Charge transfer in slow collisions of C^{4+} with H below 1 keV/amu

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We reexamined charge-transfer cross sections for $C^{4+}+H$ collisions for energies from 1 meV/amu to 1 keV/amu using the recently developed hyperspherical close-coupling method. Our results agree with several previous theoretical calculations using molecular-orbital expansion. However, these converged theoretical predictions do not agree with total cross sections from the merged-beam experiments.

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I. INTRODUCTION

Charge-transfer cross sections for slow $C^{4+}+H$ collisions have been measured in many experiments since the earlier 1980s. Using a source of slow ions from a laser-produced plasma and a hydrogen furnace as a target, Phaneuf *et al.* measured the total electron-capture cross sections in the energy range of 15–387 eV/amu [1]. Using the photon emission spectroscopy, absolute state-selected electron-capture cross sections have been measured by Hoekstra *et al.* in the impact energy range of 0.05–1.33 keV/amu [2]. Both of these early measurements have quite large error bars. More recently, Bliek *et al.* used the state-of-the-art merged-beam techniques to determine absolute total electron-capture cross sections in the energy range of 6–1000 eV/amu [3].

This collision system has also attracted considerable interest and stimulated much theoretical work, partly due to the persisting discrepancies between experimental measurements and theoretical predictions [4–12]. Various quantal and semiclassical calculations were carried out based on molecular-orbital (MO) expansion method and the adiabatic Born-Oppenheimer approximation. However, since the molecular orbitals do not satisfy the correct boundary conditions, modifications through electron translation factors (ETFs) or reaction coordinates have to be introduced to account for electron translation effects. The earlier calculations are less reliable due to neglecting some radial and angular couplings or not having enough basis functions. The pioneering work of Gargaud *et al.* [4,8,9] was based on a quantal formalism using reaction coordinates. They improved their results later by adding more basis functions and including rotational couplings in the calculations. Saha [10] used a semiclassical approach and plane-wave-type ETFs. An alternative approach is to perform semiclassical calculations using atomic orbitals (AOs) on the two collision centers as basis functions. This has been used by Fritsch and Lin [13], and later by Tseng and Lin with improved basis functions and an *ad hoc* method was used to account for trajectory effects [14] at lower energies. Most recently, Errea *et al.* [11] carried out both quantal and semiclassical calculations based on MO expansion and reaction coordinates that are different from those used by Gargaud *et al.* [9]. Their results are in good agreement with those of Gargaud *et al.* [9] and the rectilinear trajectory AO results of Tseng and Lin [14].

In spite of these experimental and theoretical efforts, discrepancies remain. All of these experiments have relatively large error bars and they do show non-negligible differences from theories. While most recent theoretical results are converging over the energy range below 1 keV/amu, they are in noticeable disagreement with the merged-beam experiment. In particular, various previous calculations were unable to confirm the sharp structure observed by Bliek *et al.* in the cross section around 500 eV/amu. In view of these controversies, we decided to employ the recently developed hyperspherical close-coupling method (HSCC) [15] to examine this collision system one more time. The HSCC method is formulated similar to the perturbed stationary-state approximation but without the well-known difficulties in that approach. No additional assumptions are needed beyond the truncation of the number of adiabatic channels included in the calculations. Therefore, the HSCC approach can also be used to evaluate the results from the various MO-ETF-type calculations. Our HSCC calculations do support these earlier theoretical results and we thus conclude that the merged-beam data reported by Bliek *et al.* are not reproducible by current theories and the origin of the discrepancy should be resolved from the experimental side.

II. THEORY

We employ in the study the hyperspherical close-coupling method recently developed by Liu *et al.* [15]. This method has proved successful in previous applications [15–17] to ion-atom collisions involving systems with one electron and two heavy nuclei (or positive ions with closed-shell electrons). This method has been described in detail in Ref. [15]. Thus we present here only a brief overview of the HSCC method.

The collision complex CH^{4+} is considered as a three-particle system consisting of an electron, a proton, and C^{4+}, which is considered as a frozen core. The system is described by mass-weighted hyperspherical coordinates. In the ''molecular'' frame, the first Jacobi vector $\boldsymbol{\rho}_1$ is chosen to be the vector from C^{4+} to H^+, with a reduced mass μ_1. The second Jacobi vector $\boldsymbol{\rho}_2$ goes from the center of mass of C^{4+} and H^+ to the electron, with a reduced mass μ_2. The hyperradius R and the hyperangle ϕ are defined as

$$R=\sqrt{\frac{\mu_1}{\mu}\rho_1^2+\frac{\mu_2}{\mu}\rho_2^2}, \tag{1}$$

$$\tan\phi = \sqrt{\frac{\mu_2}{\mu_1}}\,\frac{\rho_2}{\rho_1}, \tag{2}$$

where μ is arbitrary. Another angle θ is defined as the angle between the two Jacobi vectors. When μ is chosen equal to μ_1, the hyperradius R is very close to the internuclear distance between C^{4+} and H^+. We treat C^{4+} as an inert ionic core described by a model potential taken from the early work of Gargaud *et al.* [9]. The model potential has the form

$$V_{mod}(r) = -\frac{4}{r} + \frac{2}{r}[(1+br)e^{-\beta r} + cre^{-\gamma r}], \tag{3}$$

where $b = 4.250\,928$, $c = 0.011\,553$, $\beta = 7.788\,580$, and $\gamma = 2$.

We first introduce the rescaled wave function

$$\Psi(R,\Omega,\hat{\omega}) = \psi(R,\Omega,\hat{\omega})R^{3/2}\sin\phi\cos\phi, \tag{4}$$

then the Schrödinger equation takes the form

$$\left(-\frac{1}{2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{15}{8} + H_{ad}(R;\Omega,\hat{\omega}) - \mu R^2 E\right)\Psi(R,\Omega,\hat{\omega}) = 0, \tag{5}$$

where $\Omega \equiv \{\phi,\theta\}$ and $\hat{\omega}$ denotes the three Euler angles of the body-fixed frame with respect to the space-fixed frame. H_{ad} is the adiabatic Hamiltonian

$$H_{ad}(R;\Omega,\hat{\omega}) = \frac{\Lambda^2}{2} + \mu RC(\Omega), \tag{6}$$

where Λ^2 is the square of the grand angular-momentum operator and $C(\Omega)/R$ gives the total Coulomb interaction.

To solve Eq. (5), we expand the rescaled wave function in terms of normalized and symmetrized rotation function $\tilde{D}$, and body-frame adiabatic basis functions $\Phi_{\mu I}(R,\Omega)$,

$$\Psi(R,\Omega,\hat{\omega}) = \sum_{\nu}\sum_{I} F_{\nu I}(R)\Phi_{\nu I}(R,\Omega)\tilde{D}^J_{IM_J}(\hat{\omega}), \tag{7}$$

where ν is the channel index, J is the total angular momentum, I is the absolute value of the projection of **J** along the body-fixed z' axis, and M_J is the projection along the space-fixed z axis. $\Phi_{\nu I}$ are eigenfunctions of a reduced adiabatic Hamiltonian which does not include any J-dependent terms. To solve the hyperradial equations we divided the hyperradial space into sectors. We then used a combination of the R-matrix propagation method [18] to propagate the R matrix from one sector to the next, and a slow/smooth-variable discretization method [19] within each sector. Note that both radial and rotational couplings are fully incorporated. The R matrix is propagated to a large hyperradius (depending on the collision energy) where the solution is matched to the known asymptotic solutions to extract the scattering matrix. The electron-capture cross section for each partial wave J is then obtained from the calculated scattering matrix.

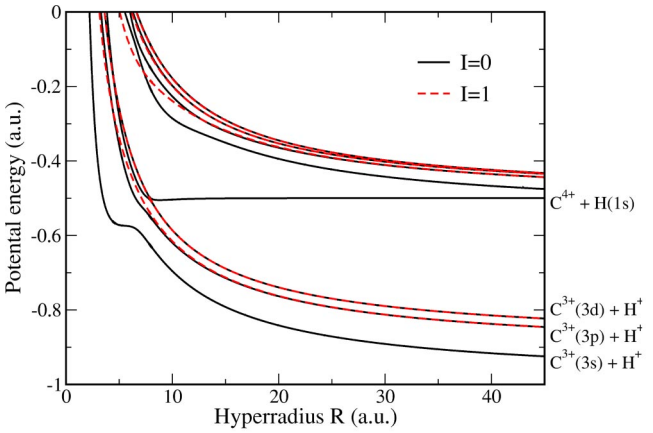

FIG. 1. Hyperspherical potential curves for CH^{4+}. This figure shows eight $I=0$ channels in solid lines and five $I=1$ channels in broken lines. The channel labels indicate the asymptotic limits of the corresponding potential curves.

The method described above has to be carried our for each partial wave J until a converged cross section is reached. Using the numerical procedure introduced in Liu *et al.* [15] such calculations can be easily carried out for many partial waves. We have checked that the results are insensitive to the matching radius within the number of channels included in the calculation.

III. RESULTS AND DISCUSSION

In this paper we applied the HSCC methods to calculate charge-transfer cross sections for $C^{4+}+H(1s)$ collisions. Figure 1 presents the hyperspherical potential curves included in the calculation for R up to 30 a.u. For clarity, only $I=0$ and $I=1$ components are shown. Note that these channels are not exact adiabatic channels since they are obtained by diagonalizing the reduced electronic Hamiltonian for each I. Therefore, we can label them with their quantum number I. Due to the avoided crossings with the initial channels, the dominant reaction channels are those corresponding to charge transfer to the $n=3$ excited states of C^{3+}. Therefore, in addition to the initial $C^{4+}+H(1s)$ channel, we include all the $I=0,1$, and 2 channels converging to C^{3+} $(n=3)+H^+$ thresholds. Also included are the $I=0$ and $I=1$ channels converging to C^{3+} $(n=4)+H^+$ thresholds. As a result, there are 14 coupled channels in total in the present calculation. The larger number of channels are included so we can extend the calculations to the higher energies. For the low-energy regime fewer channels will be adequate.

In Fig. 2, we present the charge-transfer cross sections for $C^{4+}+H(1s)$ collisions at center-of-mass energies from 1 meV/amu up to 1 keV/amu along with other theoretical and experimental results. At low energies below 1 eV/amu, the cross section varies approximately as predicted by the classical Langevin model [20], which gives a formula for the cross section

$$\sigma = \pi q\sqrt{\frac{\alpha}{E}}, \tag{8}$$

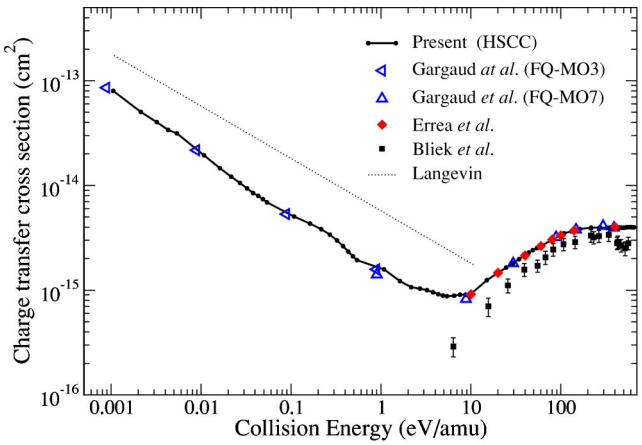

FIG. 2. Comparison of calculated and experimental total charge-transfer cross sections for the process $C^{4+}+H(1s)\rightarrow C^{3+}+H^+$. Present results are shown in dots connected by a solid line. Results of Gargaud *et al.* are obtained from fully quantal (FQ) calculations with three-MO [4] and seven-MO [9] basis functions, respectively. Results of Errea *et al.* are calculated using both quantal and semiclassical formalisms (see text for details) [11]. Experimental results of Bliek *et al.* are shown with error bars [3]. The dashed line indicates the cross section predicted by the Langevin model.

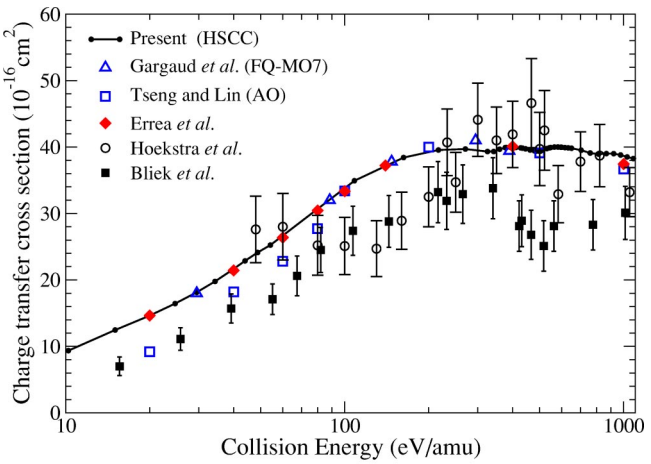

FIG. 3. Comparison of calculated and experimental total charge-transfer cross sections for the process $C^{4+}+H(1s)\rightarrow C^{3+}+H^+$. Notations are the same as in Fig. 2. Results of Tseng and Lin are obtained from semiclassical AO calculations with corrections from Coulomb trajectories [14]. (Without the corrections they agree with the present HSCC and other calculations.) Results of Hoekstra *et al.*, shown with error bars, are the sums of measured partial cross sections for electron capture into individual $C^{3+}(n=3)$ [2].

where q is the charge of C^{4+}, α is the polarizability of $H(1s)$, and E is the collision energy. Note that the Langevin model considers the incident trajectories as orbits of an attractive polarization potential

$$V(r)=-\alpha/2r^4. \tag{9}$$

The cross-section formula is derived based on the assumption that reaction occurs with *a probability of unity* should the projectile (C^{4+}) overcome the potential barrier due to the centrifugal potential and the induced dipole potential. Therefore, any energy dependence of the transition probability will result in a deviation from the $1/\sqrt{E}$ behavior. In the energy region below 1 eV, the channel corresponding to charge transfer to C^{3+} $(3d)+H^+$ is the dominant one because the major transitions occur at the avoided crossing neat $R=8$ a.u. between the initial channel and the C^{3+} $(3d)+H^+$ channel with negligible influence from coupling to other channels. Our results are in good agreement with those obtained from the three-channel calculations by Gargaud *et al.* [4].

In order to compare our results with several other theoretical and experimental ones in more detail, the total charge-transfer cross sections for the energy region between 10 eV/amu and 1 keV/amu are presented in Fig. 3. Our results agree well with those obtained by Gargaud *et al.* [9], who employed a quantal formalism using a seven-MO basis set and reaction coordinates. Results from the present calculations also agree very well with those of Errea *et al.* [11]. Note that their results, presented here in the same way as in their paper, are calculated by different formalisms at different energy regions. For $E\geqslant 140$ eV/amu, results are calculated by a semiclassical (with rectilinear trajectories) formalism using a 35-MO basis set and a common translation factor. For $E\leqslant 140$ eV/amu, quantal calculations were carried out using a 20-MO basis set and reaction coordinates different from those used by Gargaud *et al.* The semiclassical MO calculations by Saha [10], however, gives results that are qualitatively different from the present results and the other two MO calculations mentioned above.

Tseng and Lin calculated charge-transfer cross sections using an AO expansion method with plane-wave translation factors and pseudostates [14]. Their results obtained from rectilinear trajectories agree with those obtained from MO-type calculations over the energy range from 1 keV/amu down to about 10 eV/amu. They found that by introducing an *ad hoc* procedure to account for the Coulomb trajectory effect, they can get good agreement with experimental data below 100 eV/amu. Since it is not an *ab initio* calculation, the fact that the results agree better with the experimental data of Bliek *et al.* in this energy region should not be considered significant, in view of the newer quantum-mechanical calculations that, in principle, have accounted for the trajectory effects. While the total charge-transfer cross sections obtained from HSCC calculations agree well with those obtained from different MO-type calculations, they disagree with the experimental measurements by Bliek *et al.* [3]. None of these theoretical results exhibit the sharp structure near $E\approx 500$ eV/amu observed in the experiment. In addition, these theoretical total cross sections are higher than the experimental results over the energy region between 10 eV/amu and 1 keV/amu.

Here we also would like to comment on the differences between the two experimental measurements [2,3] shown in Fig. 3. Based on our results and those of Errea *et al.* [11], the contribution from channels of excited C^{3+} $(n\geqslant 4)$ are quite small, varying from about 1% at 100 eV/amu to about 5% at 1 keV/amu. Therefore, the sum of the measured cross sec-

tions for electron capture into individual l subshells of C^{3+} ($n=3$) [2] should also provide a good measure of the total charge-transfer cross sections. As can be seen from Fig. 3, the differences between these two sets of experimental data are relatively large, and the data from Hoekstra *et al.* [2] also have large error bars. While the total cross sections from Hoekstra *et al.* do not show a dip in the cross sections near 500 eV/amu, their data have their own dip near 150 eV/amu. In contrast, all the theoretical cross sections, including the present HSCC results, vary smoothly with the collision energy.

Our results for partial cross sections, presented in Fig. 4, show general good agreement with those obtained by Gargaud *et al.* [9] and by Errea *et al.* [11], except for the minor discrepancies at high energies. It is interesting to note that the differences between the two sets of results by Gargaud *et al.* [9] indicate the importance of including the δ channel (or equivalently, the $I=2$ channel in the hyperspherical representation) and that a severely truncated four-molecular-state calculation is insufficient. Overall the experimental partial cross sections of Hoekstra *et al.* agree well with these theoretical calculations except that the experiment show a plateau for the $3p$ cross section near 150 eV/amu. This plateau is reflected in the total charge-transfer cross sections in Fig. 3 as well since in this energy region electron capture predominantly populates the $3p$ state.

IV. CONCLUSIONS

In this paper we used the newly developed HSCC to calculate electron-capture cross sections for $C^{4+}+H$ collisions in the energy range from 1 meV/amu to 1 keV/amu. We were motivated by the long-standing discrepancy between the experimental data and the existing seemingly converged theoretical results for this collision system. In particular, the structure in the total electron-capture cross section near 500 eV/amu from the newer state-of-the-art merged-beam experiment was not found in all the theoretical calculations. While one may want to dismiss that all the theoretical calculations reported by Gargaud *et al.* [9] and Errea *et al.* [11] are based on similar models and thus the agreement among themselves is not surprising, the present HSCC result should resolve this doubt since it was based on a different approach without any ambiguity from the choice of different reaction coordinates.

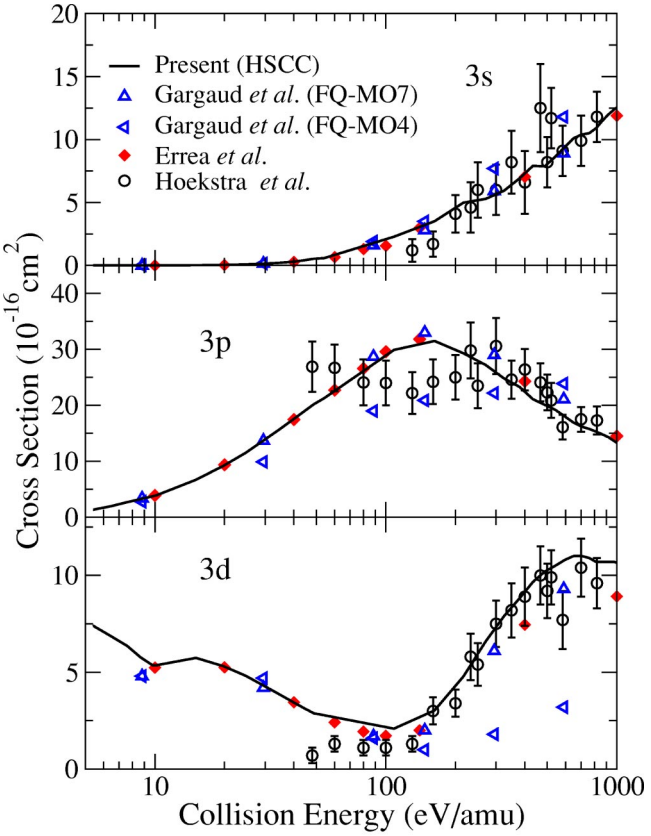

FIG. 4. The state-selective charge-transfer cross sections for electron capture into the $3l$ states of C^{3+}. Notations are the same as in Fig. 3.

Our results support these earlier theoretical calculations and we can safely conclude that the discrepancy between theory and experiment lies in the experimental data.

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