

Charge Exchange in Low-Energy H, D + C⁴⁺ Collisions with Full Account of Electron Translation

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Abstract: We report the application of the quantum approach, which takes full account of electron translation at low collisional energies, to the charge exchange process $H, D + C^{4+} \rightarrow H^+, D^+ + C^{3+}(3s, 3p, 3d)$. The partial and the total integral cross sections of the process are calculated in the energy range from 1 till 60 eV/amu. It is shown that the present results are independent from the upper integration limit for numerical solution of the coupled channel equations although nonadiabatic couplings remain nonzero up to infinity. The calculated partial and total cross sections are in agreement with the previous low-energy calculations and the available experimental data. It is shown that for low collisional energies the isotopic effect takes place. The observed effect is explained in terms of the nonadiabatic dynamics.

Keywords: Ion-atom collisions; Charge transfer; Electron translation; Molecular calculations

1 Introduction

Investigations of charge transfer processes are of both fundamental and practical importance. The most widely used approach for theoretical treatment of collisional processes, including charge exchange ones, is the so-called standard adiabatic approach based on the Born-Oppenheimer separation of the electronic and nuclear motion [1]. Within this approach the theoretical study proceeds into two steps: (i) the quantum chemical calculations of adiabatic potentials and nonadiabatic coupling matrix elements in the fixed-nuclei approximation and (ii) the subsequent treatment of the heavy particle dynamics based on the potentials and couplings obtained on the first step. From mathematical point of view the standard adiabatic approach is based on an expansion of the total wavefunction in terms of a set of electronic basis functions, which are to be found in the fixed-nuclei approximation and which contain the dependence of the total wave function on the electronic coordinates. The second step encounters the severe difficulty: in many practical cases, the coupling matrix elements do not vanish as the internuclear distance goes to infinity (see, for example, [2]-[5]), reflecting the fact that the electronic wave functions travel with one or the other of nuclei. This suggests inelastic transitions under the influence of a collision partner at an arbitrarily large distance and seems to prohibit a straightforward calculation of cross sections. In fact, the nonvanishing asymptotic couplings reflect a less obvious but more fundamental problem: The coordinates used in the standard adiabatic approach are not suited for the description of the free atom motion [6], and a single term of the total wave function expansion does not give the correct asymptotic incoming or outgoing wave functions [4].

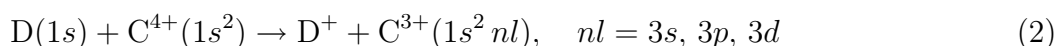
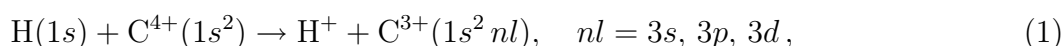
For high collision energies (typically above 1 keV), a practicable solution is known: The classical treatment of the heavy particle motion combined with the use of electron translation factors [6, 7] or common translation factors [8]. For low collision energies in contrast, where a full quantum treatment of the nuclear motion is required, there is no generally agreed simple solution to the problem. Several alternative approaches [2, 8, 9]-[17] have been discussed, practical applications of these proposals have remained limited, however. Numerical work rather was often based on an empirical treatment of the electron translation problem, and it was even asserted that a rigorous computation of collision cross sections is not possible in this way [3].

We recently proposed a new full quantum approach to account for electron translation in low-energy collisions by introducing t - or τ -matrices [4, 5], the so-called t/τ -matrix approach, and we report here the first practical application of the t/τ -matrix approach to a charge transfer process. Whereas previous approaches concentrated on a search for a formulation without nonzero

asymptotic couplings, we keep the asymptotic couplings as they are (including nonzero ones) and concentrate on an interpretation of the solutions of the coupled channel equations, obtained within the standard adiabatic approach, in the asymptotic region. It turns out that a meaningful S -matrix can be extracted by means of a simple reprojection procedure [4, 5].

In addition to the problem discussed above, there exists another problem often discussed in connection with the present one, that is, an ambiguity in the definition of nonadiabatic coupling matrix elements and coupled channel equations, in general. As observed by numerous authors, e.g., [18]-[22], nonadiabatic coupling matrix elements have different values when one chooses different origins for the electronic coordinates. This seems to make both the coupled equations and, hence, the calculation of cross sections ambiguous [23]. However, the changes in nonadiabatic couplings are compensated by additional terms in the coupled equations, and the ambiguity in the coupling matrix elements does not lead to an ambiguity in the coupled equations. The details have been worked out previously by different approaches [4, 24, 25]. We use this result without further discussion.

The H, D + C⁴⁺ charge transfer processes



have served as a model system several times in the past (see, for example, [19, 20, 26]-[31]). As the application of the t/τ -matrix approach to the processes (1) and (2) does not need additional calculations, the above processes are well suited for performing of the dynamical treatment with full account of electron translation. The recent quantum chemical data [30] obtained in the required electron coordinates open the way for the first application of the t/τ -matrix approach to the charge exchange processes, which is the goal of the present paper.

2 The theory

After the separation of the kinetic-energy operator for the centre of mass of the entire system, the Hamiltonian for a diatomic molecule can be written in the following form

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{R}^2} + H_{el}(\mathbf{r}, \mathbf{R}), \quad (3)$$

where $M = M_A M_B / (M_A + M_B)$ is the reduced mass of the nuclei A and B with corresponding masses M_A and M_B , \mathbf{R} is the vector connecting the nuclei, \mathbf{r} denotes the set of the electronic coordinates measured from the centre of nuclear mass, and $H_{el}(\mathbf{r}, \mathbf{R})$ is the so-called electronic Hamiltonian, which contains operators of the kinetic energy for the electrons and all interactions. The mass-polarization terms are neglected. The electronic Hamiltonian parametrically depends on \mathbf{R} , and its eigenstates form the fixed-nuclei adiabatic electronic basis states $|j^a\rangle$

$$H_{el}(\mathbf{r}, \mathbf{R})\phi_j^a(\mathbf{r}, \mathbf{R}) = V_j^a(R)\phi_j^a(\mathbf{r}, \mathbf{R}) \quad (4)$$

with the eigenfunctions $\phi_j^a(\mathbf{r}, \mathbf{R})$

$$\langle \mathbf{r} | j^a \rangle = \phi_j^a(\mathbf{r}, \mathbf{R}), \quad (5)$$

and the adiabatic potential energies $V_j^a(R)$. If nonadiabatic regions are narrow, it is convenient to make a transformation to diabatic or partly diabatic basis states

$$|j^d\rangle = \sum_k C_{jk} |k^a\rangle, \quad (6)$$

C_{jk} being matrix elements of a unitary transformation (see, e.g., [2, 18, 22, 32]).

It has been shown in Ref. [26] that at low collisional energies E for the charge exchange process (1) the rotational couplings can be neglected, and the theoretical treatment can be restricted to Σ states. In this case, the wave function for the total system can be written as a sum of terms $\Psi_{JM_J}(\mathbf{r}, \mathbf{R})$, each of them is characterized by the total angular momentum quantum numbers J and M_J ($M_J \geq 0$) and expanded as

$$\Psi_{JM_J}(\mathbf{r}, \mathbf{R}) = Y_{JM_J}(\Theta, \Phi) \sum_j \frac{F_j(R)}{R} \phi_j(\mathbf{r}, \mathbf{R}). \quad (7)$$

Y_{JM_J} are the spherical harmonics, Θ and Φ are the spherical coordinate angles of the vector \mathbf{R} . $\phi_j(\mathbf{r}, \mathbf{R})$ are electronic basis wave functions of either adiabatic or diabatic (including partly diabatic) states $|j\rangle$. The functions $F_j(R)$ describe the radial motion of the nuclei. Substituting the expansion (7) into the stationary Schrödinger equation $(H - E_t)\Psi_{JM_J} = 0$ [$E_t = E + V_1(\infty)$ being the total energy], multiplying it by $\phi_k^*(\mathbf{r}, \mathbf{R})$ and integrating over the electronic coordinates,

one obtains a set of the coupled channel equations [4]

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + V_j(R) + \frac{\hbar^2}{2M} J(J+1) - E_t \right] F_j(R) = -\sum_{k \neq j} \langle j | H_{el} | k \rangle F_k(R) + \frac{\hbar^2}{M} \sum_k \langle j | \frac{\partial}{\partial R} | k \rangle \frac{dF_k(R)}{dR} + \frac{\hbar^2}{2M} \sum_k \langle j | \frac{\partial^2}{\partial R^2} | k \rangle F_k(R). \quad (8)$$

$V_j(R) = \langle j | H_{el} | j \rangle$ are the potentials in a chosen representation. Note, that in a partly diabatic representation not all of off-diagonal nonadiabatic matrix elements $\langle j | \partial / \partial R | k \rangle$, $\langle j | \partial^2 / \partial R^2 | k \rangle$, and $\langle j | H_{el} | k \rangle$ are zero.

The adiabatic potentials and nonadiabatic matrix elements of the first derivative are at present usually calculated by quantum chemical programs, for example, MOLPRO [33]. The double derivative couplings are not calculated explicitly. In diabatic basis they are expected to be negligible. In adiabatic basis they are not neglected entirely, because they are required for current conservation, but they are modeled by setting [34]

$$\langle j | \frac{\partial^2}{\partial R^2} | k \rangle = \frac{d}{dR} \langle j | \frac{\partial}{\partial R} | k \rangle. \quad (9)$$

As mentioned above, the derivative coupling matrix elements used in the coupled equations (8) should be calculated with the origin of the electronic coordinates \mathbf{r} at the centre of mass of the nuclei. In these coordinates, the orbital wave functions for the active electron in the asymptotic region take the form

$$\langle \mathbf{r} | j \rangle = \phi_j(\mathbf{r} - \gamma_j \mathbf{R}) \quad \text{as } R \rightarrow \infty; \quad (10)$$

$\gamma_j \mathbf{R}$ being the vector pointing from the centre of mass of the nuclei to the nucleus, with which the electron travels:

$$\gamma_j = \begin{cases} -\frac{M_B}{M_A + M_B} & \text{for an electron travelling with the nucleus } A \\ +\frac{M_A}{M_A + M_B} & \text{for an electron travelling with the nucleus } B \end{cases}. \quad (11)$$

As a consequence, $\langle j | \partial / \partial R | k \rangle$ do not automatically go to zero at infinity. In the usual interpretation, where $F_j(R)$ gives the incoming and outgoing fluxes in the state $|j\rangle$, this would indeed predict inelastic transitions between atomic states at an arbitrarily large distance. We have recently shown, how the solutions of Eq. (8) should be used to derive meaningful transition probabilities even in the presence of nonzero asymptotic couplings [4, 5]. One solves the coupled equations (8)

numerically between a small distance and a large value R_{end} , where all couplings and potentials V_j are sufficiently constant, express the properties of the numerical solution at R_{end} by an R -matrix (\underline{R})

$$F_j = \sum_k R_{jk} \frac{dF_k}{dR} \quad \text{at } R_{end} \quad (12)$$

and compute the S -matrix as follows:

$$\underline{S} = (-1)^J \exp(-i\underline{\Phi}) \underline{\kappa}^{1/2} (\underline{\tau}^+ - i\underline{R}\underline{\tau}^+ \underline{\kappa})^{-1} (\underline{\tau}^- + i\underline{R}\underline{\tau}^- \underline{\kappa}) \underline{\kappa}^{-1/2} \exp(-i\underline{\Phi}), \quad (13)$$

where the diagonal matrices $\underline{\kappa}$ and $\exp(-i\underline{\Phi})$ respectively consist of the local wave numbers

$$\kappa_j(R) = \sqrt{\frac{2M}{\hbar^2} [E_t - V_j(R)] - \frac{J(J+1)}{R^2}} \quad (14)$$

and the elements $\exp(-i\underline{\Phi}_j)$ are the usual WKB phases of $\Phi_j(R)$. In Refs. [4, 5] the elements of the τ^\pm -matrices are expressed via dipole moment elements. For nondegenerate states they can also be evaluated via the potentials and the nonadiabatic couplings calculated in the Jacobi coordinates used in the present work

$$\tau_{kj}^\pm(R) = \delta_{kj} \pm \frac{i\kappa_j(R) \hbar^2}{M[V_k(R) - V_j(R)]} \langle k | \frac{\partial}{\partial R} | j \rangle. \quad (15)$$

The values of these quantities have to be taken at $R = R_{end}$.

The background of the relation (13) is that one has to mix the computed radial functions $F_j(R)$ in order to account correctly for the electron translation effects in asymptotic wave functions [4, 5]. This is done via the matrices $\underline{\tau}^\pm$. When the matrices $\underline{\tau}^\pm$ are replaced by the unit matrix, Eq. (13) becomes the usual relation between R - and S -matrices, which is valid in the absence of asymptotic couplings. Eq. (13) is valid in an approximation up to terms of the first order of $\sqrt{m_e/M}$ with m_e being the electron mass. Higher order corrections have turned out to be negligible in the examples treated so far. Eq. (13) is further based on the construction of a WKB type solution to the coupled equations beyond R_{end} . The WKB approximation is important only for computational convenience. It might be dropped by extending the numerical calculation to a distance, which is so large that not only variations of both the adiabatic potentials and couplings, but also the centrifugal potentials are negligible.

3 Results and discussions

3.1 Quantum chemical data

The adiabatic potentials and the radial nonadiabatic couplings for the CH^{4+} and the CD^{4+} collisional systems are calculated *ab initio* by means of the MOLPRO code [33] for the internuclear distance from $R = 0.2$ a.u. till $R = 10000$ a.u. The electronic coordinates are measured from the centre of nuclear mass. A Huzinaga Gaussian basis set ($9s4p$) [35] has been used for the hydrogen atom. For carbon, a $3d$ orbital optimized on the $1s^2 3d^2 D$ state of C^{3+} and a $4f$ orbital from the correlation-consistent polarized cc-pVTZ basis of Dunning [36] have been added to the Huzinaga basis set ($11s, 7p$) [35]. The molecular orbitals have been optimized in a state-average CASSCF calculation [37, 38] on the first six $^2\Sigma^+$ states. The seven lowest σ , the four lowest π and the two lowest δ were chosen as active orbitals. This level of calculation corresponds to the calculation labelled CASSCF-2 in Ref. [30]. The radial coupling matrix elements have been calculated by the standard numerical three points differentiation method implemented in MOLPRO [33]. A detailed description of the quantum chemical calculations is given in Ref. [30]. The calculations of Ref. [30] were restricted to internuclear distances $R \leq 32$ a.u., where the nonadiabatic couplings do not reach yet their asymptotic values. For this reason, the present calculations are performed in the extended internuclear distance range. The potentials and the nonadiabatic couplings are in good agreement with other quantum chemical calculations (see, e.g., [19]).

The quantum chemical data relevant to the process (1) are shown in Fig. 1. The potentials for the $\text{CH}^{4+}(^2\Sigma^+)$ states are plotted in Fig. 1a¹. It is seen that the potentials of the adiabatic states $|1s^a\rangle$ and $|3d^a\rangle$ asymptotically ($R \rightarrow \infty$) correlated to the $\text{H}(1s) + \text{C}^{4+}$ and $\text{H}^+ + \text{C}^{3+}(3d)$ states, respectively, are closely approaching each other at the internuclear distances $R \approx 4.46$ a.u. and $R \approx 7.93$ a.u., apparently showing two avoided crossings in these regions. Indeed the radial coupling matrix element $\langle 1s^a | \partial/\partial R | 3d^a \rangle$ depicted in Fig. 1b shows sharp peaks at the same distances confirming the avoided crossing interpretation. The area under each of the peaks is close to $\pi/2$, the situation is expected to correspond closely to the Landau-Zener model. Other radial couplings are smaller by at least one order of magnitude, as shown in Fig. 3 of Ref. [30].

In order to avoid such rapid variations in the coupling matrix elements, we transformed the

¹For the states asymptotically corresponding to $\text{H}(1s) + \text{C}^{4+}$ and $\text{H}^+ + \text{C}^{3+}(3d)$ Fig. 1a shows the diabatic potentials described below, the adiabatic potentials are not distinguishable from the diabatic ones within the figure scale.

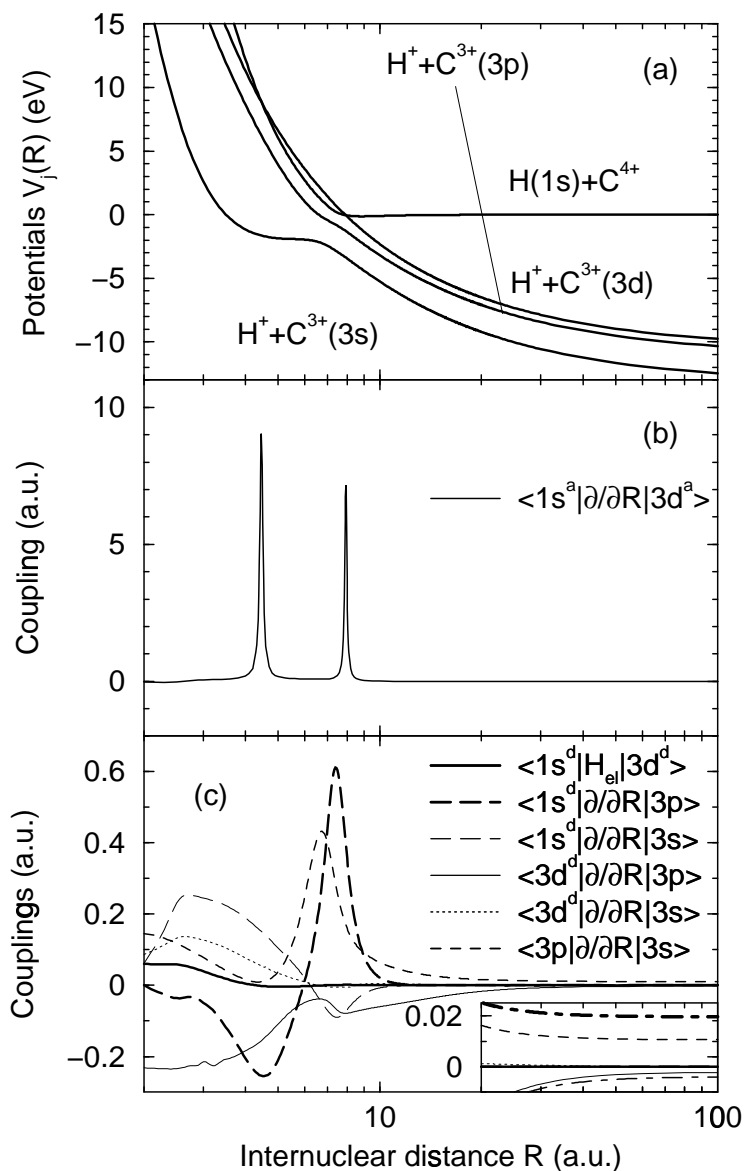


Figure 1: Quantum chemical data for the CH^{4+} quasimolecule: the potentials in the partly diabatic representation (a), the nonadiabatic radial coupling matrix element $\langle 1s^a | \partial/\partial R | 3d^a \rangle$ (b), and the couplings in the partly diabatic representation (c). The insert in (c) shows the couplings in the enlarged scale and demonstrates that some of them do not vanish as $R \rightarrow \infty$. The thick and thin dot-dashed lines are the $\langle 3p | \partial/\partial R | 3s \rangle$ and $\langle 3d | \partial/\partial R | 3p \rangle$ nonadiabatic matrix elements for the CD^{4+} quasimolecule.

adiabatic electronic basis $|nl^a\rangle$ to a partly diabatic basis $|nl^d\rangle$. The new diabatic electronic states $|1s^d\rangle \equiv |1\rangle$ and $|3d^d\rangle \equiv |2\rangle$ are constructed as linear combinations of $|1s^a\rangle$ and $|3d^a\rangle$ [see Eq. (6)] by the requirement $\langle 1s^d|\partial/\partial R|3d^d\rangle = 0$. The other states $|3p\rangle \equiv |3\rangle$ and $|3s\rangle \equiv |4\rangle$ are left unchanged. The construction of the new basis is straightforward taking into account the fact that $\langle 1s^a|\partial/\partial R|3d^a\rangle$ goes to zero at $R \rightarrow \infty$. The avoided crossings between the adiabatic potentials become real crossings between the diabatic curves $V_1(R)$ and $V_2(R)$, the other potentials are not changed. Fig. 1a shows the diabatic potentials $V_j(R)$ obtained in this manner. The coupling between the states $|1s^d\rangle$ and $|3d^d\rangle$ is now provided by an off-diagonal matrix element $\langle 1s^d|H_{el}|3d^d\rangle$ (Fig. 1c, the thick solid line) of the electronic Hamiltonian, the couplings between the states $|1s^d\rangle$ and $|3d^d\rangle$ to $|3p\rangle$ and $|3s\rangle$ occurs by new derivative couplings (Fig. 1c), the coupling between the $|3p\rangle$ and $|3s\rangle$ states is unchanged.

Nonvanishing values of the asymptotic nonadiabatic couplings are clearly recognized in the insert of Fig. 1c. They are in agreement with the analytical expression [4, 5, 19]

$$\left\langle j^a \left| \frac{\partial}{\partial R} \right| k^a \right\rangle = -\gamma_k \frac{m}{\hbar^2} (V_k^a - V_j^a) \langle j | z_{at} | k \rangle_\infty, \quad (16)$$

where z_{at} is the projection of the active electron coordinate onto the molecular axis, and m is the reduced mass of an electron and the nuclei. If one of the nuclei is replaced by its isotope, the scalar factor γ_k is changed [see Eq. (11)], and the nonadiabatic couplings have another asymptotic limits, which is shown in the insert of Fig. 1c, where the thick and thin dot-dashed lines are the $\langle 3p|\partial/\partial R|3s\rangle$ and $\langle 3d|\partial/\partial R|3p\rangle$ nonadiabatic matrix elements for the CD^{4+} quasimolecule, while the thin dashed and solid lines denote the same matrix elements for the CH^{4+} quasimolecule.

3.2 Dynamics

The program used in the present work for numerical integration of the coupled channel equations (8) is described in Ref. [34].

Fig. 2 shows typical numerical results for the transition probabilities from the initial to the final states calculated as the square of the absolute values of corresponding S-matrix elements in $\text{H} + \text{C}^{4+}$ (Fig. 2a) and $\text{D} + \text{C}^{4+}$ (Fig. 2b) collisions for collisional energy $E = 10$ eV/amu and the impact parameter $b = \sqrt{J(J+1)/(2ME)} = 1.06$ a.u. (Fig. 2a) and $b = 1.87$ a.u. (Fig. 2b). The computed results are shown as functions of the upper limit R_{end} of the numerical integration. As long as Eq. (13) is used, the computed transition probabilities (the solid lines in Fig. 2) are

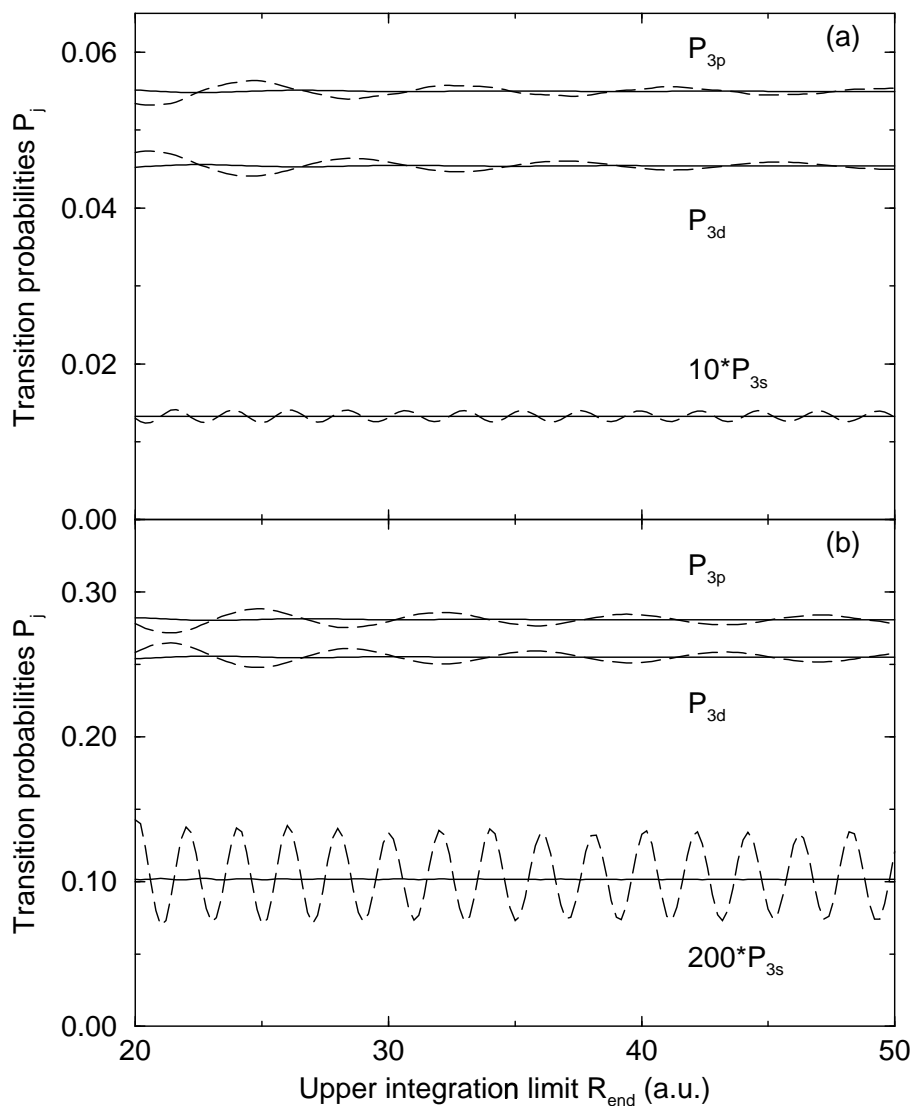


Figure 2: The transition probabilities for excitation of the $C^{3+}(nl)$ states in $H + C^{4+}$ (a) and $D + C^{4+}$ (b) collisions as functions of the upper integration limit R_{end} for the collisional energy $E = 10$ eV/amu and the impact parameters $b = 1.06$ a.u. (a) and $b = 1.87$ a.u. (b). The solid lines are the results obtained by means of the t/τ -matrix approach, the dashed lines are calculations with neglect of the electron translation ($\underline{\mathcal{T}}^\pm = \underline{\mathbb{1}}$).

essentially independent from R_{end} , when R_{end} is sufficiently large. Some minor oscillations are still exist, but they are typically by more than three orders of magnitude smaller than a corresponding transition probability. We ascribe this to the neglect of second order terms in the derivation of Eq. (15), which appears to be well justified in this way. There is no other detectable variation of the computed result, supporting the use of the WKB approximation to derive Eq. (13).

Alternatively, there are different empirical approaches to solve the coupled system. The simplest approach consists in cutting off the asymptotic couplings at an arbitrary distance \tilde{R} ; formally, this is the same as integrating numerically up to $R_{end} = \tilde{R}$ and then using Eq. (13), however with τ^\pm -matrices equal to the unit matrix. Results obtained in this way (the dashed lines in Fig. 2) show large oscillations as a function of R_{end} ; this represents the expected inelastic transitions between atomic states at large distance. The amplitudes of the oscillations vary from a few to nearly 100 percents with respect to corresponding rigorous probabilities depending on the collision conditions and the final states. Obviously the errors from the neglect of electron translation are larger for higher collisional energies [see Eq. (15)] and in cases of small transition probabilities.

Another approach consists in constructing a smooth transformation from the actual value of the coupling matrix element to zero. The numerical tests carried out in the present work show that the oscillations of the transition probabilities with the upper integration limit calculated by using this approach still exist. However, they are smaller than the ones obtained by simple cutting off the nonzero asymptotic couplings. The transition probabilities in this case are in better agreement with the rigorous results. This seems to justify numerous calculations, which have been carried out in this way in the past. However, this is a purely empirical justification, and there is no guarantee that the procedure works similarly well in other cases.

In the calculation of cross sections the influence of the electron translation neglect is expected to be reduced by integration over an impact parameter. Fig. 3 shows the result of using the present quantum approach (the solid lines) and neglecting electron translation (the dashed curves) for calculation of cross sections as a function of the upper integration limit. It is seen that the neglect of electron translation leads to variation of the cross sections, while the cross sections obtained within the t/τ -matrix approach practically do not depend on the upper integration limit, when it is large enough.

Fig. 4 shows our results for the partial and total cross sections as functions of the collisional energy for the charge transfer processes (1) and (2), the thick and the thin lines, respectively. They are compared to the data from Ref. [30], the plusses, the stars, the crosses, and the diamonds; these results were obtained by using coupling matrix elements extrapolated to zero. The good

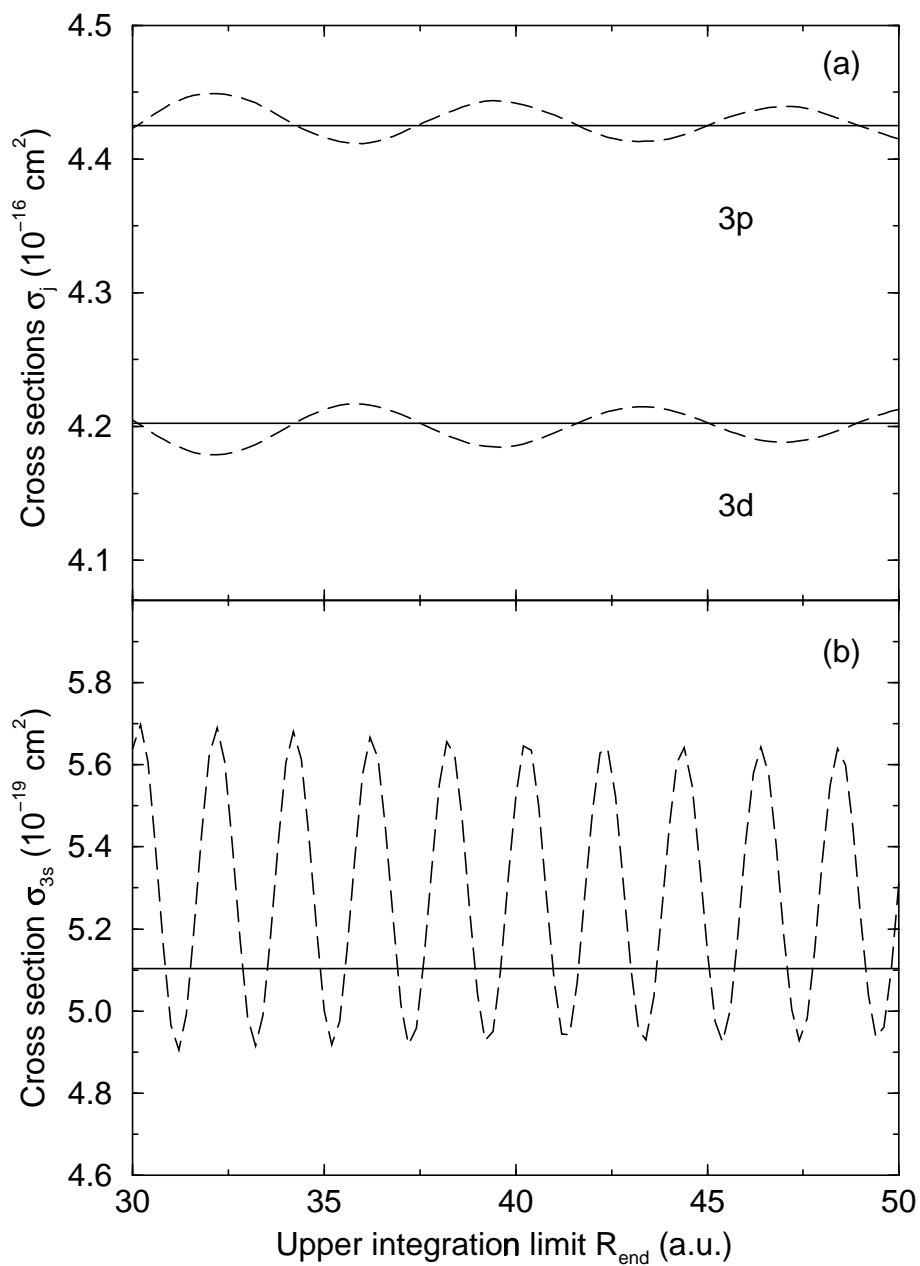


Figure 3: The charge exchange cross sections for excitation of the $C^{3+}(nl)$ states in $D + C^{4+}$ collisions as functions of the upper integration limit R_{end} for the collisional energy $E = 10 \text{ eV/amu}$. The solid lines are the results obtained by means of the t/τ -matrix approach, the dashed lines are calculations with the neglect of the electron translation ($\tau^{\pm} = \underline{1}$).

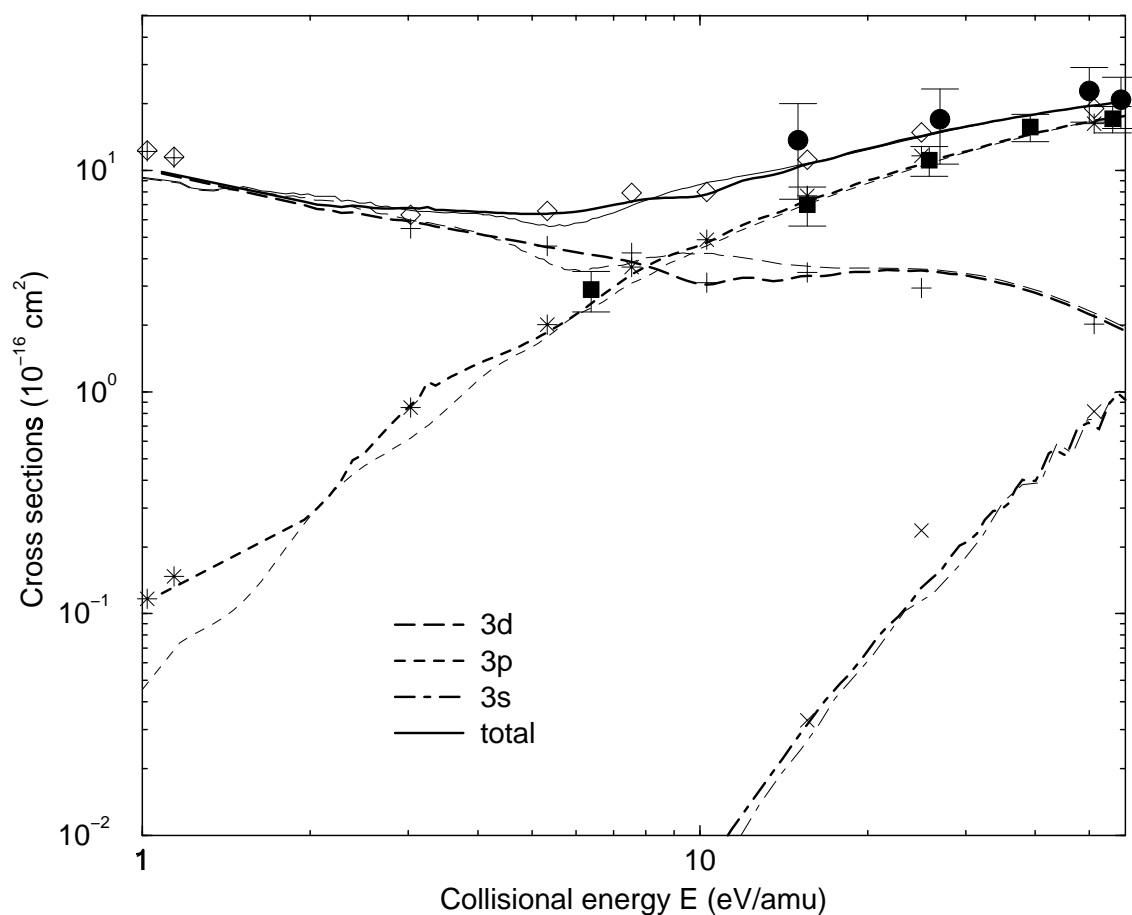


Figure 4: The partial (dashed and dot-dashed curves) and the total (solid curves) cross sections for the charge exchange processes in $\text{H} + \text{C}^{4+}$ (thick lines) and $\text{D} + \text{C}^{4+}$ (thin lines) collisions calculated in the present work. The plusses, the stars, the crosses, and the diamonds are the wave packet data [30] for the partial (3d, 3p, and 3s) and the total cross sections, respectively. The circles are experimental data for the total cross section in $\text{H} + \text{C}^{4+}$ collisions [39], while the squares are the experimental total cross section in $\text{D} + \text{C}^{4+}$ collisions [41].

agreement is to be expected in view of the good agreement of the dashed lines in Figs. 2 and 3 with the rigorous result. Except for the large distance extrapolation, the same potentials and couplings are used. However, the rest of the work was quite different: The result of Ref. [30] is obtained with a completely diabatic basis and a wave packet approach, in contrast to our time independent coupled channels approach with a partly diabatic basis. We interpret the good agreement as an indication of reliability of the treatments.

The present calculations are also in agreement with the previous calculations of Ref. [19, 20, 26, 27, 29] and the available experimental data for the total cross sections of the charge exchange processes (1) and (2) [27, 39, 40]. As the example, the experimental data [39] for H + C⁴⁺ collisions are shown in Fig. 4 by circles. The recent experimental data [41] for D + C⁴⁺ collisions at low energies are shown by squares; it is seen that these data are in good agreement with the partial cross section for the excitation of the C³⁺(3*p*) state. As discussed in the literature, the cross section [41] are smaller than both experimental [27, 39, 40] and theoretical [19, 20, 26, 27, 29, 30] total cross sections. For the detailed discussion of the theoretical results and the comparison with experiment for H, D + C⁴⁺ collisions see Ref. [30].

It is usually expected that cross sections for different isotopes should coincide for equal collisional velocities or collisional energies expressed in the eV/amu units. Fig. 4 shows that for the processes (1) and (2) this is indeed the case at relatively high collisional energies, but for energies below 20 eV/amu the isotopic effect gets remarkable. This is understandable in terms of nonadiabatic models, e.g., the Landau-Zener model, where the transition probability depends on a radial velocity in a nonadiabatic region which is different from a collisional velocity at infinity due to different (diabatic) potentials in a nonadiabatic region and at infinity. In the present case nonadiabatic transitions occur in several nonadiabatic regions (see Fig. 1), which makes the dynamics more complicated than in case of only one nonadiabatic region. In particular, the most remarkable differences in the calculated cross sections for the H and D isotopes take place at the collisional energies around 10 eV (note different collisional energies measured in the eV/amu unit), which correspond to the nonadiabatic region around $R \approx 4.46$ a.u. for H + C⁴⁺ collisions, see Fig. 1. This results in the different nonadiabatic nuclear dynamics for the different isotopes and, hence, in different transition probabilities. Fig. 5 clearly shows different types of behavior of the transition probabilities for the different isotopes for the collisional energy $E = 10$ eV/amu especially for the excitation of the C³⁺(3*d*) state. For H + C⁴⁺ collisions this energy ($E = 9.231$ eV) is nearly equal to the crossing of the 1*s* and 3*d* diabatic potentials in the nonadiabatic region, and the turning points are inside the nonadiabatic region (for small impact parameters), while for D +

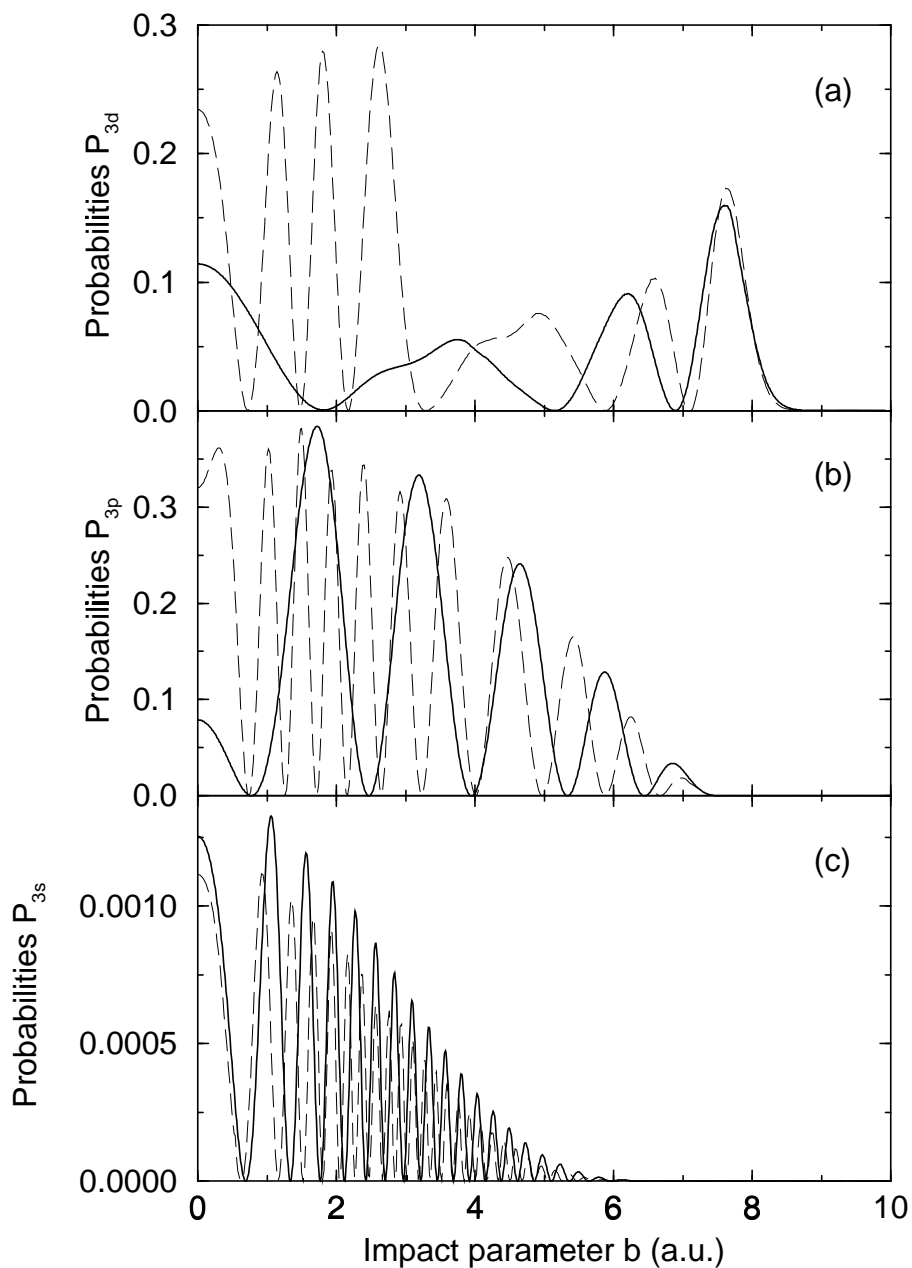


Figure 5: The transition probabilities for excitation of the $C^{3+}(3d)$ (a), $C^{3+}(3p)$ (b), and $C^{3+}(3s)$ (c) states in $H + C^{4+}$ (solid lines) and $D + C^{4+}$ (dashed lines) collisions for the collisional energy $E = 10$ eV/amu as the functions of the impact parameter.

C^{4+} collisions at the energy $E = 10$ eV/amu (the collisional energy $E = 17.143$ eV) the turning points are outside of the nonadiabatic region. As a result, the transition probabilities and the partial cross sections for excitation of the $C^{3+}(3d)$ state are significantly different in $H + C^{4+}$ and $D + C^{4+}$ collisions, reflecting, therefore, the isotopic effect for the charge exchange processes (1) and (2) at low collisional energies. The experimental evidence of violation of the scaling law is given in Ref. [42].

4 Conclusion

The charge transfer processes (1) and (2) at low collisional energies are studied theoretically with full account of electron translation by means of the t/τ -matrix approach developed recently [4, 5]. It is shown that the neglect of electron translation leads to uncertainty from a few to nearly 100 percents with respect to the upper integration limit for numerical solution of the coupled channel equations, while the results of the t/τ -matrix approach are practically independent from the upper integration limit.

The calculated partial and total cross sections are in agreement with the previous low-energy calculations [19, 20, 26, 27, 29, 30] and the available experimental data [27, 39, 40]. The recent experimental data [41] for $D + C^{4+}$ collisions at low energies are in agreement with the present partial cross section for the excitation of the $C^{3+}(3p)$ state.

It is shown that for low collisional energies the scaling law breaks down, reflecting the isotopic effect for the processes (1) and (2). The observed effect is explained in terms of the nonadiabatic dynamics.

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