J. Quant. Spectrosc. Radiat. Transfer. Vol. 14, pp. 1195–1198. Pergamon Press 1974. Printed in Great Britain.

ELECTRONIC-EXCITATION TRANSFER COLLISIONS IN FLAMES–VII. SOME ALKALI-DOUBLET MIXING CROSS SECTIONS FOR INERT GAS COLLISIONS, AT 1720 K

P. L. LIJNSE

Fysisch Laboratorium, Universiteit, Sorbonnelaan 4, Utrecht, the Netherlands

(*Received* 11 *February* 1974)

Abstract—Doublet mixing cross sections for K(4^2P)–Ar and He and for Rb(5^2P)–He collisions have been measured, in flames at 1720 K. The ratio σ_{12}/σ_{21} was measured separately and was found to agree within 2 per cent with predictions derived from detailed balance. The experiments are compared with available semiclassical theoretical results.

INTRODUCTION

DOUBLET-mixing transitions in alkali atoms, induced by collisions with inert gas atoms, have drawn much attention recently, both experimentally[1–5] and theoretically.[6–10] GALLAGHER[3] has observed a strong temperature dependence for Rb(5^2P)– and Cs(6^2P)–inert-gas doublet-mixing cross sections, in the temperature range from 300 K to 900 K, which has been explained satisfactorily by NIKITIN and coworkers.[6–8] For the lighter alkalis, Na and K, a much weaker temperature dependence is predicted theoretically,[9,14,15] but no experiments have been done to check this prediction.

In this note, we report He– and Ar–mixing cross sections for K(4^2P)– and Rb(5^2P)–doublets, measured in flames at about 1720 K.

EXPERIMENTAL RESULTS

The apparatus and experimental method have been described previously.[11] Oxygen-rich H_2/O_2 flames with a noble gas as diluent are used to ensure a favourable ratio of mixing to quenching rate constants.[11] Previously reported cross sections for H_2O and O_2[11,12] are used to correct the measurements for contributions from these molecules. Since the He-contribution to the total mixing-rate constant appeared to be dominant, the uncertainty in the H_2O and O_2 cross sections has only a minor influence on the accuracy of our He-

Table 1. Doublet mixing cross sections as measured in flames at 1720 K. The ratios σ_{12}/σ_{21} were separately measured and were found to agree with detailed balance within 2 per cent

Collision partners	$\sigma_{21}(^2P_{3/2} \rightarrow {}^2P_{1/2})$ Å^2	$\sigma_{12}(^2P_{1/2} \rightarrow {}^2P_{3/2})$ Å^2
K(4^2P)–He	55 ± 15	105 ± 30
K(4^2P)–Ar	15 ± 10	30 ± 20
Rb(5^2P)–He	11 ± 4	18 ± 6

values. This is not true for Ar. resulting in a large error. The cross sections found are given in Table 1. The ratios σ_{12}/σ_{21} were measured[11] separately and independently and were found to agree with detailed balance within 2 per cent.

DISCUSSION

Figure 1 shows our value for $(\sigma_{21})_{Rb-He}$, together with the experimental data of GALLAGHER,[3] BEAHN *et al.*[1] and PITRE *et al.*[4] An exponential extrapolation of GALLAGHER's data to 1720 K gives good agreement with our measurements. The broken line (d) in Fig. 1 represents extrapolation of the low-temperature data, according to GALLAGHER's analysis of his experiments [equation (4) of Ref. (3)]. The discrepancy between the latter extrapolation and our experimental value at 1720 K may be readily explained by uncertainties in the fitting procedure used in Ref. (3).

Figure 2 shows our values for K(4^2P)–mixing, together with data of JORDAN and FRANKEN[2] and CHAPMAN and KRAUSE.[5] The temperature dependencies for Rb– and K–mixing cross sections are clearly different.

NIKITIN *et al.*[6–8] have developed a semiclassical theory for alkali–inert-gas doublet mixing. This process was described[6–8] by non-adiabatic transitions between a restricted set of adiabatic quasi-molecular potential-energy curves. Transitions are induced, either

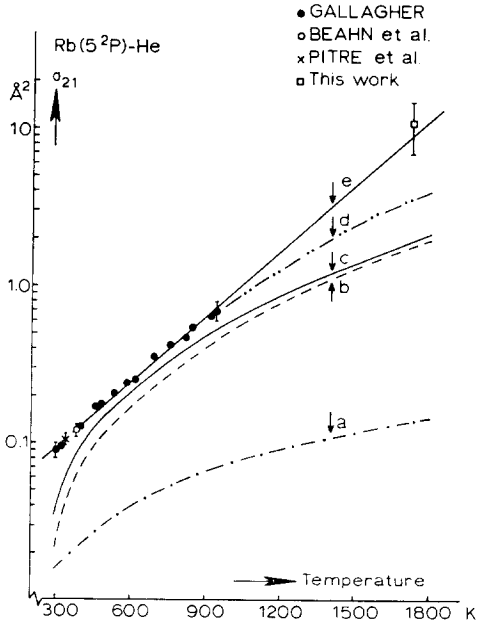

Fig. 1. Experimental and theoretical doublet mixing cross sections for Rb($5^2P_{3/2} \rightarrow 5^2P_{1/2}$) transitions induced by collisions with He-atoms, as a function of gas-temperature. The experimental values shown are those of GALLAGHER,[3] BEAHN *et al.*,[1] PITRE *et al.*[4] and our measurement. The curve *a* represents the theoretical cross section associated with a rotational-coupling mechanism, as derived by NIKITIN *et al.*,[8] curve *b* gives the cross section due to the radial-coupling mechanism,[6] whereas curve *c* gives the total cross section $(a+b)$. Curve *d* represents the extrapolation of low-temperature data according to GALLAGHER's analysis. Curve *e* gives the experimental temperature dependence with inclusion of our measurement. The experimental error in GALLAGHER's data is shown for the outermost points only.

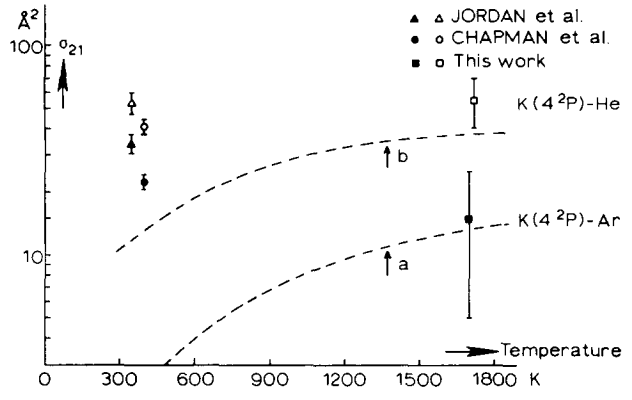

Fig. 2. Experimental and theoretical doublet-mixing cross sections for $K(4^2P_{3/2} \rightarrow 4^2P_{1/2})$ transitions, induced by collisions with He- and Ar-atoms, as a function of T. The experimental results of JORDAN *et al.*[2] and CHAPMAN *et al.*[5] are given together with our values for He and Ar.[12] Open symbols are for He, whereas closed symbols are for Ar. Curves *a* and *b* represent the theoretical cross section derived by NIKITIN,[6] for the radial-coupling mechanism, for Ar- and He- atoms, respectively.

at relatively large internuclear distances by the radial component of relative-motion of the collisions partners or, at relatively small internuclear distances, by the rotational component of relative motion. By making several additional assumptions, analytical expressions for the cross section were derived for both coupling mechanisms separately. The applicability of the theory is most seriously restricted by the condition that the collision proceeds adiabatically, i.e. the 'effective Massey parameters' γ_1 and γ_2, as defined by NIKITIN,[6,8] should be much larger than unity. For Rb–He, this condition is reasonably fulfilled for γ_1 at $T \leqq 1800$ K ($\gamma_1 \geqq 5$); but it is not fulfilled for γ_2. For K–He, neither condition is fulfilled, whereas for K–Ar the condition is only reasonably well met for γ_1 at $T \lesssim 400$ K.

In Fig. 1, we show the theoretical cross sections as predicted by Nikitin for the separate, as well as for the combined, mechanisms. In Fig. 2, we give only the theoretical cross section due to radial coupling since in these cases, the rotational coupling cannot be expected to give a correct description (see below). It appears from Fig. 1 that Nikitin's theory can explain the temperature dependence for Rb–He in the low-temperature region from 400 K upwards qualitatively. The deviation at higher temperatures may be due to the failure of the adiabatic assumption. This failure also explains why the theory does not describe the temperature dependence for K-mixing.

MASNOU-SEEUWS[9,13] has integrated the set of coupled differential equations obtained by Nikitin numerically, which makes the adiabatic criterion unnecessary. She has found that, for the $Na(3^2P)$–He mixing cross section, the neglect of rotational coupling underestimates the cross section by about a factor of two. The calculated cross section appeared to be virtually constant in a broad range of relative velocities corresponding to $T \approx 300$–2000 K.

The same conclusion may be drawn from the close-coupling calculations for Na–He, as performed by REID and DALGARNO.[14,15] Figure 2 shows that the experimental temperature dependence for $K(4^2P)$-mixing is similarly weak. Numerical calculations for $K(4^2P)$-mixing, as done for Na(3P)-mixing, are clearly derisable.

Acknowledgement—The author wishes to thank Dr. G. NIENHUIS for the many theoretical discussions and Prof. Dr. C. TH. J. ALKEMADE and Dr. P. J. TH. ZEEGERS for reading this manuscript carefully. The assistance of Mr. R. VENNINK in performing the experiments should also be mentioned.

REFERENCES

1. T. J. BEAHN, W. J. CONDELL and H. I. MANDELBERG, *Phys. Rev.* **141**, 83 (1966).
2. J. A. JORDAN and P. A. FRANKEN, *Phys. Rev.* **142**, 20 (1966).
3. A. GALLAGHER, *Phys. Rev.* **172**, 88 (1968).
4. J. PITRE, A. G. A. RAE and L. KRAUSE, *Can. J. Phys.* **44**, 731 (1966).
5. G. D. CHAPMAN and L. KRAUSE, *Can. J. Phys.* **45**, 753 (1966).
6. E. E. NIKITIN, *Opt. Spectrosc.* **22**, 379 (1967).
7. E. I. DASHEVSKAYA and E. E. NIKITIN, *Opt. Spectrosc.* **22**, 473 (1967).
8. E. I. DASHEVSKAYA, E. E. NIKITIN and A. I. REZNIKOV, *J. chem. Phys.* **43**, 1175 (1970).
9. F. MASNOU-SEEUWS, *J. Phys.* **B3**, 1437 (1970).
10. M. B. HIDALGO and S. GELTMAN, *J. Phys.* **B5**, 265 (1972).
11. P. L. LIJNSE, P. J. TH. ZEEGERS and C. TH. J. ALKEMADE, *JQSRT* **13**, 1033 (1973).
12. P. L. LIJNSE, J. C. HORNMAN, *JQSRT* **14**, 1079 (1974).
13. F. MASNOU-SEEUWS and E. ROUEFF, *Chem. Phys. Lett.* **16**, 593 (1972).
14. R. H. G. REID and A. DALGARNO, *Chem. Phys. Lett.* **6**, 85 (1970).
15. R. H. G. REID. *Abstr. VIIth I.C.P.E.A.C.*, 675 (1971).