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Sodium 3P fine-structure excitation transfer induced by collisions with rubidium and caesium atoms

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Abstract. The cross sections for the excitation energy transfer in the collisional processes $Na^*(3P_{1/2})+M(nS_{1/2})\leftrightarrow Na^*(3P_{3/2})+M(nS_{1/2})$, M being ground-state Rb ($n=5$) or Cs ($n=6$) atom, have been measured by laser fluorescence method. With either of the two sodium 3P fine-structure states optically excited, the intensity ratio of the sensitized to direct fluorescence was measured. The polarization effects due to partially polarized and anisotropic direct fluorescence were investigated. The measured cross sections ($T=530$ K) for the sodium 3P fine-structure excitation transfer induced by collisions with Rb are: $\sigma(\frac{1}{2}\rightarrow\frac{3}{2})=170$ Å^2 and $\sigma(\frac{3}{2}\rightarrow\frac{1}{2})=94$ Å^2, with an overall accuracy of 20%. The corresponding values in the Cs case are: $\sigma(\frac{1}{2}\rightarrow\frac{3}{2})=140$ Å^2, $\sigma(\frac{3}{2}\rightarrow\frac{1}{2})=83$ Å^2. The theoretical calculations reveal the decisive role of the dipole-quadrupole interaction. The obtained values are in satisfactory agreement with the experiment only if both the dipole–dipole and dipole–quadrupole interactions are taken into account, while the calculations involving the dipole–dipole term alone yield the cross section values which are as much as one order of magnitude lower than the experimentally observed ones.

1. Introduction

Collision processes involving excited atomic states have been studied for decades and these investigations led to basic understanding of atomic structure. One of the phenomena occurring in these processes is the excitation energy transfer taking place either between different atomic states of an atom due to the collisions with similar or dissimilar ground-state perturbers or from an excited atom to a ground-state collision partner of a different kind. Numerous experimental and theoretical papers in this area published up to 1975 have been summarized by Krause (1975). The body of existing experimental data in this field is of very variable accuracy and comprises an often fortuitous selection of collision species. This concerns especially the early years of these investigations due to the limitations of the available experimental techniques. The possibilities introduced by the development of laser spectroscopy have enabled more precise measurements thus prompting renewed interest in these processes. As for the theoretical aspect, calculations of the cross sections for the collisionally induced excitation energy transfer require reliable knowledge of the interatomic potentials involved and careful treatment of the collision dynamics. Since the determination of the interatomic potentials by inversion of the experimentally obtained cross sections is difficult if not impossible, the theoretical results are of great importance for interpretation of the experimental results and understanding of the basic nature of these processes, even when the agreement with the measured values is poor.

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A great deal of the investigations in this area have been related to the excitation energy transfer occurring in the collisions of alkali atoms (Krause 1975). They are very suitable for experimental investigations because their resonance lines are in a convenient spectral range and their vapours can be easily generated in cells. Studies usually concern the determination of the total (thermally averaged) cross sections, but there are significant discrepancies among the experimental result of different groups. In addition, often the theoretical cross sections for excitation transfer are much smaller than the experimental values. In particular, for mixed alkali systems these discrepancies can be of orders of magnitude. On the other hand, due to their simple hydrogen-like structure, alkali atoms are also convenient for theoretical investigations of interatomic interaction and one would expect that calculated cross sections could be obtained with reasonable accuracy.

The present work is part of the systematic investigation of the collisional excitation energy transfer in mixed alkali vapours (Knezovic *et al* 1992, Vadla *et al* 1992a, b Veza *et al* 1992, Horvatic *et al* 1993). It concerns collisionally induced transitions between the fine-structure components of the sodium first excited level due to collisions with rubidium or caesium atoms. The experiment has been carried out using the laser fluorescence method and comprises investigation of the polarization effects. Also we present the results of theoretical calculations which are in very good agreement with the measured values. The presented theoretical approach suggests that the previous calculations for similar processes (Krause 1975), resulting in values considerably different from the experimental findings, might have oversimplified the treatment of the long-range potentials or on the other hand have paid attention to interactions which seem to be of no crucial importance.

To our knowledge there are no data in the literature regarding rubidium inducing fine-structure mixing in sodium, while in the case of caesium as a perturber there is the result published by Harris and Lewis (1982). They have reported a result which is roughly two times greater than we have obtained and the possible causes of the discrepancy are discussed in section 5.

2. Experimental and method

The experimental set-up is shown in figure 1. Alkali vapours were produced in the cylindrical Pyrex glass cell, containing high-purity Rb or Cs metal (with the inevitable sodium fraction being present) in its side-arm. In the course of the experiments the fluorescence cell temperature was kept constant at 530 K, while the side-arm temperature was changed (from 450 K to 490 K and from 465 K to 505 K in the case of Rb and Cs, respectively). The temperature range covered was limited from below by the minimum of the measurable sensitized fluorescence and from above by the requirement for optical thinness of the sodium resonance lines as well as for absence of trapping effects^{10}. Accordingly, the highest sodium atom number density never exceeded $2\times10\ \mathrm{cm}^{-3}$, which was controlled by measuring the laser absorption of the Na D lines. The rubidium and caesium atom number densities were determined from white-light absorption measurements in the blue wings of the self-broadened D2 lines (Horvatic *et al* 1993). In the investigated temperature range the Rb and Cs atom number densities reached up to at most $1.6\times10^{15}\ \mathrm{cm}^{-3}$ and $4.2\times10^{15}\ \mathrm{cm}^{-3}$, respectively.

The sodium atoms were excited to the $3P_{1/2}$ or $3P_{3/2}$ state by a cw single-mode, frequency stabilized ring dye-laser (Spectra Physics model 380D, dye: RhG6), pumped by an argon-ion laser (Spectra Physics model 2020). The attenuated laser beam (about 50 μW, 2 mm in diameter) passed through the cell parallel to the cell window (z-axis, see figure 1) at the distance of about 5 mm. The fluorescence was observed at right angles (x-axis, figure 1) to the laser beam propagating direction, using a 1 m McPherson monochromator (slit width 200 μm, band pass 0.2 mm) with the RCS-20 photomultiplier.

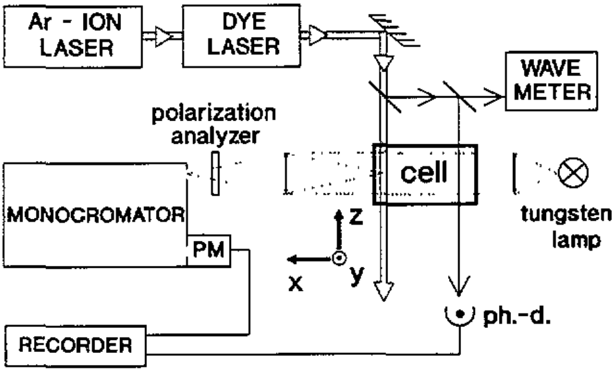

Figure 1. Experimental set-up; the coordinate system (x, y, z) indicates the directions relevant for the polarization effect analysis (see the end of section 2).

With the laser frequency being scanned over either of the two sodium D lines, the broad-band adjusted monochromator was tuned at both the wavelength of the collisionally induced (sensitized) and the directly pumped line, thus providing data on integral spectrally unresolved fluorescence intensities. The sensitized-to-direct fluorescence intensity ratio, corresponding to the case when the Na D1 line is optically excited is labelled $\eta_C = I_{\text{sens}}(\text{D2})/I_{\text{dir}}(\text{D1})$. The analogous intensity ratio in the case of direct excitation of the Na D2 line is denoted by $\eta_D = I_{\text{sens}}(\text{D1})/I_{\text{dir}}(\text{D2})$.

The data analysis has been based on a simple three-level model which involves the sodium ground state and the 3P resonance doublet with relevant collisional rates C and D for the $3P_{1/2} \rightarrow 3P_{3/2}$ and $3P_{3/2} \rightarrow 3P_{1/2}$ processes, respectively. By solving the steady-state equations for the collisionally populated levels one finds:

$$\frac{N_{\text{sens}}(3P_{3/2})}{N_{\text{dir}}(3P_{1/2})} = \frac{C}{A_{3/2} + D} \tag{1}$$

$$\frac{N_{\text{sens}}(3P_{1/2})}{N_{\text{dir}}(3P_{3/2})} = \frac{D}{A_{1/2} + C}. \tag{2}$$

Here N_{sens} and N_{dir} are the population densities of the collisionally and optically excited levels, respectivley, while A_J $(J = \frac{1}{2}, \frac{3}{2})$ denotes the spontaneous emission rate for the $3P_J \rightarrow 3S_{1/2}$ transition. In analogy with the gas kinetics, fine-structure collisional mixing rates C and D are of the form $\sigma v N$ where v is the mean relative velocity of the colliding atoms, N is the number density of the atoms inducing the transfer and σ is the corresponding cross section.

Assuming the optically thin conditions and the absence of the radiation trapping ($A_{3/2} = A_{1/2} = A$), the fluorescence intensity ratios reduce to the population density ratios, i.e.

$$\eta_C=\frac{C}{A+D} \tag{3}$$

$$\eta_D=\frac{D}{A+C}. \tag{4}$$

By combination of equations (3) and (4) and using the measured values for the intensity ratios η, perturber number density N and relative velocity v, one obtains the investigated cross sections $\sigma_C=\sigma(\frac{1}{2}\rightarrow\frac{3}{2})$ and $\sigma_D=\sigma(\frac{3}{2}\rightarrow\frac{1}{2})$.

From the general features of the fluorescence radiation it follows that the relaxation of the collisionally populated states will result in an isotopic and unpolarized emission, while the direct fluorescence due to the optical excitation by a linearly polarized laser beam is expected to be polarized and anisotropic. In order to estimate the polarization effects present in the intensity ratios η_C and η_D, the measurements were performed for two different orientations of the polarization vector of the incident laser beam with respect to the direction of the observation (x-axis, see figure 1). In the first case the vector of the electromagnetic field was in the y direction (orthogonal to the direction of observation), while in the second case it was oriented parallel to the direction of observation, i.e. along the x-axis. For both cases the resulting fluorescence light, the sensitized as well as the direct, was analysed by the polarization analyser placed in front of the monochromator entrance slit. For each particular case of laser polarization the measurements have been performed for two different orientations of the polarizer with respect to the incoming laser beam direction (z-axis). In that way two components of the fluorescence radiation were determined: in a direction parallel (z-axis) and perpendicular (y-axis) to the laser beam propagation. The corresponding sensitized-to-direct fluorescence ratios are labelled with two superscripts. The first (x or y) denotes the direction of the laser beam polarization, while the second one ($\perp$ or $\|$) indicates the orientation of the analyser with respect to the laser beam incident direction.

3. Data analysis and results

The measured values of the sensitized-to-direct fluorescence ratios plotted against the Rb and Cs number densities are shown in figures 2 and 3, respectively. In the case when the Na($3P_{1/2}$) level is directly excited, the values of the intensity ratios η_C measured at one particular perturber atom density show no sensitivity to the variation of either the orientation of the polarization vector of the laser beam or the orientation of the polarization analyser. These data, comprising $\eta_C^{x,\perp}$, $\eta_C^{x,\|}$, $\eta_C^{y,\perp}$, $\eta_C^{y,\|}$ values, are labelled simply by η_C. In contrast to the latter, in the case of the Na($3P_{3/2}$) level being directly excited, the spatial distribution of the observed fluorescence intensities differs significantly depending on the direction of the laser beam polarization. In consequence the obtained η_D data split into two groups, one denoted by η_D^* (corresponding to the (y, $\|$) case) and the other labelled η_D^{**} which comprises $\eta_D^{x,\perp}$, $\eta_D^{x,\|}$, $\eta_D^{y,\perp}$ values. The statistical accuracy of the presented η values is about 10%. Including the uncertainty in the measured perturber number density (at most 10%, see Horvatic *et al* 1993) and taking into account the possible relatively small trapping effects, we have estimated the overall accuracy to be about 20%.

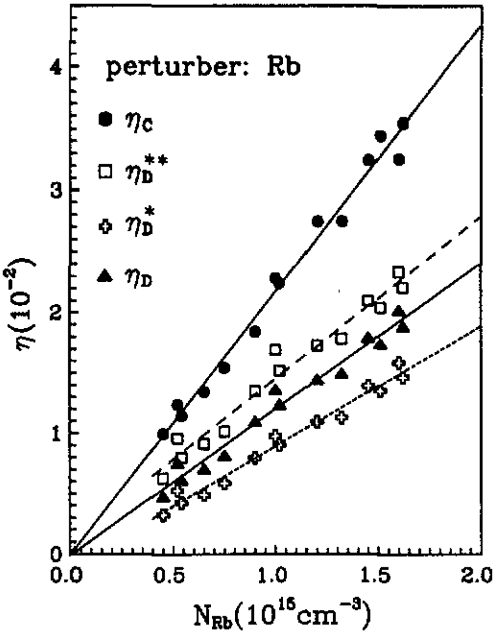

Figure 2. Sensitized to direct fluorescence intensity ratios plotted against rubidium number density. η_C (comprising $\eta_C^{x,\perp}$, $\eta_C^{x,\parallel}$, $\eta_C^{y,\perp}$, $\eta_C^{y,\parallel}$ data), the ratios obtained in the case of the directly excited Na($3P_{1/2}$) level. η_D^{*} (corresponding to the (y, $\parallel$) case) and η_D^{**} (comprising $\eta_D^{x,\perp}$, $\eta_D^{x,\parallel}$, $\eta_D^{y,\perp}$ values), the ratios obtained in the case of direct excitation of the Na($3P_{3/2}$) level. Here $\perp$ and $\parallel$ denote the orientation of the polarization analyser with respect to the propagation direction of the laser beam (z-axis, see figure 1), x or y being the directions of the laser beam polarization orientation. η_D, values obtained with polarization influence taken into account (see text).

The features of the obtained experimental data regarding the influence of the laser beam polarization orientation are in accordance with the theoretical predictions, i.e., the well known angular distribution of the dipole radiation. Namely, the direct fluorescence of the D1 line always exhibits spatial isotropy due to the fact that it corresponds to the transition between two levels with the same total angular momentum $J=\frac{1}{2}$. On the other hand, for the D2 line which corresponds to the transition $J=\frac{3}{2}\rightarrow J=\frac{1}{2}$, there exists pronounced polarization anisotropy. Although the hyperfine interaction strongly depolarizes the emitted light due to the precession of the electronic angular momentum J prior to the spontaneous emission (Walkup *et al* 1982), the resulting polarization is still significant. For a weak monochromatic incident beam of linearly polarized laser photons ε_L and linearly polarized scattered photons ε_S, the scattered light intensity I is given by:

$$I=\frac{I_T}{8\pi}\,[1+\beta P_2(\varepsilon_L\cdot\varepsilon_S)]. \tag{5}$$

Here $P_2(\varepsilon_L\cdot\varepsilon_S)$ is the second Legendre polynomial $P_2(\cos\theta)=(3\cos^2\theta-1)/2$, while I_T is the total scattered intensity. Parameter β which is proportional to the excited-state electronic alignment is simply related to the usual linear polarization degree

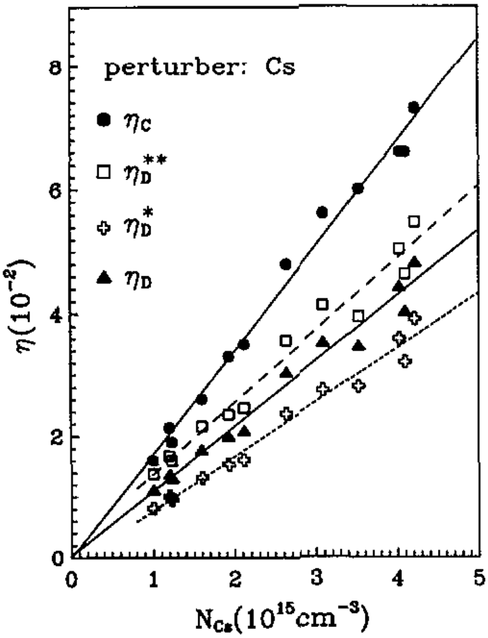

Figure 3. Sensitized to direct fluorescence intensity ratios plotted against caesium number density. The explanation of the symbols and labels is the same as in figure 2.

$P=(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ by the expression:

$$\beta=\frac{4P}{3-P}. \tag{6}$$

Applying expression (5) to the geometry in our experiment, one obtains:

$$I^{y,\perp}=I^{x,\parallel}=I^{x,\perp}=\frac{I_T}{8\pi}\left[1-\frac{\beta}{2}\right] \tag{7}$$

$$I^{y,\parallel}=\frac{I_T}{8\pi}\left[1+\beta\right] \tag{8}$$

which provides an evident explanation of the observed difference between the η_D^* and η_D^{**} data. As one can see from figures 2 and 3 in the case of the directly excited D1 line, the straight line representing the least-square fit through η_C data aims at the origin. In contrast, the corresponding straight lines for the η_D^* and η_D^{**} intersect the ordinate above and below the origin, respectively, reflecting the additional depolarization due to collisional processes. The depolarization rate depends on the perturber number density and as shown by Ballagh and Cooper (1977), in the case when collisional line broadening parameter, which is proportional to the perturber number density, is much larger than the natural line width, the polarization anisotropy disappears. For instance in the case of the rubidium being perturber, we have found that the polarization degree P decreases from 0.25 for the lowest to 0.15 for the highest investigated rubidium number density.

Obviously, due to the absence of polarization effects the data for the η_C are more reliable for the determination of the cross sections for the investigated excitation energy transfer. With the approximation $\eta_C \ll 1$, i.e. $D \ll A$ which meets our experimental conditions, equation (3) yields the expression for the cross section σ_C:

$$\sigma_C = \frac{A\eta_C}{vN_p}. \tag{9}$$

Using the value for A given by Hansen (1984) and the measured values for η_C, N_p and v, one obtains the following values for the collisional cross sections:

$$\sigma_C^{Rb} = 170 \text{ Å}^2$$

for the $Na^*(3P_{1/2}) + Rb(5S_{1/2}) \rightarrow Na^*(3P_{3/2}) + Rb(5S_{1/2})$ process, and

$$\sigma_C^{Cs} = 140 \text{ Å}^2$$

for the $Na^*(3P_{1/2}) + Cs(6S_{1/2}) \rightarrow Na^*(3P_{3/2}) + Cs(6S_{1/2})$ process. For the sodium resonance doublet the principle of detailed balance predicts $\sigma_C/\sigma_D = 2\exp(-24.5/T)$ which, for the typical temperature in our experiment (530 K), yields $\sigma_C/\sigma_D = 1.91$. Consequently the calculated values for σ_D^{Rb} and σ_D^{Cs} would be 90 Å^2 and 75 Å^2, respectively. Using the raw data for η_D^* and η_D^{**}, burdened by the polarization effects, one can obtain the values for the corresponding ratios σ_C/σ_D of about 2.2 and 1.5, respectively, i.e. above and below the expected value. Nevertheless the polarization effects can be accounted for by applying equations (7) and (8) to the set of measured η_D^* and η_D^{**} values. It follows that η_D is related to the measured ratios through:

$$\eta_D = \frac{3\eta_D^* \eta_D^{**}}{2\eta_D^* + \eta_D^{**}}. \tag{10}$$

The obtained η_D values plotted against the Rb and Cs number densities are displayed in figures 2 and 3, respectively. The straight lines representing the least-square fits through the η_D data now aim at the origin. Using a relation analogous to expression (9) one obtains the collisional cross section to be:

$$\sigma_D^{Rb} = 94 \text{ Å}^2$$

for the $Na^*(3P_{3/2}) + Rb(5S_{1/2}) \rightarrow Na(3P_{1/2}) + Rb(S_{1/2})$ process, and

$$\sigma_D^{Cs} = 83 \text{ Å}^2$$

for the $Na^*(3P_{3/2}) + Cs(6S_{1/2}) \rightarrow Na^*(3P_{1/2}) + Cs(6S_{1/2})$ process. The above values for σ_D yield the ratios σ_C/σ_D of 1.8 (perturber: Rb) and 1.7 (perturber: Cs). In both cases, the difference with respect to the prediction of the principle of detailed balance falls fairly within the error limits already stated.

Strictly speaking, the cross sections obtained include contributions for the collisions between the excited sodium atoms and both sodium and rubidium (or caesium) ground state atoms present in alkali vapour. In principle, there is also a possible contribution due to the interaction with the residue of the noble gas (argon) atoms which remain after evacuating the glass cells (up to 10^{-5} Torr). Nevertheless, using the cross section values for the sodium fine-structure excitation mixing induced Na*–Na (Huennekens and Gallagher 1983) and Na*–Ar collisions (Krause 1975), one finds these contributions to be a few orders of magnitude lower than those due to either Na*–Rb or Na*–Cs collisions.

4. Theoretical approach

We consider an alkali atom A in the first excited P state and the perturbing alkali atom B in the ground state. Neglecting the fine-structure in the perturber states, the long-range pattern for the system $A^*(P_J)+B(S_{1/2})$ is of simple form (Vadla and Niemax 1984, Movre and Beuc 1985). There are three groups of the potentials, one with $\Omega=0^+, 0^-, 1$, stemming from the $P_{1/2}$ asymptote, and the other two with $\Omega=0^+, 0^-, 1$ and $\Omega=1, 2$ stemming from the $P_{3/2}$ asymptote. The Hamiltonian matrix in diabatic basis of atomic product states for pairs $0^+, 0^-$ or 1 potentials (the other 1, 2 states remain uncoupled) is given by:

$$H_{11}=U_0-\frac{\Delta\varepsilon+V}{2} \tag{11}$$

$$H_{22}=U_0+\frac{\Delta\varepsilon+V}{2} \tag{12}$$

$$H_{12}=H_{21}=\sqrt{2}V. \tag{13}$$

Here the $P_{1/2}$ and $P_{3/2}$ states are labelled 1 and 2, respectively, $\Delta\varepsilon$ is the fine-structure splitting of the considered P_J level, while the potentials U and V are given by:

$$U_0=\frac{\Delta\varepsilon}{2}+\frac{V^\Sigma+V^\Pi}{2} \tag{14}$$

$$V=\frac{V^\Sigma-V^\Pi}{3} \tag{15}$$

where V^Σ and V^Π are the adiabatic potentials obtained with the fine-structure of the P_J level being neglected. In the long-range region the potentials are well described by the multipole expansion:

$$V=C_6R^{-6}+C_8R^{-8}+\dots \tag{16}$$

Here R is the internuclear distance and C_n are constants according to expression (15) given by:

$$C_n=\frac{C_n^\Sigma-C_n^\Pi}{3}. \tag{17}$$

A simplified semiclassical treatment of a two-state collision problem leads to the following coupled equations for the probability amplitudes $c_1(t)$ and $c_2(t)$ for the two states labelled 1 and 2 (Child 1974):

$$i\hbar\frac{d}{dt}c_1=H_{11}c_1+H_{12}c_2 \tag{18}$$

$$i\hbar\frac{d}{dt}c_2=H_{21}c_1+H_{22}c_2 \tag{19}$$

with the initial conditions $|c_2(t=-\infty)|=1$, $c_2(t=-\infty)=0$. The time dependence of the matrix elements H_{ij} is introduced assuming a straight-line trajectory

$$R(t)=\sqrt{b^2+v^2t^2} \tag{20}$$

where b is the impact parameter and v is the mean relative velocity of the colliding atoms. The cross section σ is determined according to the formula:

$$\sigma=2\pi\int_0^\infty P(b)b\,\mathrm{d}b \tag{21}$$

with $P(b)=|c_2(t=+\infty)|^2$. The U_0 part of H_{ij} leads to the common phase of c_i, and for the problem at hand, the set equations (18) and (19) is fully equivalent to

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}a_1=\frac{\Delta\varepsilon+V}{2}a_1+\sqrt{2}Va_2 \tag{22}$$

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}a_2=\sqrt{2}Va_1+\frac{\Delta\varepsilon+V}{2}a_2 \tag{23}$$

with $|a_i(t)|^2=|c_i(t)|^2$.

The numerical calculation of the cross sections was performed using the values for C_n constants published by Bussery *et al* (1987). The transformation of their results in accordance with the definition of the C_n constants used here (relation (17)) results in the following values for the Na(3P$_J$) + Rb(5S$_{1/2}$) system: $C_6=3.43\times10^{-31}\ \mathrm{s^{-1}\,cm^6}$, $C_8=-4.04\times10^{-45}\ \mathrm{s^{-1}\,cm^8}$. The corresponding values for the Na(3P$_J$) + Cs(6S$_{1/2}$) case are: $C_6=2.59\times10^{-31}\ \mathrm{s^{-1}\,cm^6}$, $C_8=-4.17\times10^{-45}\ \mathrm{s^{-1}\,cm^8}$. In the first approximation, taking the dipole–dipole term only, the calculation for either of the perturbers (Rb or Cs) yields a value for the cross section which is lower than 20 Å^2. The inclusion of the dipole–quadrupole term substantially influences the results. The values obtained are significantly larger, thus being in excellent agreement with the experimental data. With the C_8 term included, the results for σ_C are:

$$\sigma_C^{\mathrm{Rb}}=151\ \text{Å}^2$$

for the Na* + Rb and

$$\sigma_C^{\mathrm{Cs}}=142\ \text{Å}^2$$

for the Na* + Cs interaction. The values are related to the mean relative velocities which correspond to the temperature in our experiment (530 K). The influence of the dipole–quadrupole term on the calculated cross sections is illustrated in figure 4. The transition probability for the Na*(3P$_{1/2}$)→Na*(3P$_{3/2}$) transfer due to collisions with ground-state Cs atoms is displayed as a function of the impact parameter within the region from 7 Å to 12 Å. With the dipole–quadrupole terms included the function $P(b)$ begins to be significant at distances below 11 Å. Otherwise, without this term the probability is almost negligible in the same region, remaining low even at much smaller (down to 4 Å) distances. However, for values $b<4$ Å, where it begins to oscillate with maximal amplitude, the assumed form of the potential (C_6/R^6) is not applicable at all.

The importance of dipole–quadrupole terms in describing Na*(3P$_J$)—other alkali systems was shown by Vadla and Niemax (1984) via lineshape measurements of the sodium D lines. In the view of their investigation one can also conclude that the electrostatic interaction is valid for internuclear distances down to about 7 Å, which additionally confirms the reliability of the presented results.

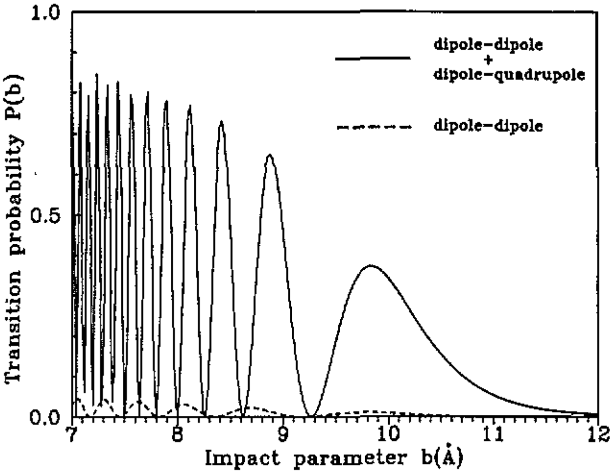

Figure 4. The transition probability for the $Na^*(3P_{1/2}) \rightarrow Na^*(3P_{3/2})$ transfer due to collisions with ground-state Cs atoms displayed as a function of the impact parameter. Full curve, the result obtained for both the dipole–dipole and the dipole–quadrupole terms being included. Broken curve, the result obtained when only the dipole–dipole interaction is considered.

5. Discussion and conclusion

To our knowledge there are no available data in the literature on the cross sections for fine-structure mixing between sodium $3P_J$ states due to collisions with rubidium atoms. In the case of caesium as the perturber there are data given by Harris and Lewis (1982) who reported values about two times larger than we have obtained. Except for the polarization measurements, in both experiments the same method (laser fluorescence) was applied, but the experimental conditions were somewhat different what may be the cause of the discrepancy of the results. Harris and Lewis (1982) performed measurements covering the Cs number density in the range from 5×10^{15} to $3 \times 10^{16}\,cm^{-3}$ whereas in our experiment the highest value has been about $4 \times 10^{15}\,cm^{-3}$. Although they pointed out the high purity (99.98%) of the caesium used, precise information about the sodium number density in their experiment is missing. The caesium we have used was several times redistilled and its vapour contained sodium in the ratio 5×10^{-6} which, according to our experience, cannot be significantly lowered by further distillation. Therefore we suppose that the caesium purity in the experiment of Harris and Lewis (1982) was not higher than in ours. Consequently, we suppose that they worked in a range of higher sodium number densities (between 5×10^{10} and $10^{11}\,cm^{-3}$), where trapping effects are non-negligible. Moreover, if our assumption is correct, according to Holstein (1951), under such conditions one can expect about 1.5 to 2 times lower effective spontaneous emision rate for the sodium D lines, what reflects itself directly in greater measured values of the cross sections.

Figure 5 shows the relationship between cross sections σ_C and the fine-structure splitting of the first resonance levels of alkali atoms colliding with ground-state caesium atoms. The data were obtained at different temperatures, but comparison makes sense because the corresponding temperatures lie in a relatively narrow range (520 ± 50 K). As one can see, the data for K*–Cs (Knezovic *et al* 1992), Rb*–Cs (Vadla *et al* 1992a),

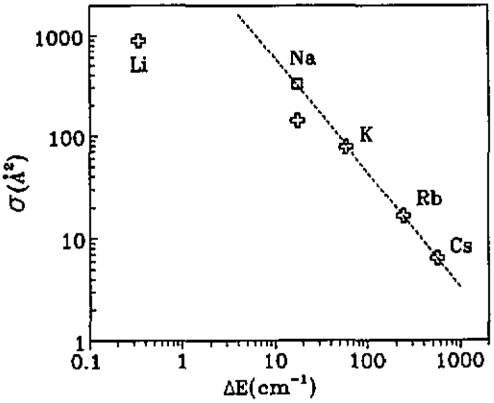

Figure 5. The relationship between the cross sections for the $M^*(nP_{1/2}) + Cs(6S_{1/2}) \rightarrow M^*(nP_{3/2}) + Cs(6S_{1/2})$ process (M = Li (Vadla *et al* 1992b), Na (□, Harris and Lewis 1982; ✥, present result), K (Knezovic *et al* 1992). Rb (Vadla *et al* 1992a), Cs (Czajkowski and Krause 1965)) and the fine-structure splitting of the first resonance levels for alkali atoms.

and Cs*–Cs (Czajkowski and Krause 1965) fall on a straight line. In the Na*–Cs case, the result obtained by Harris and Lewis (1982) also lies on the same line, while our result, being a factor of two smaller, lies below. On the other hand the Li*–Cs (Vadla *et al* 1992b) cross section represents a clear exception from the assumed 'straight-line' rule. Such general behaviour resembles that found for alkali–noble gas and alkali-similar alkali pairs. In the former cases, Li* and Na* collide with noble gas atoms 'suddenly', but other alkalis tend towards the 'adiabatic' limit, leading to a decrease of the cross sections at temperatures $T < 600$ K (Krause 1975). In the suddent limit the time scale for the collision τ_c is short compared to the time scale of the transition $\hbar/\Delta E$ and the transition probabilities are large. The opposite, adiabatic limit leads to less efficient transitions. These adiabatic trends can be correlated with the exponential energy gap law $\exp(-\Delta E/kT)$. For Li and Na, the energy gaps are so small compared to thermal translational energies that exponential damping is not important. Furthermore, as pointed out by Lewis (1980) in discussing the trends of the cross sections of fine-structure transitions for collisions between like atoms, when the typical collision time τ_c is compared to $\hbar/\Delta E$ for sodium, it is to be expected that the cross section is more likely determined by time-of-flight considerations. The deviation of our result from systematic behaviour can be understood in that way too.

The agreement between the presented results for the measured and calculated cross sections can be regarded as excellent, especially bearing in mind the rather significant discrepancies between theory and experiment in this field. As pointed out before, the calculations including only the dipole–dipole term give values of the cross sections about one order of magnitude lower than the experimental findings. The values that we have used for C_n constants, published by Bussery *et al* (1987) fit with our experimental results better than those given by Vadla and Niemax (1984). The former are also supposed to be more accurate, since they have been calculated in a larger basis. Unfortunately, Bussery *et al* (1987) did not discuss the possible uncertainty of their values, but in order to get more insight into the accuracy of our calculations of the cross sections, we have varied the C_6 and C_8 constants in an interval of ±20% and ±30%, respectively. These variations have resulted in values of σ_C^{Rb} ranging from 110 Å^2

to 161 Å^2. The corresponding values of σ_C^{Cs} have fallen in the interval between 136 Å^2 and 149 Å^2. Thus, the poorer agreement (although within the declared error bar) between the calculated and measured cross sections in the Na*-Rb case may be accounted for by the more pronounced sensitivity of the theoretical values to the choice of the C_n values. This can additionally confirm our conclusion that in the case of collisions between excited sodium atoms and rubidium or caesium ground-state atoms, the fine-structure mixing of the sodium first resonance level is caused by a long-range potential. As already found for the broadening of sodium D lines (Vadla and Niemax 1984), the investigated mixing process is also essentially determined by the dipole–quadrupole electrostatic interaction.

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