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Cross sections for the Na(4D) → Na(4F) excitation energy transfer induced by collisions with He, Ar and Na atoms

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Abstract. The cross sections for the Na(4D) → Na(4F) excitation energy transfer induced by collisions with He, Ar and Na ground-state atoms have been measured. The sodium atoms in the 4D state have been produced by two-photon excitation using cw laser radiation at 578.89 nm. Within a model which takes into account collisional population and depopulation of the 4F level as well as radiative relaxation (direct or cascade) of the 3D, 4P, 4D and 4F states ending in the 3P level, the rate for the Na(4D) → Na(4F) collisional transfer turns out to be related to the ratio of the steady-state populations created in 3D and 4D states. They have been determined by measuring the fluorescence intensities of the 3D → 3P and 4D → 3P transitions. The measurements yield the following cross section values for those processes investigated: $\sigma^{\mathrm{Na-He}}_{\mathrm{4D}\to\mathrm{4F}} = (60 \pm 10) \times 10^{-16}$ cm^2, $\sigma^{\mathrm{Na-Ar}}_{\mathrm{4D}\to\mathrm{4F}} = (28 \pm 6) \times 10^{-16}$ cm^2 and $\sigma^{\mathrm{Na-Na}}_{\mathrm{4D}\to\mathrm{4F}} = (410 \pm 50) \times 10^{-16}$ cm^2, at $T \approx 630$ K.

1. Introduction

The cross sections for collisional mixing of sodium nd states with $l > 2$ states of the same n (l-mixing cross sections) due to collisions with noble gases have been investigated both experimentally and theoretically covering a wide range of n values. Experimental results, concerning He, Ne and Ar as collision partners, have been reported by Gallagher *et al* (1975, 1977). Since this work, no experimental investigations regarding these processes have been reported. The first theoretical investigations of the l-mixing processes in sodium, induced by collisions with noble gases, were by Gersten (1976), Olson (1977), Hickman (1978) and de Prunelé and Pascale (1979). These early results, comprising the cross sections for l-mixing induced by collisions with He, Ne and Ar, as well as numerous subsequent contributions, were recently reviewed by Gallagher (1994) and Beigman and Lebedev (1995).

The excitation transfer cross sections for the Na(nD) → Na(nF) processes induced by collisions with noble gases, have not yet been experimentally investigated in the case of $n = 4$. As for theoretical predictions, the cross sections for He which concern the case $n = 4$ have been reported in all the theoretical papers mentioned above. The existing results for the corresponding cross sections for Ar are less numerous and the calculated values are probably too high (Gersten 1976, de Prunelé and Pascale 1979).

The estimate of the cross section for the Na(4D) → Na(4F) energy transfer induced by collisions with sodium ground-state atoms was previously reported by Allegrini *et al* (1985). It was obtained within the frame of the experiment designed primarily to determine the cross section for the Na(3P) + Na(3P) → Na(4F) + Na(3S) energy-pooling process. As stated by Allegrini *et al* (1985), the cross section for the Na(4D) → Na(4F) transfer could

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not be determined with an error of less than ±50%, since the experiment was not suitable for the measurement of this particular transfer process.

This experiment is concerned exclusively with the Na(4D) → Na(4F) transfer. Helium, argon and sodium have been investigated as collisional partners. The cross section for the collisional mixing induced by sodium ground-state atoms has been determined with an improved accuracy (±12%) and the value obtained is more than two times smaller than the one formerly reported (both experiments were carried out at a similar temperature). To our knowledge, the cross sections for this process caused by collisions with He and Ar atoms are reported here for the first time. An assessment is given of how our results fit into the scheme of the existing experimental and theoretical cross sections for the *l*-mixing processes in sodium induced by collisions with the noble gases.

2. The Na(4D) → Na(4F) collisional excitation transfer

Figure 1 shows the partial term diagram of sodium. The energy levels involved in the determination of the collision rate for the Na(4D) → Na(4F) transfer, and the pumping scheme of the Na(4D) level, are indicated. The Na(4D) population was created by two-photon excitation from the Na(3S) ground state, while the population of the Na(4F) level arose from collisions with the perturbers. The depopulation channels for the Na(4D) level comprise 4D → 4F collisional transfer and radiative relaxation to the lower-lying 3P and 4P levels as shown in figure 1. The Na(4F) level decays radiatively to the Na(3D) and collisionally by back transfer to the Na(4D) level. The rate equations for the steady-state populations $N(4\mathrm{F})$, $N(4\mathrm{P})$ and $N(3\mathrm{D})$, subsequent to the two-photon excitation of the Na(4D) level, read as follows:

$$\frac{\mathrm{d}N(4\mathrm{F})}{\mathrm{d}t} = 0 = -A_{4\mathrm{F}}N(4\mathrm{F}) - DN(4\mathrm{F}) + CN(4\mathrm{D}) \qquad (1)$$

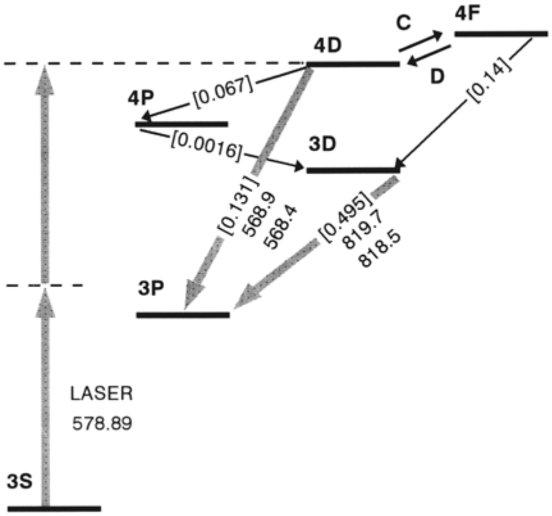

Figure 1. Partial term diagram of sodium. Energy levels involved in the determination of the collision rate for Na(4D) → Na(4F) transfer and the pumping scheme of the Na(4D) level are shown. The wavelength in nanometres and the spontaneous emission coefficients in 10^8 s^{-1} (numbers in brackets) for the transitions of interest are also indicated.

$$\frac{\mathrm{d}N(4\mathrm{P})}{\mathrm{d}t} = 0 = -A_{4\mathrm{P}}N(4\mathrm{P}) + A_{4\mathrm{D}\to 4\mathrm{P}}N(4\mathrm{D}) \tag{2}$$

$$\frac{\mathrm{d}N(3\mathrm{D})}{\mathrm{d}t} = 0 = -A_{3\mathrm{D}}N(3\mathrm{D}) + A_{4\mathrm{F}}N(4\mathrm{F}) + A_{4\mathrm{P}\to 3\mathrm{D}}N(4\mathrm{P}). \tag{3}$$

Here, $A_{4\mathrm{F}}$, $A_{4\mathrm{P}}$ and $A_{3\mathrm{D}}$ are the total spontaneous emission rates of the levels indicated by the corresponding subscript, $A_{4\mathrm{D}\to 4\mathrm{P}}$ and $A_{4\mathrm{P}\to 3\mathrm{D}}$ are the spontaneous emission rates for the 4D → 4P and 4P → 3D transitions, respectively, while C and D denote Na(4D) ↔ Na(4F) collisional mixing rates.

By solving the system of equations (1)–(3), we obtain:

$$\frac{N(3\mathrm{D})}{N(4\mathrm{D})} = \frac{A_{4\mathrm{F}}}{A_{3\mathrm{D}}}\frac{C}{A_{4\mathrm{F}} + D} + \frac{A_{4\mathrm{P}\to 3\mathrm{D}}}{A_{3\mathrm{D}}}\frac{A_{4\mathrm{D}\to 4\mathrm{P}}}{A_{4\mathrm{P}}}. \tag{4}$$

The populations of the 3D and 4D states were probed by measuring the fluorescence intensities of the lines corresponding to the $3\mathrm{D}_{3/2,5/2} \to 3\mathrm{P}_{3/2}$ ($\lambda_1 = 819.7$ *nm*) and $4\mathrm{D}_{3/2,5/2} \to 3\mathrm{P}_{3/2}$ ($\lambda_2 = 568.9$ *nm*) transitions. The fluorescence intensity of the spectral line corresponding to the $j \to i$ transition is $I = h\nu_{j\to i}N_jA_{j\to i}$, where $\nu_{j\to i}$ is the frequency of the line centre, N_j is the population of the upper state and $A_{j\to i}$ is the corresponding spontaneous emission coefficient. Since the populations of the $\mathrm{D}_{3/2}$ and $\mathrm{D}_{5/2}$ sublevels are in the ratio of their statistical weights (4:6), it follows that the fluorescence intensities of the λ_1 and λ_2 lines are $I_{\lambda_{(n-2)}} \propto N(n\mathrm{D})[0.4A_{n\mathrm{D}_{3/2}\to 3\mathrm{P}_{3/2}} + 0.6A_{n\mathrm{D}_{5/2}\to 3\mathrm{P}_{3/2}}]/\lambda_{(n-2)}$, where $n = 3$, 4 and $N(n\mathrm{D})$ represents the total population in the particular D level. Therefore, substituting the numerical values for the spontaneous emission coefficients from previous literature (Wiese *et al* 1969), and using the principle of detailed balance for the rates C and D ($C/D = (g_{4\mathrm{F}}/g_{4\mathrm{D}})\exp[-\Delta E/kT] = 1.3$ at $T \approx 630$ K), we obtain from equation (4) the following expression for the rate C:

$$C = 1.82 \times 10^7 \frac{\mathcal{R} - 0.0060}{0.968 - \mathcal{R}} \tag{5}$$

where $R = I_{819.7}/I_{568.9}$ is the ratio of the measured fluorescence intensities.

3. Experiment

The sodium vapours were produced in a resistively heated, T-shaped stainless-steal heat-pipe oven. Argon or helium was used as a buffer gas. The total pressure in the heat pipe was measured with a MKS Baratron manometer.

The sodium atoms were excited to the 4D state by two-photon excitation from the ground state using the 578.89 nm radiation from a single-mode, frequency stabilized ring-dye laser (Spectra Physics model 380 D, dye: Rh6G), pumped by an argon-ion laser (Spectra Physics model 2020). The wavelength of the dye-laser radiation was measured with a Burleigh wavemeter. The dye-laser beam, having a total power of 110 mW, was focused in the middle of the sodium-vapour column. The cross section of the beam in the focused region was 0.2 mm^2. The fluorescence from the excitation zone was observed at right angles to the laser beam propagating direction and analysed using a 1 m McPherson monochromator (slit width 100 μm) supplied with the RCA S-20 photomultiplier.

In order to measure the Na ground-state number density the dye laser was tuned to the wavelengths in the blue wing of the Na D2 line. For this purpose the laser beam was not focused and its power was reduced using neutral density filters down to 10 μW. The dye laser was scanned across the blue wing of the Na D2 line and the intensity transmitted through the sodium-vapour column of length $L = (7 \pm 1)$ cm was detected by a photodiode and recorded as a function of the wavelength. Applying the method described previously in Horvatic *et al* (1993) the sodium ground-state number density N_{Na} was determined from the set of measured values for the absorption coefficient $k(\lambda)$, according to the relation which holds for the blue wing of the Na D2 line :

$$N_{\mathrm{Na}} = \alpha\sqrt{k(\lambda)}\,\frac{\Delta\lambda}{\lambda}\left[\sqrt{1+\gamma\frac{\Delta\lambda}{\lambda}}\right]^{-1} \tag{6}$$

where $\alpha = 3.352 \times 10^{19}$ cm$^{-5/2}$, $\gamma = 543.33$, $\Delta\lambda$ is the detuning from the line centre and $k(\lambda)$ is measured in cm^{-1}. In the experiment, the Na ground-state number density varied from 4.7×10^{14} cm^{-3} to 2.3×10^{15} cm^{-3}. The accuracy of the N_{Na} is ±7%, and is mainly due to the error in vapour-column length determination.

With N_{Na} being determined in the former way, the temperature of the vapour was subsequently read off from the vapour pressure curve (Nesmeyanov 1963). During the measurements the temperature ranged from 595 to 635 K. These values were used in the evaluation of the Maxwellian mean relative velocity $\bar{v}$ of the colliding species. Taking into account the probable uncertainty in the vapour pressure curve, we have estimated the error in $\bar{v}$ to be less than ±2% (at typical experimental temperatures an uncertainty of ±20 K accounts for the stated error).

At each particular constant heating of the heat pipe, the pressure of the buffer was varied in the range 0.4–4 mbar. Since the heat pipe was not running in heat-pipe mode, the number density N_{ng} of the noble gas in the region of the sodium-vapour column was determined from the ideal-gas equation:

$$p = N_{\mathrm{Na}}kT + N_{\mathrm{ng}}kT \tag{7}$$

where k is the Boltzmann constant, p is the total pressure measured by the manometer, while the N_{Na} and T values are determined in the way described above.

4. Data analysis and results

With the dye laser being locked at the frequency of the two-photon Na(3S) → Na(4D) excitation, the fluorescence intensities of the $3D_{3/2,5/2} \rightarrow 3P_{3/2}$ and $4D_{3/2,5/2} \rightarrow 3P_{3/2}$ transitions were measured by scanning the monochromator over the 819.7 and 568.9 nm lines, respectively. Typical spectra are shown in figure 2. The fluorescence-intensity ratio $\mathcal{R} = I_{819.7}/I_{568.9}$ was measured as a function of both the sodium ground-state number density N_{Na} and the noble gas $N_{\mathrm{ng}}(\mathrm{ng} = \mathrm{Ar}, \mathrm{He})$ number density. At certain constant heatings of the heat pipe, the total pressure p was changed in the range 0.4–4 mbar by varying the buffer gas (Ar or He) pressure. The dependence of $\mathcal{R}$ on the pressure p, measured at several different heatings, is shown in figure 3 for argon and helium. The monochromator response at particular wavelengths has been accounted for in the displayed $\mathcal{R}$ values. The temperatures $\bar{T}$ assigned to the displayed curves represent the mean temperature value along the particular curve, the meaning of which is clarified in the following.

The measurement of each $\mathcal{R}$ ratio along the particular $\mathcal{R}$ versus p curve in figure 3 was accompanied by the measurement of the optical depth $k(\nu)L$ across the blue wing of the Na D2 line. The absorption measurements showed that, although the heating was constant, the $k(\Delta\nu)L$ observed at constant detuning $\Delta\nu$ changed with the variation of the buffer-gas pressure. This is to be expected as a consequence of either the change of the vapour-column length L or $k(\Delta\nu)$. The latter is due to a change of the Na ground-state number density corresponding to the temperature variation caused by the altered efficiency of heating. In

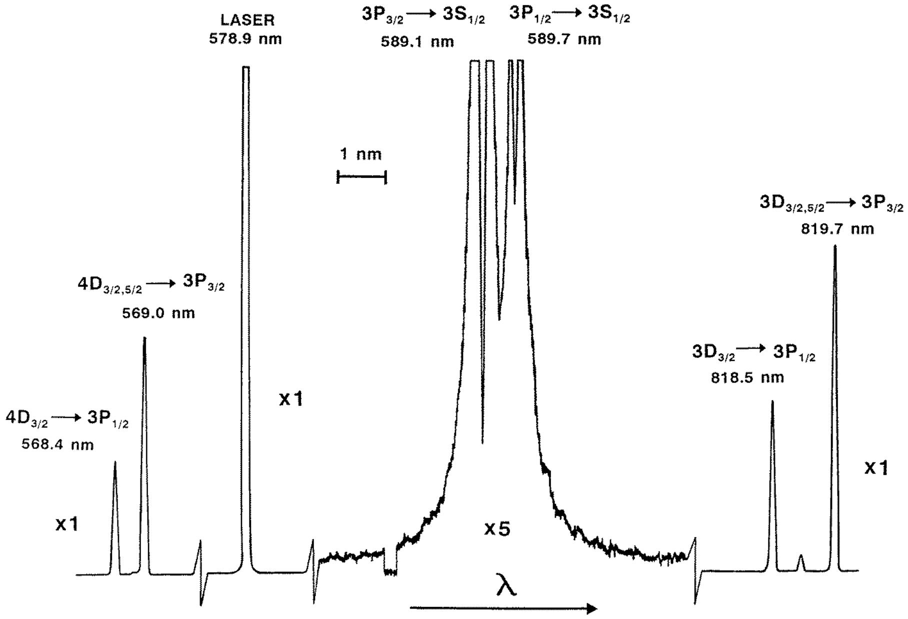

Figure 2. Typical fluorescence spectra obtained by scanning the monochromator, while the dye laser was locked at the frequency of the two-photon Na(3S) → Na(4D) transition. Note that the figure displays the raw spectra, i.e. the intensities do not comprise the correction for the spectral response of the system.

order to resolve between the two we did the following. The dye laser was tuned at a certain fixed detuning $\Delta\nu$ in the quasistatic blue wing of the Na D2 line and the optical depth $k(\Delta\nu)L$ was measured as a function of the pressure p. Afterwards the dye laser was tuned to pump sodium in the wing of the D1 line and the fluorescence of the D2 line wing was observed at the same detuning $\Delta\nu$ depending on the pressure p. In the quasistatic wing of the resonance line the absorption coefficient is proportional to N_{Na}^2. The same is also valid for the fluorescence intensity I_{res} in the resonant quasistatic wing since $I_{\mathrm{res}} \propto N_{\mathrm{Na}} N_{\mathrm{Na(3P)}}$, while $N_{\mathrm{Na(3P)}} \propto P_{\mathrm{laser}} N_{\mathrm{Na}}$, where P_{laser} is the pump power and $N_{\mathrm{Na(3P)}}$ is the atom number density of the excited 3P state. Therefore, if no change in the vapour-column length L is caused by variation of the buffer-gas pressure, the ratio $I_{\mathrm{res}}(\Delta\nu)/k(\Delta\nu)L$ should not exhibit pressure dependence. Indeed, no systematic trend of this ratio with respect to the pressure was observed and it was found that it can be regarded constant within a margin of ±5%. Accordingly, within the error stated, the observed change of the $k(\Delta\nu)L$ can be attributed solely to a change in $k(\Delta\nu)$. Furthermore, it means that the measurement of the $k(\nu)L$ across the wing of the line for each particular pressure p is sufficient to obtain the proper corresponding value of the sodium ground-state number density N_{Na} from equation (6). The accompanying value of the noble gas number density for each pair of N_{Na} and $\mathcal{R}$ values, measured along the curves displayed in figure 3, is determined according to equation (7) as explained in section 3. The temperature variation accompanying the change of the pressure along the particular $\mathcal{R}$ versus p curve was about ±7 K around the corresponding $\bar{T}$ value denoted in figure 3.

In analogy with the gas kinetics the collisional mixing rate is defined as a product $N\sigma\bar{v}$, where N is the number density of the perturbers inducing the excitation transfer, σ is the cross section for the particular transfer process and $\bar{v}$ is the mean relative velocity of the

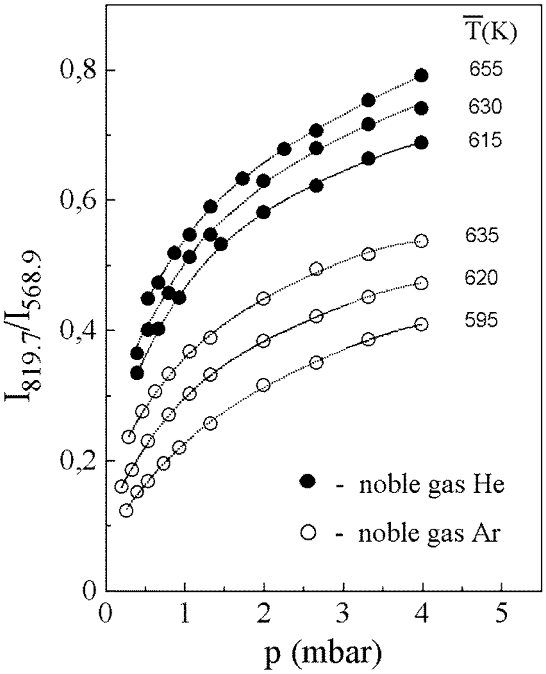

Figure 3. The fluorescence intensity ratio $I_{819.7}/I_{568.9}$ as a function of the total pressure p, measured at several different heatings. The results obtained with argon (open symbols) and helium (full symbols) as a buffer gas are displayed (dotted lines are only to guide the eye). The associated temperatures represent the mean temperature value corresponding to the particular curve (see text for detailed explanation).

colliding atoms. Here it is justified to use the mean Maxwellian relative velocity for $\bar{v}$, since as shown by Vadla *et al* (1987), though the two-photon excitation yields the velocity-selective population, the difference between the actual mean relative velocity of colliding partners and the Maxwellian one is negligible so far as the excitation occurs within a Doppler profile, which was fulfilled in this experiment.

Since the heat pipe was not running in the heat-pipe mode, the rate C includes contributions due to collisions between excited sodium atoms and both sodium and noble gas ground-state atoms. Namely,

$$C = N_{\mathrm{Na}}\sigma_{\mathrm{Na-Na}}\bar{v}_{\mathrm{Na-Na}} + N_{\mathrm{ng}}\sigma_{\mathrm{Na-ng}}\bar{v}_{\mathrm{Na-ng}} \qquad (8)$$

where N_{ng} denotes the number density of the noble gas.

The rates C were evaluated according to equation (5) using the intensity ratio data $\mathcal{R}$ shown in figure 3. At this point it is worth noting that the values of the intensity ratio amount to at most 0.8. The importance of this fact is evident bearing in mind that the expression (5) diverges for $\mathcal{R} = 0.968$. The relative error in the determination of the rate C increases as $\Delta C/C = [\Delta\mathcal{R}/\mathcal{R}]f(\mathcal{R})$, where $f(\mathcal{R}) = -0.962\mathcal{R}/[(\mathcal{R}-0.006)(\mathcal{R}-0.968)]$. Therefore, as the inset in figure 4 shows, despite the relative error in $\mathcal{R}$ being small ($\pm 2\%$), the relative error $\Delta C/C$ remains below the acceptable limit of $\pm 10\%$ only for $\mathcal{R}$ values below ≈ 0.8.

Since for each obtained C value the corresponding N_{Na}, N_{ng}, $\bar{v}_{\mathrm{Na-Na}}$ and $\bar{v}_{\mathrm{Na-ng}}$ values were determined in the way described above, it is possible to determine $\sigma_{\mathrm{Na-Na}}$ and $\sigma_{\mathrm{Na-ng}}$

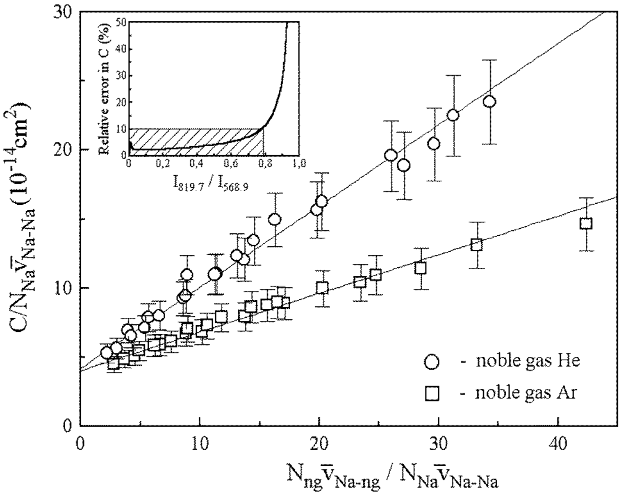

Figure 4. The rate C for the Na(4D) → Na(4F) excitation energy transfer induced by collisions with argon (□) and helium (○) divided by the corresponding sodium number density N_{Na} and relative velocity $\bar{v}_{\mathrm{Na-Na}}$ and plotted against the ratio $N_{\mathrm{ng}}\bar{v}_{\mathrm{Na-ng}}/N_{\mathrm{Na}}\bar{v}_{\mathrm{Na-Na}}$. In this plot the parameters of the straight line fit (intercept and slope) determine the cross sections $\sigma_{\mathrm{Na-Na}}$ and $\sigma_{\mathrm{Na-ng}}$, respectively.

from the following plot:

$$\frac{C}{N_{\mathrm{Na}}\bar{v}_{\mathrm{Na-Na}}} = \sigma_{\mathrm{Na-Na}} + \sigma_{\mathrm{Na-ng}}\frac{N_{\mathrm{ng}}\bar{v}_{\mathrm{Na-ng}}}{N_{\mathrm{Na}}\bar{v}_{\mathrm{Na-Na}}} \tag{9}$$

where the cross sections of interest, $\sigma_{\mathrm{Na-Na}}$ and $\sigma_{\mathrm{Na-ng}}$, represent the intercept and the slope of the straight line defined by equation (9). The results of measurements performed in argon and helium are shown in figure 4. The plotted error bars represent the total relative error in the determination of the quantity $C/N_{\mathrm{Na}}\bar{v}_{\mathrm{Na-Na}}$. The least-square fits through the data weighted by the plotted error bars yield the values $\sigma_{\mathrm{Na-Ar}} = (28 \pm 3) \times 10^{-16}$ cm^2 and $\sigma_{\mathrm{Na-He}} = (59 \pm 4) \times 10^{-16}$ cm^2 for the slopes of the displayed straight lines. Accounting for an uncertainty of ±10% in the abscissa values (for visual clarity the corresponding error bars are not plotted), the cross sections for the Na(4D) → Na(4F) excitation energy transfer induced by collisions with Ar and He atoms are found to be:

$$\sigma_{\mathrm{Na-Ar}} = (28 \pm 6) \times 10^{-16}\ \mathrm{cm}^2 \qquad \text{and} \qquad \sigma_{\mathrm{Na-He}} = (60 \pm 10) \times 10^{-16}\ \mathrm{cm}^2$$

respectively.

The measurements performed enable a double check of the cross section $\sigma_{\mathrm{Na-Na}}$ for the Na(4D) → Na(4F) energy transfer, caused by collisions with sodium atoms. Namely, the intercepts of the straight lines in figure 4 yield two independent results for the $\sigma_{\mathrm{Na-Na}}$ value, $\sigma_{\mathrm{Na-Na}} = (402 \pm 32) \times 10^{-16}$ cm^2 and $\sigma_{\mathrm{Na-Na}} = (419 \pm 40) \times 10^{-16}$ cm^2. Since the obtained $\sigma_{\mathrm{Na-Na}}$ data lie well within mutual error bars, we declare the cross section value $\sigma_{\mathrm{Na-Na}}$ as the arithmetic mean of the mentioned values, i.e.

$$\sigma_{\mathrm{Na-Na}} = (410 \pm 50) \times 10^{-16}\ \mathrm{cm}^2.$$

5. Discussion and conclusion

The excitation transfer cross sections for the $\mathrm{Na}(n\mathrm{D}) \rightarrow \mathrm{Na}(n\mathrm{F})$ processes induced by collisions with noble gases have not yet been experimentally investigated in the case of $n = 4$. However, for higher values of n, there are experimental results of Gallagher *et al* (1975, 1977). In these two papers the authors reported the cross sections σ_l for the collisional mixing of the sodium nd states with the $l > 2$ states of the same n (named 'l-mixing cross sections' by the authors), using He, Ne, and Ar as collision partners. In the case of He and Ne the cross sections were measured for $6 \leqslant n \leqslant 15$, while for Ar the range was $5 \leqslant n \leqslant 15$.

Theoretically, the l-mixing processes in sodium due to collisions with noble gases were investigated by Gersten (1976) (He: $4 \leqslant n \leqslant 6$; Ar: $4 \leqslant n \leqslant 7$), Olson (1977) (He, Ne: $4 \leqslant n \leqslant 20$; Ar: $5 \leqslant n \leqslant 20$), Hickman (1978) (He: $4 \leqslant n \leqslant 15$) and de Prunelé and Pascale (1979) (He, Ne, Ar: $4 \leqslant n \leqslant 20$).

Both experimentally and theoretically, the cross sections σ_l were found to rise sharply with increasing n up to $n = 10$–12, and then decrease for larger values of n. In the range $n \leqslant 10$, which is of interest for the present discussion, the cross sections were found to reflect the geometric size of the orbit of the of the excited Na atom, i.e. to increase as n^4. A satisfactory agreement between the measured and calculated σ_l values, especially for higher n values, was found. For the scope of this discussion it is sufficient to mention that the calculations are concerned with the problem of binary collision between the neutral perturber and the excited electron which is very weakly bound to the atomic core and perturbed by the interaction of the short-range character. Additionally, in order to make the problem tractable, some assumptions regarding electron–noble-gas scattering were made (see for instance Beigman and Lebedev 1995). In this way the correlation between l-mixing processes and the scattering of a free electron on the noble gas atom, at kinetic energies corresponding to those of the excited electron in the atomic-core field, is established. The kinetic energies E_n which concern the electron in sodium atoms excited in the states with $n = 4$–15 and $l > 2$, are in the low-energy limit, i.e. in the range between 0.06 eV and 0.85 eV ($E_n = 13.6/n^2$ eV). The relation to the low-energy electron scattering is introduced through a choice of the type of interaction in which standard electron–noble-gas scattering length L (Gersten 1976, Olson 1977) or effective scattering length L_{eff} (Hickman 1978) is involved ($L_{\mathrm{eff}} = [\sigma_{\mathrm{el}}(E_n)/4\pi]^{1/2}$, where $\sigma_{\mathrm{el}}(E_n)$ is the total elastic free-electron scattering cross section for the mean kinetic energy of the orbital motion). In the semiclassical model of de Prunelé and Pascale (1979) the actual energy dependence of the free-electron scattering cross sections averaged over the momentum distribution was taken into account. The approach involved in the papers by Gersten (1976) or Olson (1977) is less advantageous, since it in fact correlates the l-mixing cross section with the zero-energy electron scattering cross section $\sigma_{\mathrm{el}}(0) = 4\pi L^2$. If the electron scattering cross section in the low-energy range does not change much from its zero-energy value (as in the case of He and Ne; see O'Malley (1963), McEachran and Stauffer (1983a, b)), the scattering length L is a valid parameter to base the correlation upon. If, however, the electron scattering cross section curve exhibits the Ramsauer–Townsend effect, known to exist for electron–heavy-noble-gas scattering (here it concerns Ar), this approach might turn out to be inadequate in some aspects (see discussions in Hickman (1978), de Prunelé and Pascale (1979) and review articles by Gallagher (1994), Beigman and Lebedev (1995)).

In the case of He as a perturbing partner, there are four theoretical results for the $\mathrm{Na}(4\mathrm{D}) \rightarrow \mathrm{Na}(4\mathrm{F})$ transfer cross section for comparison with our results. The oldest result was given by Gersten (1976). Compared with his value of about 150×10^{-16} cm^2 our result is too small. The values given by Olson (1977) and Hickman (1978) are similar and amount to $\approx 40 \times 10^{-16}$ cm^2 (as read from the graph). In the paper by Olson (1977) there is a remark that the calculated cross section is a good representation of the Boltzmann-averaged cross section for 430 K, i.e. it is to be expected that the measured thermally averaged cross section at 430 K should be about 30% higher than the corresponding theoretical value. Since Hickman (1978) carried out the calculation for the same collision energy as Olson (1977), we presume this remark should also be applicable to Hickman's (1978) result. Bearing in mind that our experimental value $\sigma_{\mathrm{Na-He}} = (60 \pm 10) \times 10^{-16}$ cm^2 has been measured at 630 K, the agreement with the values of Olson (1977) and Hickman (1978) is acceptable. The calculations reported by de Prunelé and Pascale (1979) yielded the lower and upper limits to the cross section for the Na(4D) → Na(4F) transfer process, which are roughly 150×10^{-16} cm^2 and 600×10^{-16} cm^2, respectively. de Prunelé and Pascale (1979) stated, that for the lowest values of n their calculation should give values that are too large because the applied model probably underestimates the elastic processes in that case. Our $\sigma_{\mathrm{Na-He}}$ value seems to support this expectation.

The theoretical cross sections for Ar inducing the Na(4D) → Na(4F) transfer are available from Gersten (1976) and de Prunelé and Pascale (1979), who reported $\sim 170 \times 10^{-16}$ cm^2 and 130–500 $\times 10^{-16}$ cm^2, respectively. In view of the arguments above our $\sigma_{\mathrm{Na-Ar}}$ value is predictably smaller.

As for the relationship between the He and Ar l-mixing cross sections, the results of Olson (1977) and de Prunelé and Pascale (1979) show that for low n values ($4 \leqslant n \leqslant 6$–8) the σ_l for Ar is smaller than for He, while for higher values of n this relationship is inverted. The calculations of Gersten (1976) yielded a cross section for Ar higher than for He, regardless of the n value. The finding of Olson (1977) and de Prunelé and Pascale (1979) are to be expected from the aspect of the low-energy electron scattering cross sections σ_{el}. Namely, only in a narrow electron-energy range close to zero the σ_{el} for Ar is higher than the σ_{el} for He (O'Malley 1963, McEachran and Stauffer 1983a, b, Ferch *et al* 1985, Weyhreter *et al* 1988), while the opposite is fulfilled in the whole electron-energy range between 0.034 and 0.85 eV, or equivalently for $20 \geqslant n \geqslant 4$. When averaged over the quantum-mechanical velocity distribution of the Rydberg electron the cross sections σ_{el} are higher for Ar than for He only when $n > 12$ (de Prunelé and Pascale 1979). Thus, regarding the theoretical predictions of Olson (1977) and de Prunelé and Pascale (1979) as well as the correlation with low-energy electron scattering cross sections, the relationship between our cross sections ($\sigma_{\mathrm{Na-Ar}} < \sigma_{\mathrm{Na-He}}$) for sodium 4D–4F mixing is in accordance with the expectations.

An additional argument in favour of the l-mixing cross section for Ar being smaller than the one for He in the case of $n = 4$, concerns the relative velocity of colliding species. The peculiarity of 4D–4F mixing in comparison to all other nd–nf pairs of levels with $n > 4$, regards the energy separation ΔE between the levels involved. Namely, the Na(4D) and Na(4F) states are separated by 39.8 cm^{-1} (Wiese *et al* 1969), which is more than the fine-structure splitting $\Delta E_{\mathrm{fs}} = 17$ cm^{-1} of the Na(3P$_J$) states. The energy separations of all higher nd–nf states are close to (20 cm^{-1} for $n = 5$) or smaller (for $n > 5$) than the ΔE_{fs}. In contrast to the collisions inducing fine-structure mixing of Na(3P$_J$) levels, which are entirely nonadiabatic, the collisions responsible for the 4D–4F mixing in sodium should (given the typical thermal energies of the collisions) behave more like those, for instance, inducing the fine-structure mixing between 4P$_J$ states in potassium, which occur nearly adiabatically. Theoretical investigations of Nikitin (1965) showed that if the adiabatic limit is applicable to the collision, the cross section of the energy transfer, for given energy defect ΔE, depends on the relative velocity between the alkali atom and the noble gas and the characteristic collision radius at which the transition between different potential curves occurs. Since the characteristic collision radii of Na*–He and Na*–Ar are expected to be similar (Nikitin 1965), the magnitudes of the cross sections reflect the relationship between the corresponding relative velocities (higher velocity implies greater cross section). Thus, from this aspect too, the mutual relationship between the cross sections for the Na(4D) + He, Ar → Na(4F) + He, Ar processes reported here meets expectations.

In the following we will assess how our data fit into the scheme of the existing experimental results of Gallagher *et al* (1977), which represent extension and refinement of their initial (Gallagher *et al* 1975) measurements. Although in both papers the authors declared that the σ_l increased as n^4 for $n \leqslant 10$, the single analysis of the functional dependence was presented in the initial paper, and that one concerned only the case of argon where the σ_l had been shown to exhibit $\sim n^{3.8(5)}$ growth. However, subsequent analysis is possible due to the numerical values with the corresponding error bars listed in the paper. When fitted to a power law (using the error bars as a weight), the results reported by Gallagher *et al* (1977) show that the l-mixing cross sections increase as $n^{2.6(5)}$, $n^{2.8(5)}$ and $n^{3.8(5)}$ in the case of He, Ne and Ar, respectively. The extrapolation of the fits down to $n = 4$ yields values of about 160×10^{-16} cm^2 and 145×10^{-16} cm^2 for He and Ar, respectively. Compared with the extrapolated values, our results $\sigma_{\mathrm{Na-He}} = 60 \times 10^{-16}$ cm^2 and $\sigma_{\mathrm{Na-Ar}} = 28 \times 10^{-16}$ cm^2 lie too low.

In the case of helium, the inclusion of our $\sigma_{\mathrm{Na-He}}$ datum in the set of σ_l values obtained by Gallagher *et al* (1977) has a very agreeable consequence. Namely, in that case, when fitted to a power law, the cross sections exhibit $\sim n^{3.7(4)}$ dependence (see figure 5). Granted that, due to the inclusion of result for $n = 4$, the agreement with the expected $\sim n^4$ behaviour is improved without increasing uncertainty in the exponent, we may say that our $\sigma_{\mathrm{Na-He}}$ cross section fits reasonably in the previous experimental results and different theoretical models which are well founded for helium.

As for the Ar results, the existing data (Gallagher *et al* 1977) alone reproduce n^4 dependence quite good. The inclusion of our datum in the set to be fitted only spoils the picture, since the resulting dependence goes as $\sim n^{5.7}$. To all appearances our $\sigma_{\mathrm{Na-Ar}}$ cross

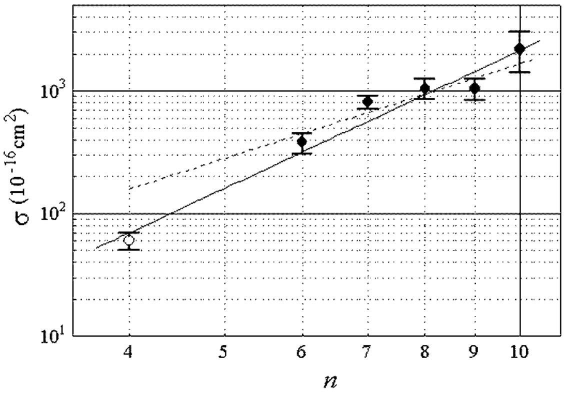

Figure 5. The cross sections for collisional mixing of sodium nd states with the $l \geqslant 2$ states of the same n due to collisions with He, plotted against n. Full symbols: the results of Gallagher *et al* (1977); open symbol: present investigation; dotted line: power fit through the data of Gallagher *et al* (1977) exhibiting $\sim n^{2.6(5)}$ cross section growth; full line: power fit through the set of data comprising the result of the present investigation displaying $\sim n^{3.7(4)}$ cross section dependence.

section is simply too small to fit into the results obtained by Gallagher *et al* (1977). For all investigated values of n, the σ_l cross sections measured by Gallagher *et al* (1977) increased in sequence from Ne to He to Ar. Our results explicitly contradict that finding in the part which concerns He and Ar, since we have obtained $\sigma_{\mathrm{Na-He}} > \sigma_{\mathrm{Na-Ar}}$. Given all that has been said in the preceding discussion regarding this particular point, the relationship between σ_l for He and Ar observed by Gallagher *et al* (1977) for low n values, opposes the predictions mentioned above from all discussed points of view. This disagreement, as well as the one regarding our $\sigma_{\mathrm{Na-Ar}}$ value being apparently too small, could be explained if, for some reason, their Ar cross sections happen to be too high.

The initial investigations of these l-mixing processes in sodium due to collisions with the noble gases were reported in the paper by Gallagher *et al* (1975). Two years later (Gallagher *et al* 1977), the investigation was extended to higher values of n, the initial measurements were refined and the accuracy of the results was improved (±20% compared with the former ±40%). In fact, only the data for He and Ne were reinvestigated, while the Ar results were simply quoted from the initial paper. The results for Ne, for instance, underwent a decrease in value by a factor of 2.5–4, incompatible with either the former or the latter error bar declared. The data for He suffered a minor alteration (decrease) when remeasured. We cannot speculate on the origin of these changes, because no comment, regarding the differences in the Ne case at least, was given in the paper by Gallagher *et al* (1977). No experimental difficulties associated exclusively with the measurements involving Ne, which would make them less reliable than Ar data, were reported in the paper by Gallagher *et al* (1975). The subsequent experiment (Gallagher *et al* 1977) employed the same experimental method as previously, the only difference being the more powerful N_2 laser. Given the fact that the Ar cross sections were not reinvestigated, while those for He and Ne exhibited lower values in the refined measurements, our presumption about Ar cross sections being too high might not be completely unfounded. Therefore, we feel that the l-mixing cross sections in sodium for Ar inducing the transfer deserve to be reinvestigated experimentally in the range of low n values.

As already mentioned in the introduction, the meticulous measurements of the cross section for the Na(4D) → Na(4F) energy transfer process induced by collisions with the sodium ground-state atoms have not been performed up to now. An estimate of 1000×10^{-16} cm^2 was reported previously by Allegrini *et al* (1985) accompanied with 50% indeterminacy since the experiment was not suitable for the measurement of this particular transfer process. Our value $\sigma_{\mathrm{Na-Na}} = 410 \times 10^{-16}$ cm^2 is determined with much greater accuracy (±12%) and, in fact, results from two independent experiments which yielded consistent cross section values, thus substantiating the reliability of the result. The relatively large uncertainty of the result by Allegrini *et al* (1985) still does not help to overlap the mutual error bars.

Theoretical calculation of the cross section for this process has not been reported in the literature so far. The Na(4D) → Na(4F) transfer induced by the sodium ground-state atoms is much more complicated than in the case of the noble-gas perturbers due to the presence of ^{3}P resonance in e^-–Na scattering. This concerns both of the two different points of view, one involving the free electron model and the other based on coupled-channel calculations. The ionic curve correlated to the $\mathrm{Na}^-[^3\mathrm{P}]$ state is responsible for the avoided crossing at $R_c = 13.7 \times 10^{-8}$ cm in the $^3\Pi$ curves (Magnier *et al* 1994) stemming from the $\mathrm{Na(3S)} + \mathrm{Na(4D, F)}$ asymptotes. Furthermore, there is an avoided crossing within the $^3\Sigma$ manifold (located at 12.2×10^{-8} cm) corresponding to an ionic state which could probably be identified as a mixture of Na^- resonances lying above the ^{3}P resonance (Magnier *et al* 1994). Regarding the interatomic distances at which these avoided crossings occur, the rule of thumb estimate of the cross section value $\sigma = \pi R_c^2/2$ yields $\sim 300 \times 10^{-16}$ cm^2. Calculations employing a more thorough approach to the problem are currently being considered.

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References

Allegrini M, Gabbanini C, Moi L and Colle R 1985 *Phys. Rev.* A **32** 2068

Beigman I L and Lebedev V S 1995 *Phys. Rep.* **250** 95

Ferch J, Granitza B, Masche C and Raith W 1985 *J. Phys. B: At. Mol. Phys.* **18** 967

Gallagher T F 1994 *Rydberg Atoms* (Cambridge: Cambridge University Press)

Gallagher T F, Edelstein S A and Hill R M 1975 *Phys. Rev. Lett.* **35** 644

——1977 *Phys. Rev.* A **15** 1945

Gersten J I 1976 *Phys. Rev.* A **14** 1354

Hickman A P 1978 *Phys. Rev.* A **18** 1339

Horvatic V, Movre M, Beuc R and Vadla C 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 3679

Magnier S, Aubert-Frécon M, Bouty O, Masnou-Seeuws F, Millie Ph and Ostrovsky V N 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 1723

McEachran R P and Stauffer A D 1983a *J. Phys. B: At. Mol. Phys.* **16** 255

——1983b *J. Phys. B: At. Mol. Phys.* **16** 4023

Nesmeyanov A N 1963 *Vapour Pressure of the Elements* (New York: Academic)

Nikitin E E 1965 *J. Chem. Phys.* **43** 744

Olson R E 1977 *Phys. Rev.* A **15** 631

O'Malley T F *Phys. Rev.* **130** 1020

de Prunelé E, Pascale J 1979 *J. Phys. B: At. Mol. Phys.* **12** 2511

Vadla C, Lawrenz J and Niemax K 1987 *Opt. Commun.* **63** 293

Weyhreter M, Barzick B, Mann A and Linder F 1988 *Z. Phys.* D **7** 333

Wiese W L, Smith M W and Miles B M 1969 *Atomic Transition Probabilities* (NSRDS-NBS 22) vol 2 (Washington DC: US Govt Printing Office)