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Electron capture in K^+ ion collisions with Na(4d)

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Abstract. Close-coupling calculations have been performed for the $K^+ + Na(4d)$ system for laboratory energies in the range 0.3–3.5 keV. Total cross sections for electron capture from the different magnetic substates of the 4d manifold are compared with existing experimental data. The predicted dependence of the capture cross section on the magnetic quantum number of the initial state is interpreted in terms of the probability of finding the 4d electron close to the collision plane. We also comment on the difference between choosing the quantization axis to be parallel or perpendicular to the beam axis.

1. Introduction

In recent years the electron capture process in collisions of ions with excited target atoms has been studied experimentally as well as theoretically. All but a few cases, however, have been directed towards capture from excited p-states. Experimental studies of electron capture from different magnetic substates of d-orbitals have been done by Campbell *et al* (1990), who measured relative capture cross sections for the $K^+ + Na(4d)$ system and, more recently, by Wörmann *et al* (1993), who studied collisions between Ar^+ ions and Na Rydberg d states. At lower energies, Robinson *et al* (1990a, b) and Driessen *et al* (1991) have studied the excitation of laser-excited $Ca(4p^2\,{}^1D_2)$ and $Ca(4s4f\,{}^1F_3)$ states in thermal collisions with rare-gas atoms. There are no careful theoretical studies for collisions between ions and laser-excited target atoms in the d states. In this paper, we have chosen to investigate the $K^+ + Na(4d)$ system theoretically. We compare the theoretical results with the experiment of Campbell *et al* (1990) where cross sections for capture from the different magnetic substates of Na(4d) were reported.

The following section briefly describes the theoretical approach, while the comparison and analysis of experimental and theoretical results are done in section 3. In section 4 we comment on existing data for related collision systems. Concluding comments are given in section 5.

2. Theory

In our theoretical model, the $K^+ + Na(4d)$ collision is treated as a one-electron system in a time-dependent two-centre potential, taking the effect of the core electrons in each atom into account by using model potentials. The model potential for each atom is of the form $V_A(r) = -1/r - ((Z_A - 1)/r + \alpha_A r)\exp(-\gamma_A r)$, where Z_A is the charge of the nucleus A and α_A and γ_A are fitting parameters. The parameters are varied until the eigenenergies obtained from the model potential are in good agreement with the experimental energies for

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the first few excited states of the atom. For Na and K we found $\alpha_{Na} = 85.0$, $\gamma_{Na} = 4.3$ and $\alpha_K = 83.7$, $\gamma_K = 2.9$ in atomic units, respectively.

The calculation of electron capture cross sections is carried out within the semiclassical impact parameter approximation where the time-dependent electronic wavefunction is expanded in terms of travelling atomic orbitals on each collision centre, see Fritsch and Lin (1991). Galilean invariance is ensured by including a plane-wave electronic translational factor (ETF) on the projectile states.

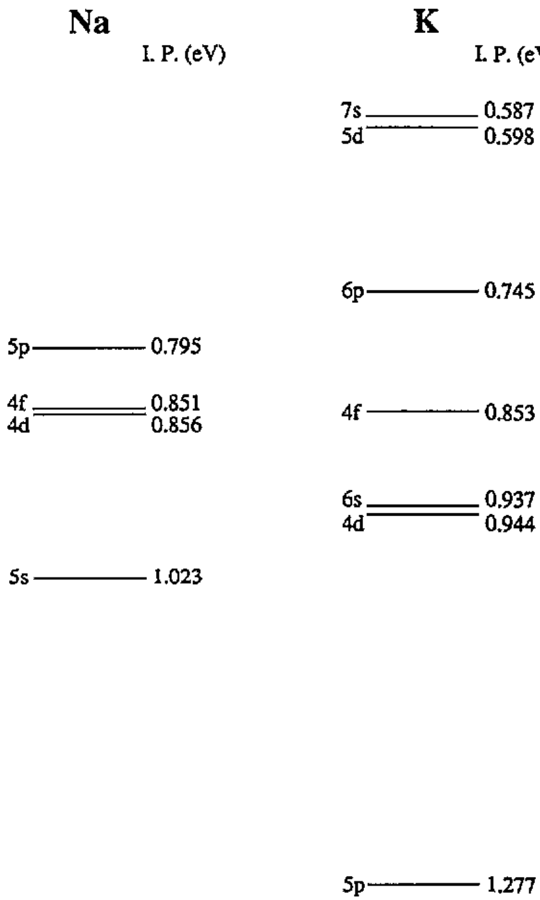

Figure 1. Energy levels diagram for Na and K based on experimental data.

The complication of the present collision system lies in the fact that there are many states, both on the target and on the projectile, which are nearly degenerate with the initial Na(4d) state (see figure 1). Thus the number of states that should be included in the close coupling calculation is quite large. In the present calculation the basis set consists of the 5s, 4d, 4f and 5p Na states and the 4–9s, 4–9p, 4d, 5d and 4f states of K, making a total of 16 Na and 41 K states. The Na states are obtained by diagonalizing the model Hamiltonian within a set of seven s, four p, two d and one f Slater orbitals. In the same way we have obtained the K states using ten s, nine p, four d and one f Slater orbitals. This procedure gives eigenenergies that differ from experimental energies within at most a few percent, except for the K(9s) and K(9p) states, which are pseudo states with energies 0.224 and 0.138 au respectively.

3. Results

The discussion of the results is divided into two subsections. In the first part only theoretical data are presented, while a comparison of experimental and theoretical data is given in the second part.

3.1. Theoretical results

In this section we look for a possible pattern in the dependence of the electron capture cross section on the magnetic quantum number m of the initial target state, with m being defined with respect to the beam axis. We also examine the dependence of the final-state distribution on m with the hope that it will reveal more details about the capture process.

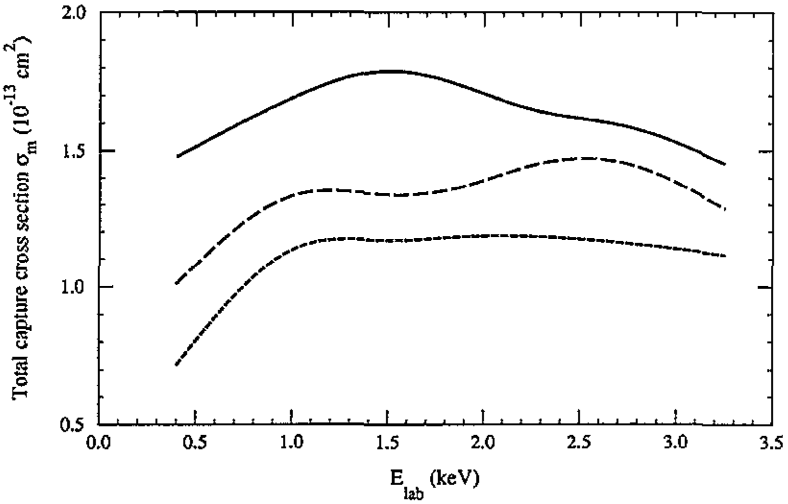

Figure 2. Total cross section σ_m for capture from different magnetic substates, $|m|$, as function of laboratory energy. $|m|$ is defined with respect to the beam axis. Full curve, $|m| = 0$; long dashes, $|m| = 1$; short dashes, $|m| = 2$.

The total cross section $\sigma_{|m|}$ for capture from the magnetic substates $|m| = 0$, 1 and 2 of the Na(4d) manifold is shown in figure 2 as a function of projectile energy in the 0.5–3.2 keV region. The calculations predict that the cross section decreases as $|m|$ is increased. Since the magnetic quantum number, m, is defined with respect to the beam axis (z axis in figure 3(a)) the cylindrical symmetry allows the capture cross section to be calculated by $\sigma_{|m|} = 2\pi \int b P_{|m|} \, db$, where the capture probability $P_{|m|}(b)$ refers to a specific collision plane, e.g. the $+x, z$ halfplane in figure 3(a). Typically $P_{|m|}$ is about the same for all ms for impact parameters in the range 0–40 au, while for larger impact parameters the ordering $P_0 > P_1 > P_2$ appears (not shown), and thus gives rise to the m dependence of $\sigma_{|m|}$ seen in figure 2. This pattern has also been observed by Toshima and Lin (1994) for the $H^+ + H(4fm)$ system. One might speculate that the more likely it is to find the electron close to the collision plane, e.g. the xz plane in figure 3(a), the more likely capture is and hence the bigger the capture cross section is (an idea that has been discussed previously by Toshima and Lin (1994) and by Lundsgaard and Lin (1992)). In figure 3(b) the probability $\wp_{|m|}(h)$ of finding the electron within a distance less than h from

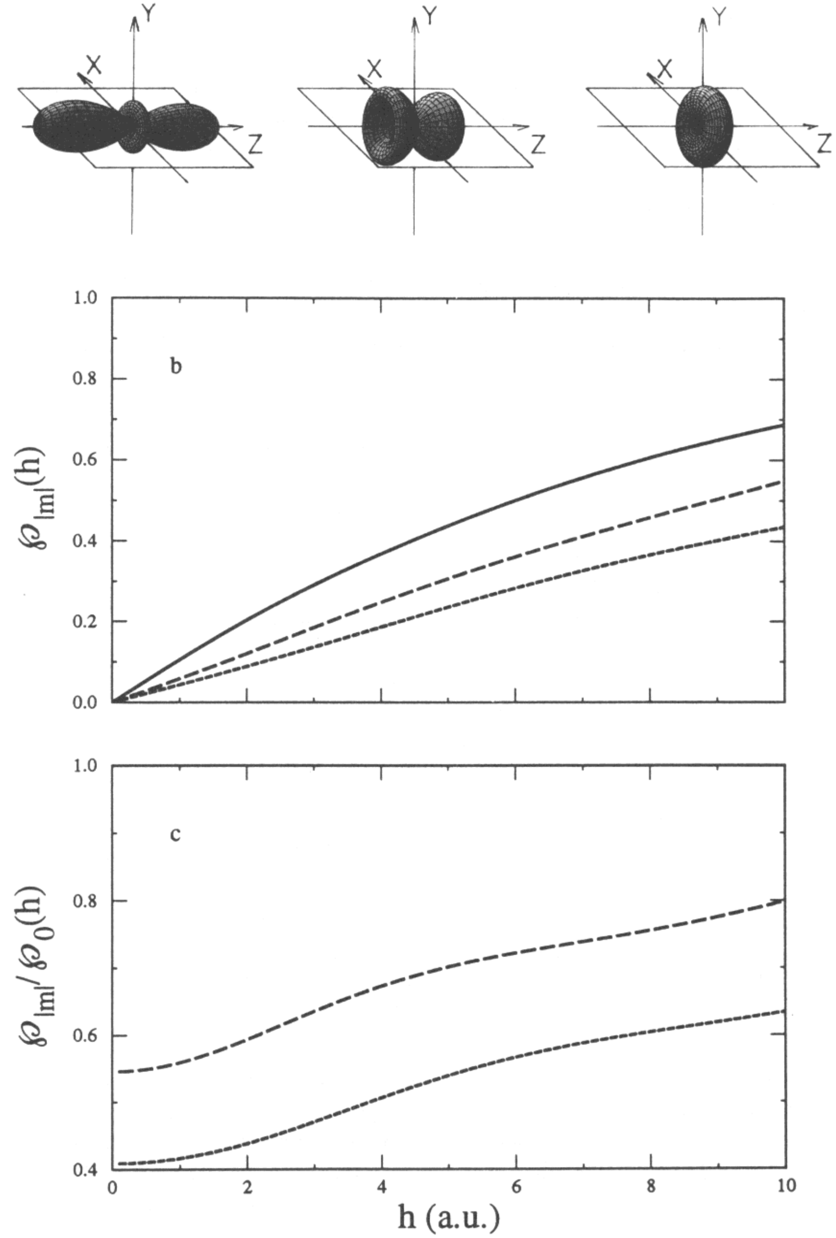

Figure 3. (a) The angular distribution of the 4dm states, m increasing by one from 0 to 2 when going from left to right. In the experiment by Campbell *et al* (1990) the beam is moving along the quantization axis (z axis). (b) The probability, $\wp_{|m|}$, of finding the electron within a distance h from the collision plane (e.g. the xz plane): full curve, $|m| = 0$; long dashes, $|m| = 1$; short dashes, $|m| = 2$. (c) The ratio of $\wp_{|m|}$ to $\wp_0$: long dashes, $|m| = 1$; short dashes, $|m| = 2$.

the xz plane (see figure 3(a)), which is taken to be the collision plane, is plotted. We notice that for all h the probability $\wp_{|m|}(h)$ is a decreasing function of m just as the capture cross sections $\sigma_{|m|}$ are. In an attempt to make a more quantitative comparison between $\sigma_{|m|}$ and $\wp_{|m|}(h)$ we show the ratio $\wp_{|m|}(h)/\wp_{m=0}(h)$ in figure 3(c). We find that these ratios are close to the corresponding $\sigma_{|m|}$ ratios and, for the velocity region studied here, we might at least partially attribute the dependence of $\sigma_{|m|}$ on m to the distribution of the electron cloud with respect to the collision plane used in the calculation of $P_{|m|}$.

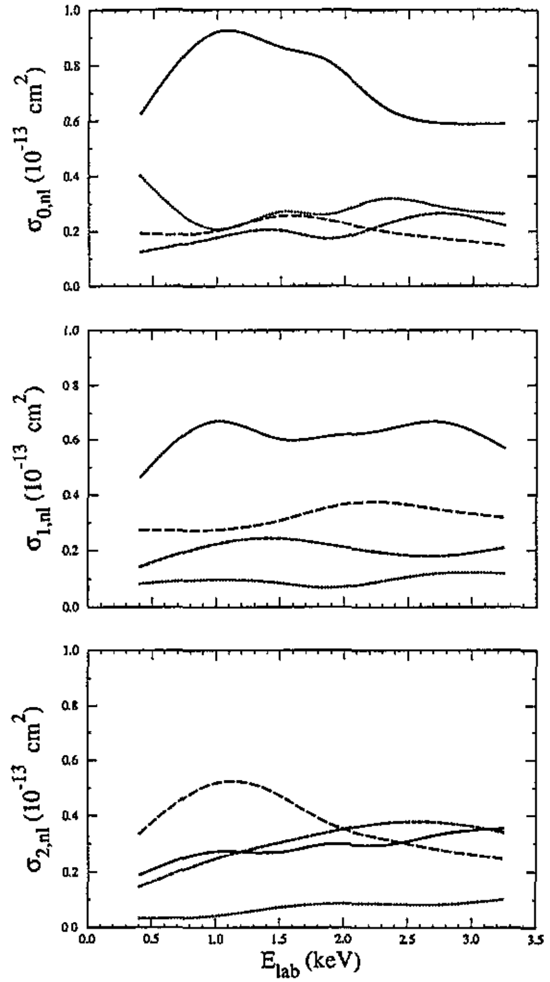

Figure 4. Cross section, $\sigma_{|m|,nl}$, for capture from different magnetic substates, $|m|$, into specific K(nl) states: full curve, 4d; long dashes, 4f; short dashes, 6p; dotted curve, 6s.

For a given initial $|m|$ of the target atom we next examine which final capture states are more likely to be populated. In figure 4 the cross section, $\sigma_{|m|,nl}$, for capture from $4d|m|$ into the most important nl substates of K are shown. For both $m = 0$ and $|m| = 1$ capture into the K(4d) manifold dominates, contributing about 50% to the total capture cross section in the entire energy range studied. For the $|m| = 2$ initial state, which has the smallest total capture cross section of the different initial states, the picture is more mixed. For energies up to 2 keV the K(4f) channel is largest, while 6p and 4d become comparable with and even larger than 4f at higher energies. At the level of impact parameter dependence we find that capture into K(4d) is important at large impact parameters ($b > 40$), while capture into K(4f) mainly takes place at smaller impact parameters.

3.2. Comparison of experimental and theoretical results

Before comparing the experimental and theoretical results, we first discuss the sources that could influence the measured capture signal. Next we make a comparison between the signal obtained from the theoretical calculation with the measured one, and finally we compare the relative cross sections extracted from the experiment with the calculated ones.

In the experiment by Campbell *et al* (1990) a beam of K^+ ions is crossed with a beam of neutral Na atoms that have been excited from the 3s ground level to the 4d level by two lasers. The capture signal is measured as a function of the angle β that the polarization direction of the laser beams make with the ion beam. If only the 4d manifold of Na was populated in the excitation scheme, then the total electron capture signal $I(\beta)$ would depend on β in the following way:

$$I(\beta) = A(B,C) + B\cos(2\beta) + C\cos(4\beta) \tag{1}$$

where $A(B,C) = 1/5 + B/3 + C/15$. The coefficients B and C depend on the real multipole moments of the optical preparation and the relative capture cross sections, ρ_m (see Campbell *et al* (1990) equation (13)). Here ρ_m ($= \rho_{|m|}$) is defined as $\sigma_m/\sum\sigma_m$. The real multipole moments can be obtained by solving the rate equation for the pumping scheme (see Campbell *et al* 1990), and the ρ_ms can be determined by fitting expression (1) to the measured capture signal, and solving $B = B(\rho_m)$ and $A = A(\rho_m)$ for ρ_m under the normalization constraint $\rho_0 + 2\rho_1 + 2\rho_2 = 1$.

According to Campbell *et al* (1990), however, the relative population of the 4d states is only 28% at stationary pumping conditions and one might have to worry about capture from other states. The most important possible ones are the (i) 3s, (ii) 3p and (iii) 4p states which have a relative population of 25%, 25% and 18% respectively.

(i) Measurements by Vermeeren *et al* (1988) and Aquilanti and Bellu (1974) of the capture cross section for the $K^+ + Na(3s)$ system in roughly the same energy range as in the experiment of Campbell *et al* (1990) have given values typical of the order of a few Å^2. This is three orders of magnitude smaller than the cross section for capture from the 4d state as obtained by the present close-coupling calculations. Thus contribution to the capture cross section from ground-state Na atoms is not important.

(ii) In the case of Na(3p) Campbell *et al* (1990) reported that the capture signal drops by almost a factor of 100 when the second laser used for the 3p–4d excitation is turned off. Also, assuming that the capture cross section is roughly the same for K^+ projectiles as for H^+ projectiles, one may use calculations (Courbin *et al* 1990) and measurements (Richter *et al* (1990)) for the $H^+ + Na(3p)$ system to estimate the cross section for the $K^+ + Na(3p)$ system. In this way we estimate that the cross section for capture from 3p is less than 5% of the cross section for capture from 4d and we conclude that capture from Na(3p) is of minor importance and henceforth neglect it.

(iii) Since neither experimental nor theoretical data for capture from Na(4p) are available, we did a close-coupling calculation for the $K^+ + Na(4pm)$ system at one energy point, $E = 1.5$ keV, adding the Na(4p, 3d) and K(3d) states to the basis set previously mentioned. We found that the average cross section for capture from Na(4p) is about 30% of the cross section for capture from Na(4d). As about 18% of the Na atoms are in the 4p state and 28% in the 4d states the present close-coupling calculations suggest that roughly 15% of the experimental capture signal is due to capture from Na(4p). Neglecting capture from the 4p states in the analysis of the experimental capture signal therefore gives rise to an inherent error in the relative 4d cross sections extracted from the fit to equation (1).

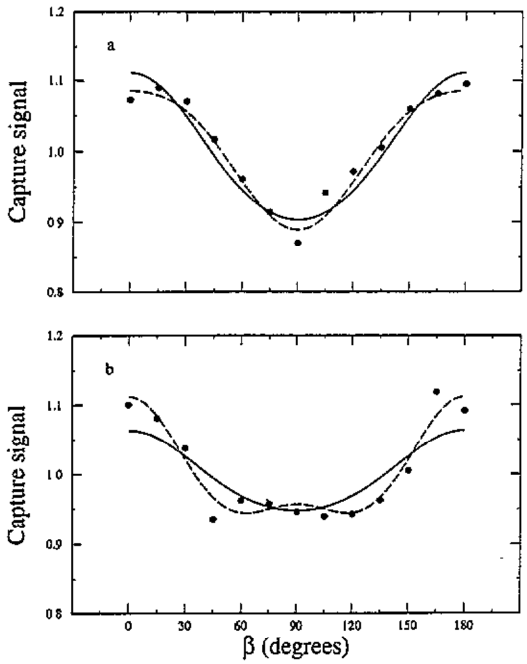

Figure 5. Capture signal as function of polarization direction β for (a) $E = 0.4$ keV and (b) $E = 1.5$ keV. Both curves are based on equation (1). Dots, experimental data; long dashes, least-squares fit to experimental data; full curve, present calculations. For $E = 0.4$ keV the fitted and the calculated values of B/A and C/A are (0.098, −0.013) and (0.10, 0.0069) respectively. For $E = 1.5$ keV the ratios are (0.078, 0.034) from the fitting and (0.058, 0.0054) from the calculation.

With these considerations in mind we may now compare the experimental data with the theoretical calculations.

By combining the multipole moments reported by Campbell *et al* (1990) and the relative cross sections obtained by our close-coupling calculations we can get the coefficients B/A and C/A, and hence by means of equation (1) make a direct comparison with the experimental capture signal. In figure 5 such a comparison is shown for projectile energies of 0.4 and 1.5 keV. On the general dependence of the capture signal on polarization direction the theory and the experiment agree and both reveal a clear energy dependence of the effect of the initial alignment. The coefficients obtained from the least-squares fit of equation (1) to the experimental data, however, differ somewhat from the theoretical ones. For $E = 0.4$ keV and $E = 1.5$ keV one finds respectively $(B/A, C/A) = (0.098, -0.013)$ and $(B/A, C/A) = (0.078, 0.034)$†, whereas at the same energies we find (0.10, 0.0069) and (0.058, 0.0054) for $(B/A, C/A)$. The relative big difference between the values of C/A based on the experiment and based on the close-coupling calculations does not manifest itself clearly in figure 5, since the B/A coefficient dominates C/A.

Another, but more indirect way of comparison is to check the relative cross sections, ρ_m, derived from the experimental data with those calculated. While theory provides ρ_m directly, we can only deduce ρ_m from the experiment by fitting the measured capture cross section signal as a function of polarization angle to equation (1) as described above. In the linear expression for the ρ_ms, C is typically weighted ten times more than B, i.e. the relative cross sections are just as sensitive to C as to B. Hence, the experimentally derived ρ_ms depend sensitively on the fitted values of C. In figure 6, the theoretical and experimental data for ρ_m are plotted as a function of energy. Within the whole energy range considered here the theory does not show much energy dependence of ρ_m, while the experimental data

† For $E = 1.5$ keV Campbell *et al* (1990) report $(B/A, C/A)$ to be (0.076, 0.024). These values of B/A and C/A do not reproduce the ρ_ms given in table 8 of the paper by Campbell *et al* (1990), while the numbers given in this text do.

do scatter significantly. Since total capture cross sections, in general, are smooth functions of energy we find that the apparent structure in the experimental data most likely is caused by the uncertainty in fitting expression (1) to the measured electron capture signal.

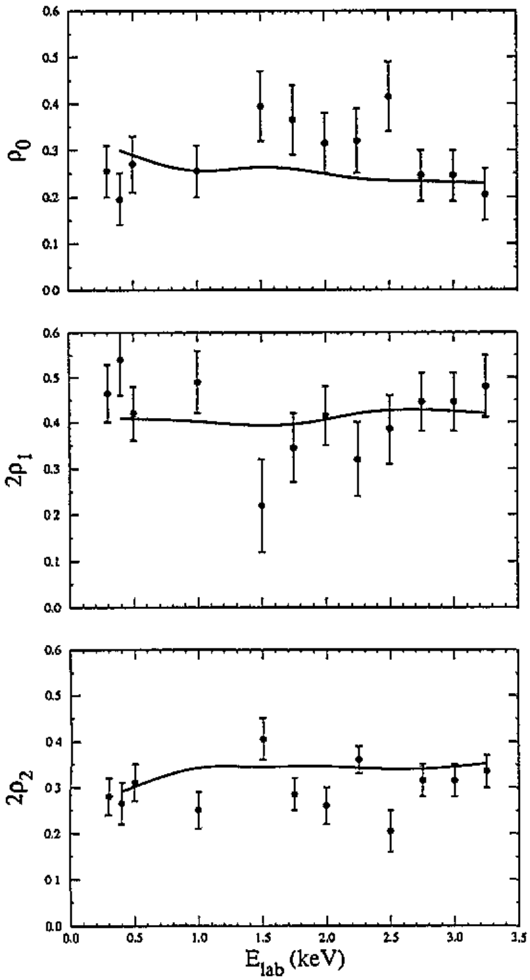

Figure 6. Relative capture cross sections, $\rho_{|m|}$, for different magnetic substates, $|m|$, as a function of laboratory energy: dots, experimental data; full curves, present calculation.

4. Comments on related collision systems

In recent ion–atom experiments the dependence of the electron capture cross section on both the initial alignment of the target atom (Wörmann *et al* 1993) and the angle between the incident beam and the symmetry axis of the orbital of the active target electron (Hansen *et al* 1993a, b, Richter *et al* 1990) have been studied. Even though these collision systems typically involve Rydberg targets and hence are not obviously comparable to the present $K^+ + Na(4dm)$ system, it is still worthwhile to look for common trends in the dependence of the capture cross section on the above mentioned parameters. Below we make the following observations.

Wörmann *et al* (1993) have measured electron capture from the magnetic m substates of Na(nd) Rydberg atoms ($n = 20$–28) by Ar^+ ions, i.e. the target electron has the same initial angular distribution as in the experiment by Campbell *et al* (1990). In a relative velocity region of [0.8;1.6] they find that σ_1/σ_0 is almost constantly equal to 0.8, while σ_2/σ_0 has a strong velocity dependence in the interval [0.8;1.2] decreasing from about 0.9 at $V_r = 0.8$ to about 0.5 at $V_r = 1.2$. For $V_r = 0.7$ and 1.0 our close-coupling calculation for the present system gives $\sigma_1/\sigma_0 = 0.76$ and 0.93 respectively, i.e. showing the same trend as seen by Wörman *et al.* For σ_2/σ_0, though, we find practically no velocity dependence in the region of interest here, σ_2/σ_0 decreasing from 0.56 at $V_r = 0.7$ to 0.54 at $V_r = 1.0$.

Experiments on electron capture from circular Rydberg atoms by Hansen *et al* (1993a, b) have shown that the cross section for capture from circular states is largest when the classical orbital plane is parallel to the beam axis (e.g. the beam is moving along the x axis in figure 3(a)) and smallest when it is perpendicular to the beam axis. None of the initial states considered here is circular ($l \neq l_{\max}$) but the 4d2 resembles a circular state. By choosing the beam axis to be the quantization axis, we have so far studied the case where the classical orbital plane of a circular state is perpendicular to the beam axis. To obtain the cross section, $\sigma^{\perp}_{|m'|=2}$, for capture from the initial state $|4dm'\rangle_{\perp}$, where m' refers to a new quantization axis perpendicular to the beam axis, we need only to rotate the old quantization axis 90°. One finds $\sigma^{\perp}_{|m'|=2} = 3/8\sigma_{|m|=0} + 1/2\sigma_{|m|=1} + 1/8\sigma_{|m|=2}$. The experiment by Hansen *et al* (1993a, b) was done at relative velocities around 1, corresponding to an energy of 61 keV for the K^+ + Na(4d) system. At this energy and at $E = 30.2$ keV ($V_r = 0.7$) we find the ratio $\sigma^{\perp}_{|m'|=2}/\sigma_{|m|=2}$ to be 1.7 and 1.5 respectively in qualitative agreement with the observation of Hansen *et al* (1993a, b), who for the Na^+ + Li ($n = 25$, circular) system finds the ratio to be roughly 1.4 at $V_r = 1.05$ and 1.2 at $V_r = 0.81$.

With respect to alignment the $|d, m = 0\rangle$ initial state resembles the $|p, m = 0\rangle$ state, for which studies on the effect of the direction of the initial alignment, parallel versus perpendicular to the beam axis, on the total capture cross section exist (Richter *et al* 1990, Esry *et al* 1993, Aumayr *et al* 1992). The present calculation shows that capture is more probable, when the 4d, $m = 0$ state is aligned along with the beam axis than when it is aligned perpendicular to the beam axis, the cross section in the latter case being given by $\sigma^{\perp}_{|m'|=0} = 1/4\sigma_{|m|=0} + 3/4\sigma_{|m|=2}$. The same observation has been made in the experiment by Richter *et al* (1990) on the H^+ + Na(3p) system and in calculations by Esry *et al* (1993) on the H^+, He^{2+} + H(2p) systems, while Aumayr *et al* (1992) find the opposite effect in their experiment on the He^{2+} + Na(3p) system.

5. Conclusion

We conclude that the present close-coupling calculations for the K^+ + Na(4d) system, in general, agree with the experimentally observed dependence of the capture signal of both polarization direction and energy. The relative cross sections deduced from experimental data show a strong energy dependence, which was not reproduced by the theoretical calculations. The observed decrease of the capture cross section with increasing magnetic quantum number $|m|$ of the initial 4d state is interpreted in terms of the decreasing probability of finding the electron close to the collision plane as $|m|$ is increased. We examined the final states that are populated by the electron capture processes well. For the initial Na(4d, $m = 0, 1$) states (m referring to the beam axis) the dominant final state on K is 4d. For the $m = 2$ initial state, the distribution of the populated final states on K is less selective. We also compared the results for the present collision system with results from collisions involving Rydberg target atoms where the dependence of electron capture cross sections on the orientation or the alignment of the initial state were investigated.

Acknowledgments

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References

Aquilanti V and Bellu G P 1974 *J. Chem. Phys.* **61** 1618–20
Aumayr F, Gieler M, Schweinzer J, Winter H and Hansen J P 1992 *Phys. Rev. Lett.* **68** 3277–80
Campbell E E B, Hülser H, Witte R and Hertel I V 1990 *Z. Phys.* D **16** 21–33
Courbin C, Allan R J, Salas P and Wahnon P 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 3909–24
Driessen J P J, Smith C J and Leone S R 1991 *J. Phys. Chem.* **95** 8163–9
Esry B D, Chen Z, Lin C D and Piacentini R D 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 1579–86
Fritsch W and Lin C D 1991 *Phys. Rep.* **202** 1
Hansen S B, Ehrenreich T, Horsdal-Pedersen E, MacAdam K B and Dubé L J 1993a *Phys. Rev. Lett.* **71** 1522–5
Hansen S B, Ehrenreich T, Horsdal-Pedersen E and MacAdam K B 1993b *Proc. XVIII ICPEAC* pp 828–35
Lundsgaard M F V and Lin C D 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** L429–34
Richter C, Dowek D, Houver J C and Andersen N 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 3925–32
Robinson R L, Kovalenko L J and Leone S R 1990a *Phys. Rev. Lett.* **64** 388–91
Robinson R L, Kovalenko L J, Smith C J and Leone S R 1990b *J. Chem. Phys.* **92** 5260–9
Toshima N and Lin C D 1994 *Phys. Rev.* A **49** 397–401
Vermeeren L, De Bisschop P, Lievens P and Silverans R E 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 3417–22
Wörmann Th, Roller-Lutz Z and Lutz H O 1993 *Phys. Rev.* A **47** R1594–6