{N_{4^2D}(t)}{N_{4^2F}(t)} \sim \frac{5}{7} e^{+\Delta E/kT} \quad ,$$

leading to linear dependence of the two equations.

IV. CONCLUSION

In conclusion, we have extended previous measurements on excitation transfers in the $n = 3$ lithium atoms to the $4\,^2D \rightleftharpoons 4\,^2F$ transfer processes. In the lower pressure ranges, the identification method allowed us to determine the excitation transfer rate coefficients for collisions with Li, He, Ar, and the radiative and collisional quenching rate coefficients. The collisional data are compared to experimental values obtained in Na for the *l*-mixing processes $n^2D \rightarrow N^2L \geq 3$ and with the theoretical work of Gersten. Transition from the *l*-changing ($4\,^2D \rightarrow 4\,^2F$) to the *l*-mixing ($4\,^2D \rightleftharpoons 4\,^2F$ saturated) collision regimes was studied in the particular case of the Li-Ar system by increasing the Ar pressure up to 8 Torr. In this range the $4\,^2D$ and $4\,^2F$ populations are roughly in the statistical ratio, and the identification method fails to give the correct transfer coefficients. It provides reliable information only on the apparent lifetime of the mixed levels. Thus, great care must be taken in the interpretation of the physical content of time-resolved laser fluorescence experiments, particularly when *l*-mixing situations are not recognized.

[1]C. Chaleard, B. Dubreuil, and A. Catherinot, Phys. Rev. A 26, 1431 (1982).

[2]C. Chaleard, Thèse de Troisième Cycle, Université d'Orléans, 1982.

[3]B. Dubreuil and M. Harnafi, Abstracts of the E.S.C.A.M.P.I.G. 82. (European Physical Society, 1982).

[4]B. Dubreuil, Phys. Rev. A 27, 2479 (1983).

[5]B. Dubreuil and A. Catherinot, Ann. Phys. (Paris) 7, 359 (1982), and references therein.

[6]B. Dubreuil and A. Catherinot, Phys. Rev. A 21, 188 (1980).

[7]A. Catherinot and B. Dubreuil, Phys. Rev. A 23, 763 (1981).

[8]W. L. Wiese, H. W. Smith, and B. M. Glennon, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 1, 4 (1966).

[9]J. Heldt and G. Leuchs, Z. Phys. A 291, 11 (1979).

[10]W. Hansen, J. Phys. B 16, 933 (1983).

[11]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A 15, 1945 (1977).

[12]J. I. Gersten, Phys. Rev. A 14, 1354 (1976).

[13]F. B. Dunning and R. F. Stebbings, Adv. Electron. Electron Phys. 59, 79 (1982).

[14]R. E. Olson, Phys. Rev. A 15, 631 (1977).

[15]A. P. Hickman, Phys. Rev. A 18, 1339 (1978).

[16]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 35, 644 (1975).