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LETTER TO THE EDITOR

On the discrepancies of the calculated $C^{5+}(n = 5)$ capture cross sections in C^{6+}–H collisions

Jérémie Caillat†, Alain Dubois† and Jan Petter Hansen‡

† Laboratoire de Chimie Physique-Matière et Rayonnement§, Université Pierre et Marie Curie, 11, rue Pierre et Marie Curie, F 75231 Paris Cedex 05, France

‡ Institute of Physics, University of Bergen, Allégaten 55, N-5007 Bergen, Norway

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Abstract. We present new results for electron transfer cross sections in C^{6+}–H collisions at low and intermediate impact energies (0.1–500 keV amu^{-1}). The impact parameter semiclassical method is used within the atomic-state close-coupling approach. Special attention is concentrated on the $C^{5+}(n = 5)$ capture channels, for which severe discrepancies have been reported at low impact energies. We identify and discuss the mechanisms giving rise to the discrepancies in terms of avoided crossings in the molecular energy diagram. Trajectory effects are also introduced with the use of channel-selective deflection patterns obtained by classical trajectory Monte Carlo calculations.

The C^{6+}–H collision system has been widely studied for more than 20 years, partly motivated by the need for accurate cross sections in high-temperature plasma physics (see, e.g., [1, 2] and references therein). Electron transfer, especially to the $C^{5+}(n = 4)$ states, dominates completely over excitation and ionization [3,4], which simplifies the computations of the cross sections. Secondary but non-negligible capture channels involve the $C^{5+}(n = 5)$ manifold. Excellent agreements for total capture cross sections have been obtained between various theoretical predictions and the few available experimental results, e.g. [1–13]. However, when considering $C^{5+}(n = 5)$ capture at low energies, two trends in the cross sections predicted by theoretical calculations are observed with differences reaching one order of magnitude at 0.1 keV amu^{-1} [2]. The semiclassical methods behind these data are all non-perturbative but differ from each other by:

(i) the type and the size of the basis expansion;
(ii) the choice of internuclear trajectories (straight-line or curved trajectory approximation).

Among the most important results at low energies we mention the atomic orbital (AO) based works of Fritsch and Lin [11] (basis including $H(1s) + C^{5+}(n = 4, 5)$ states with unscreened Coulomb potential trajectories) and Caillat *et al* [6] ($H(1s) + C^{5+}(n = 1–6)$ states with straight-line trajectories). The alternative molecular orbital (MO) calculations were performed by Green *et al* [10] with a basis spanning asymptotically the $C^{5+}(n = 3–6)$ manifolds, with curved trajectories based on average molecular potential, and Harel *et al* [5] with inclusion of all states correlated with channels up to $C^{5+}(n = 8)$ states and straight-line trajectories. Note also the calculations of Kimura and Lin [13] using a mixed AO/MO approach spanning the $C^{5+}(n = 4, 5)$ states, with Coulomb trajectories for energies below 1 keV amu^{-1}.

§ Unité Mixte de Recherches du CNRS, UMR 7614.

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The goal of this letter is to resolve the reasons for this low-energy discrepancy between the various calculations of electron transfer to the $C^{5+}(n = 5)$ states. For the discussion semiclassical straight-line atomic orbital coupled channel (AOCC) results obtained with different basis sets are used and connected to classical trajectory Monte Carlo (CTMC) results for the analysis of trajectory effects. A simple model is proposed to fold the semiclassical probabilities with CTMC channel-selective deflection functions. The convergence of the results obtained with different methods and the validity of the straight-line approximation are discussed.

The present semiclassical calculations follow from the AOCC method as described in [6, 16]. The relative motion of the two heavy particles is described by straight-line trajectories. The electronic wavefunction is expanded onto a set of eigenstates of the target and projectile centres, modified by the electron translation factors. The basis set used (B_1) consists of the initial H(1s) state and all states spanning $C^{5+}(n = 1–6)$ shells, i.e. 92 states. This basis set is appropriate to describe capture channels for energies below 50 keV amu^{-1} where excitation and ionization processes are negligible [3, 4]. However, a few calculations have been performed at low energies with a restricted basis set (B_2) including only H(1s) and $C^{5+}(n = 4, 5)$ capture states.

In the CTMC method the dynamics of the three particles is described by classical mechanics. The initialization of the H(1s) target electron is performed through a microcanonical distribution with energy fixed to -0.5 au [17]. The final $C^{5+}(n\ell)$ states are identified as in [12]. The results have been further analysed for the prediction of realistic relative trajectories between the two collision partners. Attention will be especially focused on the closest approach distance with respect to impact parameter, for given channels and impact velocities.

In figure 1 cross sections for the important capture channels are presented. As mentioned above, a general agreement within 10% is obtained for $C^{5+}(n = 4)$ capture: this can be seen when comparing our results to the analytical fit proposed by Janev *et al* [2]. The systematic overestimation of our results at high energies (above 50 keV amu^{-1}) is due to the absence of ionization and excitation channels in our basis set. The same remarks can be drawn for $C^{5+}(n = 5)$ capture at high energies. However below 25 keV amu^{-1} a severe disagreement is observed: a flat behaviour (present work and [5, 6, 10]) or a strong drop-off for decreasing energies [11, 13] (cf figure 4 for a blow-up of the important region).

The mechanisms responsible for these processes at low energies are identified with the adiabatic molecular curves, obtained with the full basis B_1, presented in figure 2(a). As mentioned in previous studies, e.g. [11], capture to $n = 4$ arises through the avoided crossings around $R = 7$ au (framed) between the $5g\sigma$ curve correlated asymptotically with H(1s) and the $4f\sigma$ merging into the $C^{5+}(n = 4)$ manifold. On the other hand capture to $n = 5$ is a two-step process involving first the mechanism described above and then the avoided crossings around $R = 3$ au (framed) between the curves correlated with the $n = 4$ and 5 manifolds. The importance of these crossings is illustrated in figure 2(c) where the $n = 4$ and 5 capture probabilities for a typical low energy are presented: while $n = 4$ capture extends up to impact parameter $b = 8$ au, $n = 5$ capture only takes place at smaller impact parameters with a cut-off just below $b = 4$ au.

The first point to investigate for the analysis of the discrepancies for $n = 5$ capture is the quality of the description of the couplings which give rise to the avoided crossings mentioned above. The size and the type of the basis sets used in the different calculations should be invoked for that purpose. Figure 1 clearly shows that the MO expansion of Harel *et al* [5] and the present AO expansion give very close results. In fact in these works convergence is achieved for low impact energies and the only discrepancy observed at 0.06 keV amu^{-1}

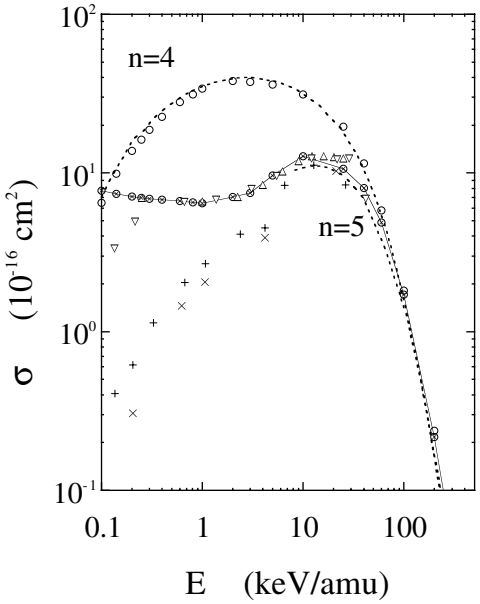

Figure 1. Cross sections for electron capture from H(1s) to $C^{5+}(n = 4, 5)$ shells as a function of impact energy. For $C^{5+}(n = 4)$: ○, [6] and present straight-line (SL) results using basis set B_1; - - - -, recommended data [2]. For $C^{5+}(n = 5)$: ——⊗——, [6] and present SL results using set B_1; - - - -, recommended data [2]; △, Harel *et al* [5]; ▽, Green *et al* [10]; +, Fritsch and Lin [11]; ×, Kimura and Lin [13].

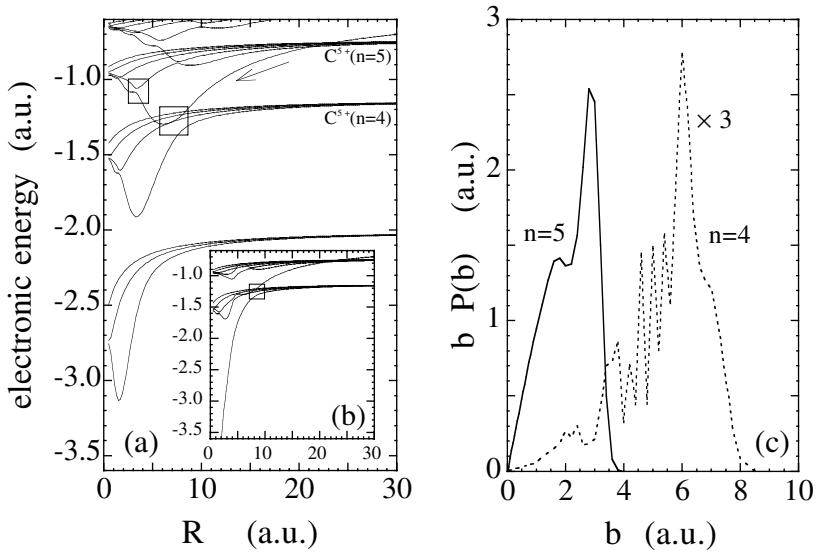

Figure 2. (*a*) and (*b*) Adiabatic potential energy curves of the Σ states for the $(CH)^{6+}$ system: (*a*) using basis set B_1 (the two important avoided crossings commented on in the text are framed); (*b*) using restricted basis set B_2. (*c*) Reduced probability $b \times P(b)$ as a function of impact parameter b (au) for impact energy $E = 0.05$ keV amu^{-1}: - - - -, $C^{5+}(n = 4)$ capture; ——, $C^{5+}(n = 5)$ capture.

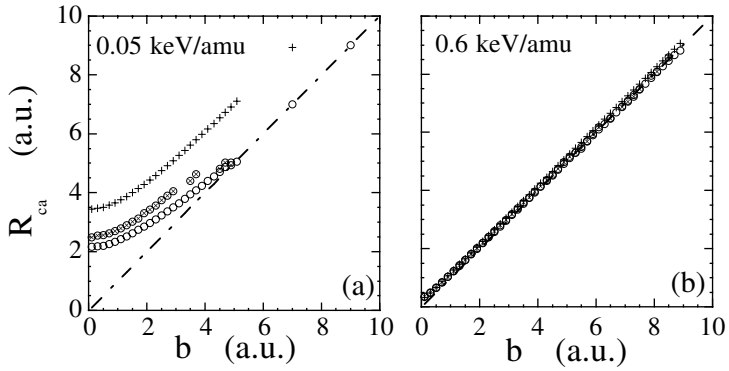

Figure 3. Closest approach distance R_{ca} between the two nuclei as a function of impact parameter b for two impact energies: (*a*) $E = 0.05$ keV amu^{-1} ($v = 0.0447$ au) and (*b*) $E = 0.6$ keV amu^{-1} ($v = 0.155$ au). ○, mean values from CTMC trajectories leading to $C^{5+}(n = 4)$ capture; ⊗, mean values from CTMC trajectories leading to $C^{5+}(n = 5)$ capture; +, $6/R$ potential model; — · —, straight-line model ($R_{ca} = b$).

may be explained by slight differences in the description of the molecular energy curves at small internuclear separations. Note that these two semiclassical approaches used the same description of the internuclear trajectory (straight line). The MO expansion of Green *et al* [10] is based on molecular curves comparable to ours with respect to the two important crossings. Though the basis set is smaller than ours the $n = 5$ capture cross sections are very close to the results reported here and in [5] down to about 0.6 keV amu^{-1}. Below this limit the choice of internuclear trajectory based on average molecular potentials in [10] can explain, as commented in the following, the observed differences. On the other hand the two studies [11, 13] which predict much smaller cross sections at energies below 5 keV amu^{-1} (cf figures 1 and 4) are based on AO or mixed AO/MO expansions spanning the $C^{5+}(n = 4$–$5)$ manifolds to describe only the important capture channels. The effects of such restricted basis sets on the description of the molecular curves is however dramatic, as can be seen in figure 2(*b*) (diagonalization performed with basis B_2). When the AOs related to deep bound states are missing the MOs created by LCAO shift to low energies, following the variational principle. This is indeed what is shown in figure 2(*b*), where one of the MOs, normally correlated with the $n = 4$ shell of the united atom, falls strongly. This effect propagates to higher MOs, so the avoided crossing at about 3 au is not present with such a restricted basis. This mechanism no longer works and $C^{5+}(n = 5)$ capture cross sections are then predicted to be much smaller at low velocities. We have performed coupled-channel calculations with the restricted basis set (B_2) and we observed that indeed the $C^{5+}(n = 5)$ capture cross sections dropped by an order of magnitude, as in [11, 13].

The second point to investigate is the choice of internuclear trajectory in the semiclassical models. For that purpose we have performed CTMC calculations in the low-energy range (below 1 keV amu^{-1}). The CTMC method has given results in reasonable agreement with other methods at energies above 50 keV amu^{-1} [12]. The use of the CTMC method at lower energies is questionable: in fact we observed total capture cross sections two or three times too large and a bad shell selectivity ($n = 5$ underestimated and $n = 4$ overestimated). However, the main point of these calculations was to model realistic internuclear trajectories, which are essentially classical in nature. From the CTMC calculations and for given channels we selected the distance of closest approach R_{ca} between the two heavy particles to parametrize the deflection. In figure 3 this parameter for the trajectories giving rise to $C^{5+}(n = 5)$ capture

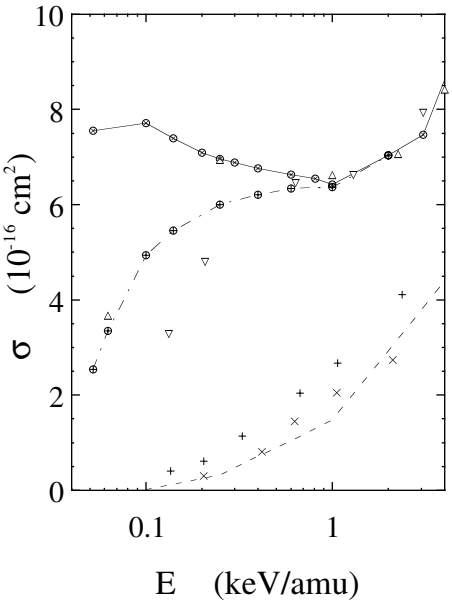

Figure 4. $C^{5+}(n = 5)$ cross sections as a function of impact energy. ——⊗——, present straight-line results using set B_1; — · —⊕— · —, present straight-line (B_1) results folded with the CTMC $R_{ca}(b)$ functions; – – –, present straight-line (B_2) results folded with the $6/R$ potential $R_{ca}(b)$ functions; △, Harel *et al* [5]; ▽, Green *et al* [10]; +, Fritsch and Lin [11]; ×, Kimura and Lin [13].

is presented as a function of impact parameter and for two typical velocities. It is compared with the closest approach distances corresponding to an unscreened $+6/R$ Coulomb potential. Figure 3(b) shows that no important deflection is observed for an energy of 0.6 keV amu^{-1}. The three models presented in this figure give very close results: for that energy the trajectory model implemented in the semiclassical methods cannot be of importance for the prediction of the cross sections, in agreement with the conclusion of Green *et al* [14]. However, for the lowest energy, $E = 0.05$ keV amu^{-1} (figure 3(a)), the deflection is clear. For this energy the closest approach distance is about 2.5 au for $b = 0$. Therefore the $C^{5+}(n = 5)$ capture probability pattern obtained with the straight-line approximation (figure 2(b)) is partially spurious since it is related to forbidden internuclear distances. It is interesting to note that the deflection by a 6/R potential is larger and that the closest approach is at least 3.5 au. When considering the mechanism involving the avoided crossing around 3 au it is clear that this model, implemented in a close-coupling approach, would lower drastically and artificially the corresponding cross sections.

In this letter, to account for the observed deviation from straight-line trajectories, a simple model is proposed: it is based on the straight-line probabilities obtained in our present calculations and the deflection functions obtained in the CTMC calculations. The cross sections are then computed through the usual integration with probabilities evaluated at closest approach instead of initial impact parameter. This simple model is similar to those proposed by Tseng and Lin [18], with the improvement that more realistic closest approach distances are used.

The cross sections evaluated with this simple model are presented in figure 4, together with the data relevant in the low-energy range. The trajectory effects predicted from the CTMC calculations are clearly seen to affect the cross sections only for energies below 1 keV amu^{-1}. The disagreement shown in figure 4 between [11, 13] and the other data is therefore mainly

due to the truncation of the basis, which implies a bad description of the avoided crossing at 3 au. It is interesting to note from figure 4 that this model applied to our B_2 basis results, folded with $6/R$ potential deflection, gives results close to the ones reported in [11, 13] using the same internuclear scattering potential.

Finally the same model to account for trajectory effects has been applied to the $C^{5+}(n = 4)$ capture cross sections. There the CTMC calculations predict similar, somewhat smaller, deflection than for $C^{5+}(n = 5)$ capture. However, their effects on the cross sections are quite minor since the probabilities extend up to about 8 au (figure 2(*c*)) while the deviation from a straight line is only important below impact parameter 5 au, cf figure 3(*a*).

In conclusion our analysis explains the discrepancies observed in previous works for the prediction of capture cross sections in C^{6+}–H collisions at low energies. The dynamical features responsible for $C^{5+}(n = 5)$ capture are identified with the help of avoided crossings observed in adiabatic molecular curves. The effects of both trajectory and basis size are discussed within this frame. To account for the internuclear interaction we have proposed a model to fold straight-line coupled-channel results with deflection functions obtained by CTMC calculations. In the 0.1–10 keV amu^{-1} energy range the $C^{5+}(n = 5)$ capture cross sections evaluated with the present model are in good agreement with the data of Green *et al* [10]. This validates an extension of the fits proposed by Janev *et al* [2] by the use of these results at low energies.

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