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Atomic-basis study of electron transfer into $C^{3+}(nl)$ orbitals in $C^{4+}+H$ and $C^{4+}+Li$ collisions

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Abstract. A modified two-centre atomic-orbital expansion is used in an investigation of electron transfer in collisions of C^{4+} with H and with Li atoms in the energy range 0.1–20 keV amu^{-1}. Calculated total transfer cross sections constitute the first published origin-independent results for these systems and are found to be in good agreement with experiment. Partial transfer cross sections have been compared with recent, preliminary experimental data for the case of $C^{4+}+Li$ collisions, and qualitative agreement is found for the n distributions. Significant discrepancies, however, are found between calculated and measured l-subshell distributions.

Electron capture in ion–atom collisions is a process of outstanding fundamental and practical interest. Much progress has recently been achieved in the efficient theoretical description of one-electron and quasi-one-electron collision systems at intermediate collision energies where the very number of competing physical channels precludes an understanding by simple models. The standard procedure consists of decomposing the time-dependent electronic wavefunction either into a set of travelling atomic orbitals (AO), with additional pseudostates representing molecular binding effects or contributions of the electronic continuum, or into a set of travelling molecular orbitals (MO), and subsequent solution of the coupled differential equations which are equivalent to the Schrödinger equation within the basis chosen (Fritsch and Lin 1982, 1984a, Bransden *et al* 1983, Kimura and Thorson 1983, and references in these works). With basis sets sufficiently large to represent the important physical channels, total transfer cross sections have been successfully calculated over one to two orders of magnitude of collision energies around the transfer maximum. Even the more sensitive predicted partial transfer into individual nl subshells of the projectile is now being confirmed in experimental work (Aumayr *et al* 1984, Boellaard 1984). For a discussion of the Stark effect in atomic collisions and its possible use for reducing the size of numerical calculations, see the recent investigation by Salin (1984).

In this paper we present and discuss calculated cross sections for electron transfer into individual nl subshells and into all orbitals of the projectile in the collision systems

$$C^{4+}+H \rightarrow C^{3+}(nl)+H^{+} \tag{1}$$

and

$$C^{4+}+Li(2s) \rightarrow C^{3+}(nl)+Li^{+} \tag{2}$$

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in the energy range 0.1–20 keV amu^{-1} for system (1) and 1–7 kev amu^{-1} for system (2). While experimental data have been published for total transfer in both system (1) (Phaneuf *et al* 1982, Gardner *et al* 1980, Crandall *et al* 1979) and system (2) (Dijkkamp *et al* 1983, Brazuk *et al* 1984), corresponding theoretical information is available in the literature only for system (1). Moreover, above 0.4 keV amu^{-1} the calculations for system (1) display features indicative of a limited-size basis study. The present study is intended not only to make available reliable theoretical total transfer cross sections for both systems (1) and (2), but also to support the current experimental thrust towards the determination of partial transfer cross sections in collisions between highly charged ions and hydrogen or lithium.

The calculations reported here are based on the modified two-centre AO expansion method ('AO+ method') in which account is taken of the molecular binding effect in slow collisions by including some more tightly bound orbitals of the united atom at the collision centres (Fritsch and Lin 1982). Adopting one-electron potential models for processes (1) and (2), the respective effective electronic two-centre Hamiltonian H_{el} is constructed from the atomic potential V_1 of the projectile after capture, C^{3+}, and that of the target, V_2,

$$H_{el} = T + V_1 + V_2. \tag{3}$$

The model potentials V_1 and, in the case of system (2), V_2 have been chosen to be of the form (in atomic units)

$$V_i(r_i) = -(q_i/r_i) - (2/r_i)(1+\alpha_i r_i)\exp(-\beta_i r_i) \tag{4}$$

where r_i is the radial electronic coordinate measured from centre i, the charge parameters q_i ($q_i = 4$ and 1 for C^{3+} and Li respectively) ensure the correct asymptotic behaviour of the atomic potentials V_i as r_i tends to zero or infinity, and the parameters α_i and β_i are taken from the works of Gargaud *et al* (1981) (for C^{3+}) and Allan *et al* (1983) (for Li). Atomic orbitals of C^{3+} and Li have been calculated by diagonalising the respective atomic potentials $T + V_i$ in a set of Slater orbitals or hydrogenic orbitals, and plane-wave translational factors have been attached to them. Classical straight-line trajectories are assumed for the atomic centres above 1 keV amu^{-1} while below that energy Coulombic trajectories have been adopted corresponding to two colliding bare nuclei of charges 4 and 1 (system (1)). The model description of the collision and the calculational procedures used here are very close to the methods in our investigation of $H^+ + Li$ and $He^{2+} + Li$ collisions (Fritsch and Lin 1983). Calculated transfer cross sections in that work were, at the time of publication, partly at variance with existing experimental data but are in very good agreement with latest measurements (Boellaard 1984, Varghese *et al* 1984) and calculations (Sato and Kimura 1983).

The choice of the atomic orbital basis (AO+ basis) is related to the particular transfer mechanism operating in the collision system under consideration. These mechanisms have been discussed in the literature for both systems (1) and (2) and are also given here in short form for convenience.

$C^{4+} + H$ collisions. As has been already discussed (Harel and Salin 1977) for the analogous one-electron system $Be^{4+} + H$, low-energy electron transfer in $C^{4+} + H$ collisions occurs predominantly into the $n = 3$ shell through MO of σ symmetry, which diabatically correlate in the united-atom (UA) limit with the UA 3d and 4f states. For a more complete representation of the collision dynamics, Olson *et al* (1978) have included in their semiclassical MO study all the σ or π MO which correlate to the initially populated 1s H and the 3s, 3p, 3d, 4s C^{3+} orbitals for large separations R. In

fully quantum-mechanical calculations at very low energies, Gargaud *et al* (1981) and Bottcher and Heil (1982) have restricted themselves to including those four σ orbitals which correlate to the $n=1$ H and $n=3$ C^{3+} shells. Translational factors are not explicitly taken into account in any of these studies.

In the present work the basis set has been chosen to consist of the 1s H and the $n=2,3,4$ C^{3+} orbitals, plus some hydrogenic and Slater orbitals which are included in order to represent the $n=2,3$ UA orbitals at the H centre and the $n=2,3,4$ UA orbitals at the C centre. There are ten orbitals in total at the H centre and 33 orbitals at the C centre. The exact $n=2,3,4$ eigenenergies of the C^{3+} atomic Hamiltonian with potential (4) are reproduced by our expansion to better than 1% while they agree with the experimental energy levels to better than 0.1% (Gargaud *et al* 1981).

Figure 1 shows the calculated total transfer cross sections in $C^{4+}+H$ collisions. Partial transfer cross sections σ_n for transfer into the C^{3+} n shells as well as the normalised l distributions P_l for each shell n are given in table 1. As is seen from figure 1, the calculated total transfer cross sections are in good agreement with experimental data of Phaneuf *et al* (1982) and Crandall *et al* (1979) while the single point found by Gardner *et al* (1980) is slightly higher. The AO+ results agree with the results of the MO study by Gargaud *et al* (1981) and that by Bottcher and Heil (1982) at low energy, and they show that the oscillations observed in the MO calculation by Olson *et al* (1978) are probably spurious. Deviations from the latter results at low energies are likely to be due to their using a straight-line internuclear trajectory for all energies, while deviations at higher energies may be due to their failure to include translational factors in the calculations. Indeed, the AO+ results are very close to results of a recent nine-state MO calculation (Kimura 1984) in which translational factors are taken into account in first order of the collision velocity. We note that the remaining discrepancies between the present results and those from the work by

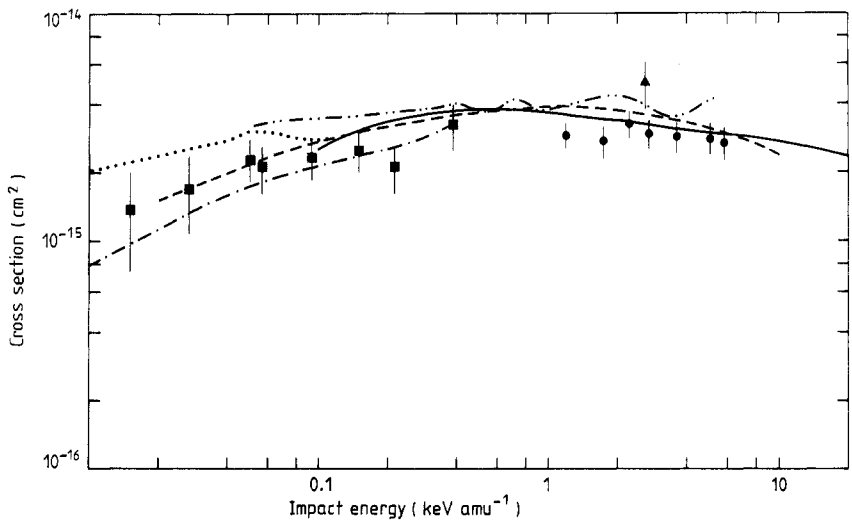

Figure 1. Electron transfer in $C^{4+}+H$ collisions. Theory, full curve, AO+ expansion calculation, this work; other curves are from MO expansion calculations by Gargaud *et al* (1981; chain curve), Bottcher and Heil (1982; dotted curve), Olson *et al* (1978; double dotted chain curve) and Kimura (1984; broken curve). Experimental data are by Phaneuf *et al* (1982; squares), Crandall *et al* (1979; circles) and Gardner *et al* (1980; triangle).

Table 1. Cross sections (in 10^{-15} cm^2) for electron transfer into $C^{3+}(n)$ subshells (σ_n) and into all states (σ_{tot}) in $C^{4+}+H$ collisions. For each n, P_l denotes the normalised l distribution.

E (keV amu^{-1})	n	σ_n	P_0	P_1	P_2	P_3	σ_{tot}
0.1	3	2.31	0.01	0.95	0.04		2.35
	4	0.04					
0.2	3	3.24	0.07	0.84	0.09		3.33
	4	0.09					
0.5	3	3.57	0.22	0.56	0.22		3.77
	4	0.16	0.01	0.47	0.35	0.18	
1.0	3	3.43	0.34	0.42	0.24		3.65
	4	0.19	0.08	0.50	0.28	0.14	
2.0	3	3.12	0.43	0.30	0.27		3.41
	4	0.24	0.11	0.18	0.45	0.26	
4.0	2	0.01					3.07
	3	2.68	0.40	0.25	0.36		
	4	0.30	0.04	0.10	0.47	0.40	
10.0	2	0.03	0.06	0.94			2.79
	3	2.19	0.18	0.27	0.56		
	4	0.56	0.05	0.08	0.28	0.59	
20.0	2	0.05	0.18	0.82			2.34
	3	1.71	0.07	0.20	0.74		
	4	0.56	0.04	0.12	0.28	0.57	

Gargaud *et al* (1981), who also employ the Hamiltonian (3)–(4), are probably caused by the small basis size of only four σ orbitals in the MO work, and only to a minor extent by their more refined, quantum-mechanical description of the internuclear motion. At energies below about 0.1 keV amu^{-1}, however, trajectory effects may become important. Therefore, the AO+ calculations were not extended below that energy.

In table 1 we observe that of the dominant capture channels, i.e. capture into $n=3$ orbitals, the 3p, 3s and 3d orbitals are each in turn the most likely channel with increasing energy. At the low-energy end of our calculations, this is in agreement with the results derived by Gargaud *et al* (1981) and Kimura (1984), who both find the 3p channel to be clearly the dominant one below 0.1 keV amu^{-1}. In the investigation of Kimura, however, capture into 3s orbitals is dominant in the energy region 1–10 keV amu^{-1}, in contrast to the results in table 1. As for capture into shells $n \neq 3$, capture into the $n=4$ shells become increasingly important for energies beyond the cross section maximum. Capture into still higher shells probably also contributes above about 10 keV amu^{-1}. Measured partial transfer cross sections are not available to date but are presently being extracted in experiments by the FOM group (Dijkkamp 1984). Preliminary results from that group in the energy range 0.5–10 keV amu^{-1} agree well with the present calculations. In particular, this latter agreement lends strong support to the model potential approach adopted in the present work; the partial transfer cross sections calculated in the one-electron system $Be^{4+}+H$ (Fritsch and Lin 1984b) are significantly different from those derived here.

$C^{4+}+Li$ collisions. For a discussion of electron transfer in $C^{4+}+Li$ collisions, the target atom Li can be considered as consisting of one 2s electron in the model potential (4). Since the Li 2s electron is less bound ($\varepsilon_{2s}=-0.1982$ au) than the 1s H electron, capture occurs at larger distances, into higher n shells and hence with larger cross

sections than in the $C^{4+}+H$ case, as has been observed and discussed earlier (Dijkkamp *et al* 1983, Brazuk *et al* 1984). For illustration, figure 2 shows an energy diagram of $m=0$ 'Stark states' in the $C^{4+}+Li$ system, which is derived by plotting the energies formed out of atomic energies in the presence of the respective collision partner at separation R. Figure 2 is representative of an energy diagram of partly diabatised molecular orbitals. It illustrates that transfer occurs predominantly into $n=5$ orbitals at and below impact parameters of some 25 au, in agreement with arguments given previously (Brazuk *et al* 1984). Figure 2 also shows that Li 2p orbitals have to be included in any detailed discussion of $C^{4+}+Li$ collisions.

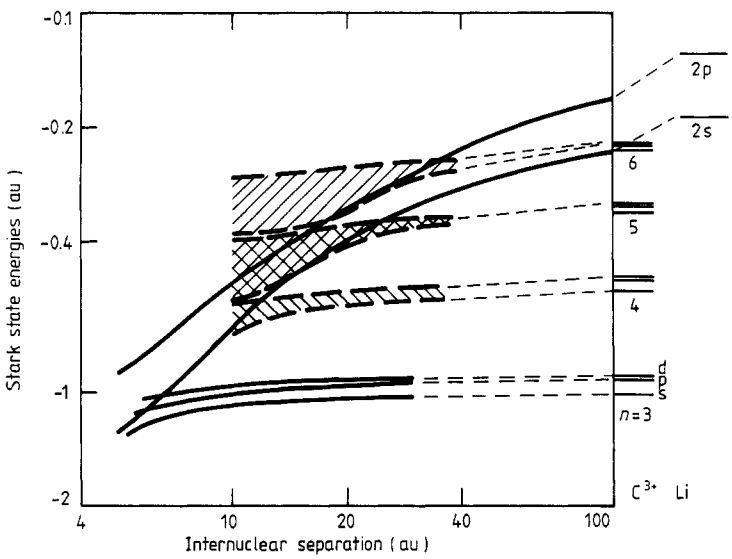

Figure 2. Energy levels of $m=0$ Stark states in the collision system $C^{4+}+Li$. Levels correlating to C^{3+} nl states of given $n \geq 4$ are combined in hatched areas.

In the dynamical calculations the Li 2s and 2p orbitals have been represented by, respectively, four and two hydrogenic basis orbitals, leading to Li energies $\varepsilon_{2s}=-0.1977$ au and $\varepsilon_{2p}=-0.1289$ au. Thus, according to our earlier experience (Fritsch and Lin 1983), the Li orbitals are included in the calculations with sufficient accuracy. At the carbon centre, all 46 C^{3+} orbitals with $4 \leq n \leq 6$ have been taken into account. They have been represented by the corresponding hydrogenic orbitals with charge number 4, which, when diagonalised with the model potential (4), give eigenenergies in agreement with those in the literature (Lindgaard and Nielsen 1977) to better than 1.5% for s states and better than 0.2% for p–g states. Since charge transfer is dominated by distant collisions, united-atom orbitals have not been included.

Calculated partial and total transfer cross sections for $C^{4+}+Li$ collisions are given in table 2, and are compared with experiment (Dijkkamp *et al* 1983, Brazuk *et al* 1984, Dijkkamp 1984) in both table 2 and figure 3. In the dynamical calculations, population of $n=5$ orbitals clearly dominates the transfer process as expected, and also some sizable population of $n=6$ and, to a lesser degree, $n=4$ orbitals is observed. At the two higher energy points, cross sections for transfer into l subshells, within a given n shell, rise smoothly with quantum number l as is known to occur at intermediate

Table 2. Cross sections (in 10^{-15} cm^2) for electron transfer in $C^{4+}+Li$ collisions.

E (keV amu^{-1})	n	σ_n	σ_n†	P_0	P_1	P_2	P_3	P_4	P_5	σ_{tot}
1.0	4	2.3		0.23	0.23	0.24	0.30			24.8
	5	20.3		0.17	0.13	0.15	0.23	0.32		
	6	2.2		0.07	0.13	0.18	0.19	0.18	0.24	
2.5	4	1.9	4.0	0.13	0.25	0.24	0.38			22.4
	5	16.8	10.9	0.07	0.09	0.15	0.31	0.38		18.5†
	6	3.7	3.5	0.06	0.10	0.12	0.20	0.25	0.27	
5.0	4	1.6	3.1	0.15	0.16	0.30	0.39			22.0
	5	15.5	10.4	0.02	0.05	0.11	0.28	0.54		18.7†
	6	4.9	5.3	0.02	0.04	0.08	0.12	0.28	0.46	
6.667	4	2.0	3.4	0.12	0.13	0.32	0.42			20.5
	5	13.9	19.4	0.01	0.04	0.11	0.27	0.56		17.8†
	6	4.6	5.0	0.02	0.04	0.08	0.15	0.25	0.46	

† Preliminary experimental results (Dijkkamp 1984).

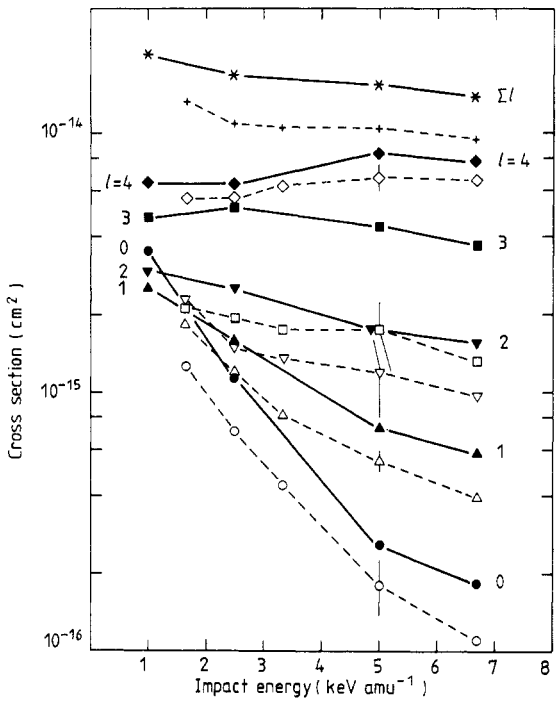

Figure 3. Capture cross sections for capture into $C^{3+}(n=5)$ orbitals in $C^{4+}+Li$ collisions. Symbols ●, ▲, ▼, ■ and ◆ denote calculated $l=0,1,\ldots,4$ subshell cross sections, respectively, while the corresponding open symbols denote experimental results (Dijkkamp 1984). Asterisks and crosses denote calculated and measured summed cross sections, respectively. Error bars at 5 keV amu^{-1} illustrate averaged experimental uncertainties for each l. Lines are drawn to guide the eye.

energies in one-electron systems from calculations (Fritsch and Lin 1984b and references therein). At the lower energies, irregularities in the l distribution may reflect details of the molecular structure of the system. We point out that the calculated cross sections are affected by some 'statistical' error, due to oscillations in the transfer probabilities

that depend on the impact parameter (b) and the finite b mesh in the calculations ($\Delta b = 0.75$ au). The smallest cross sections at the lowest energy may well change by some 20% in a calculation with smaller b mesh.

When comparing with experimental results we first note that the calculations confirm the magnitude of the measured total transfer cross sections within the quoted error margin (some 30%); cf table 2. Second, not surprisingly, the measured and calculated partial cross sections for transfer into C^{3+} n shells deviate more strongly from each other. Finally, the most significant disagreement lies in the calculated and measured l distribution. This is illustrated in figure 3 for the $n = 5$ partial cross sections. While all other measured $n = 5$ cross sections could be made to agree with the calculations by applying a common, energy-independent normalisation factor of about 0.8, the measured 5f population is much smaller than the calculated one (factor of about 0.35). We note that, in experiment, the 5f population is determined, in conjunction with other populations, by measuring a number of transition lines (Dijkkamp 1984) and using published branching ratios (Lindgaard and Nielsen 1977). The element of redundancy in this method is expected to work as a safeguard against errors.

The calculations presented here should be very appropriate for the $C^{4+} + Li$ system where large internuclear separations are involved in both the primary capture process and the final distribution of the captured electron over l orbitals. Moreover, since the present description apparently works for $C^{4+} + H$ collisions it should work even better for the $C^{4+} + Li$ case. Of course, the calculations could be improved by adding higher orbitals to the AO expansion and by further improving the representation of those orbitals which are already included. The former modification, however, would affect calculated capture into $n = 6$ orbitals primarily and $n = 5$ orbitals less so. We would not expect the latter modification to induce any *qualitative* change of the relative n or l population. Actually, with a different, slightly worse representation of the 2s Li orbitals, similar results to those in table 2 have been derived. Even with a simple Be^{4+} potential at the carbon centre, the relative l distribution of transfer into the $n = 5$ shell is found to look qualitatively similar to that presented here at the highest energy. In support of the calculations we also mention here that the integration of the coupled-state equations has been carried out to sufficiently large internuclear separations $R \simeq 60$ au so that any remaining couplings between C^{3+} nl orbitals are very small in the *space-fixed* coordinate system.

In conclusion, cross sections for electron transfer into individual nl and all projectile shells have been calculated for $C^{4+} + H$ and $C^{4+} + Li$ collisions. The calculated total transfer cross sections are in good agreement with experiment for both systems. Calculated partial transfer cross sections have been compared with experiment for the case of $C^{4+} + Li$ collisions. Significant deviations are observed in the relative l distribution within a given n shell where, for the dominating transitions into the $n = 5$ shell, the measured 5f population is much smaller than the calculated one. A satisfactory explanation for this discrepancy has not been offered here. It is hoped that further experimental and theoretical investigations will be stimulated by the present communication, and that they might help to resolve the problem.

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