P H Y S I C A L   R E V I E W   L E T T E R S

Strong Isotope Effects on the Charge Transfer in Slow Collisions of He^{2+} with Atomic Hydrogen, Deuterium, and Tritium

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Probabilities and cross sections for charge transfer by He^{2+} impact on atomic hydrogen (H), deuterium (D), and tritium (T) at low collision energies are calculated. The results are obtained using an *ab initio* theory, which solves the time-dependent Schrödinger equation. For the H target, excellent agreement is achieved between the present and previous results. Differences by orders of magnitude are observed between the cross sections for H, D, and T. A method is introduced to separate the contributions of charge-transfer mechanisms due to radial and rotational coupling. The large differences observed for H, D, and T are attributed to isotope effects in the rotational coupling mechanism.

Helium ''ash'' is the main end product in a fusion reactor. Bare helium ions $^4He^{2+}$, i.e., alpha particles, are produced in fusion plasmas between deuterium (D) and tritium (T) and constitute an important ingredient in the dynamics of maintaining the plasma. Alpha particles, which have been slowed down by elastic collisions and reach the cooler outer plasma boundary, can recombine along various pathways into excited He^+ states and thus contribute to radiative cooling [1]. The latter helps to accommodate the large power flux from the plasma core onto the surrounding walls and the divertor target plates.

In view of this rather complex scenario, it is evident that a satisfactory understanding of the transport behavior and charge balance of neutral and ionized He in the plasma boundary is highly desirable. In the boundary layer a significant fraction of neutral D and T atoms, which are being desorbed and sputtered from the walls, is available for charge exchange reactions with alpha particles. Such charge exchange reactions involve sizeable cross sections [2] and can therefore play an important role. In order to understand and assess the particular role of the collisions of alpha particles with atoms, a detailed knowledge of the relevant cross sections is necessary.

As a fundamental three-particle problem, $He^{2+} + H$ is the benchmark system of charge-transfer theory, for which numerous theoretical approaches have been applied (for references to previous theoretical and experimental studies, see [3,4]). At energies above 1000 eV/amu, excellent agreement among the different calculated cross sections is achieved. At lower energies the data from earlier work deviate, in general. Recent studies, employing reaction coordinates (RC) by Le *et al.* [5] and the hidden crossing coupled channel (HCCC) approach by Krstić [6], have yielded converging cross sections. Since the results of these calculations [5,6], based on essentially different

methods, agree within 5%, reliable cross sections for the $He^{2+} + H$ system became available at collision energies as low as 10 eV/amu.

At low impact energies, charge transfer can be interpreted in terms of couplings of adiabatic potential curves as shown in Fig. 1. It is commonly accepted [4,6] that charge transfer in $He^{2+} + H$ collisions is dominated by radial coupling between the $2p\sigma$ and $3d\sigma$ molecular orbitals at
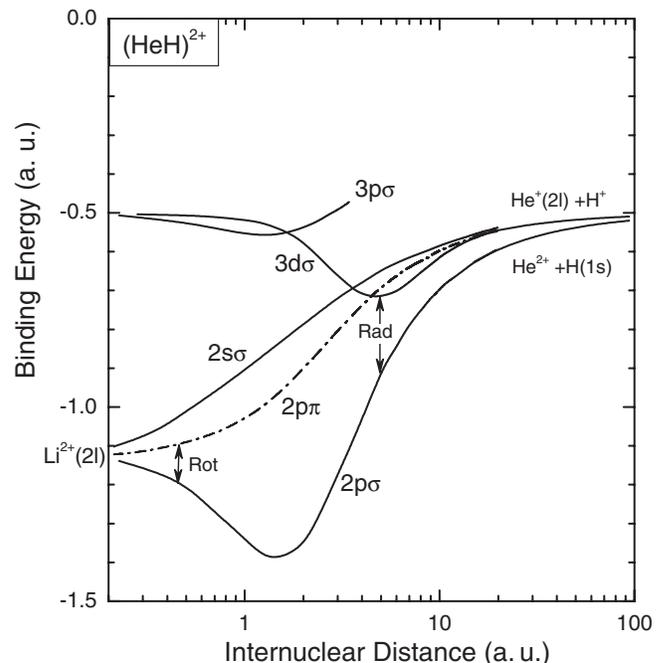
FIG. 1. Molecular orbital diagram for the system (HeH)$^{2+}$. The arrows labeled ''Rot'' and ''Rad'' denote the approximate locations for transitions due to rotational and radial couplings, respectively. (See Havener *et al.* [4].)

large internuclear distances (~ 6 a.u.) and rotational coupling between the $2p\sigma$ and $2p\pi$ orbitals at small internuclear distance (~ 0.5 a.u.). Radial coupling dominates at collision energies around 1000 eV/amu. However, its contribution decreases exponentially with decreasing energy, which is characteristic for transitions between orbitals separated by a significant energy gap [7,8]. Since the radial coupling loses significance, the rotational coupling gains importance at lower energies giving rise to significant capture cross sections around 100 eV/amu [6]. At energies below 40 eV/amu the significance of the rotational coupling diminishes and the radial coupling again becomes dominant.

In view of the extensive studies of $He^{2+} + H$ collisions, one would expect that the collisions with the target atoms D and T would have received similar considerations. Charge exchange has been studied in $Cl^{7+} + D$ collisions [9]. However, to the best of our knowledge, no investigation for He^{2+} impact on D and T has yet been performed. As mentioned, these systems are of considerable interest for modeling the plasma in a fusion reactor and their cross sections are highly desirable.

In the present work, we have calculated cross sections for charge transfer in collisions of alpha particles with atomic H, D, and T. The calculations were performed using the theoretical approach, known as electron nuclear dynamics (END) [10], which explicitly solves the time-dependent Schrödinger equation. The results for the $He^{2+} + H$ system are shown to agree well with previous cross sections [5,6] providing confidence that the present approach yields reliable results. Within the energy range, where the rotational coupling dominates, the capture cross sections for the target atoms D and T exceed those for H by orders of magnitude.

The END theory is an explicitly time-dependent, direct method that accounts for nonadiabatic coupling terms between the nuclear and the electronic dynamics as described in the review by Deumens *et al.* [10]. The equations that govern the time evolution of the system state vector are derived using a time-dependent variational principle and form a set of coupled first-order differential equations. The time dependence is carried by the wave function parameters: average nuclear positions, average nuclear momenta, and complex molecular orbital coefficients. The nuclei are described with Gaussian wave packets in the narrow width limit, i.e., they move as classical particles. The electronic wave function is described as a linear combination of Gaussian functions centered on the nuclei and endowed with electron translation factors. This application of the END theory using a nonrelativistic Coulombic Hamiltonian, apart from the nuclei being classical and the electronic wave function expressed in a finite basis, has no further approximations. The theoretical predictions agree well with measured differential and integral cross sections for ion-atom and ion-molecule collisions (see the recent work by Cabrera-Trujillo *et al.* [11] and references therein).

In the present calculations, the electronic states centered at H and He are expressed in terms of the correlation consistent, polarized-valence double Z basis sets aug-cc-pVDZ and aug-cc-pVTZ, respectively, from Dunning [12]. They have been augmented with two diffuse orbitals to insure a proper description of the hydrogenic excited states. These bases yield the binding energies for $n = 1$, 2, and 3 within 1% of their exact values. The grid for the impact parameters b was divided into two regions: (i) close collisions for which b is varied in steps of 0.05 a.u. from 0 to 1 a.u. and (ii) soft collisions for which b runs in steps of 0.1 a.u. from 1 to 10 a.u. These regions will be denoted *inner* and *outer* regions, respectively.

Figure 2 shows the calculated charge-transfer probabilities, $P(b)$, for the collisions systems $He^{2+} + H$ and $He^{2+} + T$ as a function of the impact parameter. The inner and outer regions of the impact parameter are separated by the vertical lines drawn near 1 a.u. Although somewhat arbitrary, the separation into two impact parameter regions is useful, as it provides information about the contributions of the rotational and radial coupling mechanisms. It is recalled that the internuclear distances for the two processes differ by an order of magnitude.

In the outer region the probability $P(b)$ exhibits oscillatory structures, which are due to well-known interference effects treated in the early work by Stueckelberg [13]. The
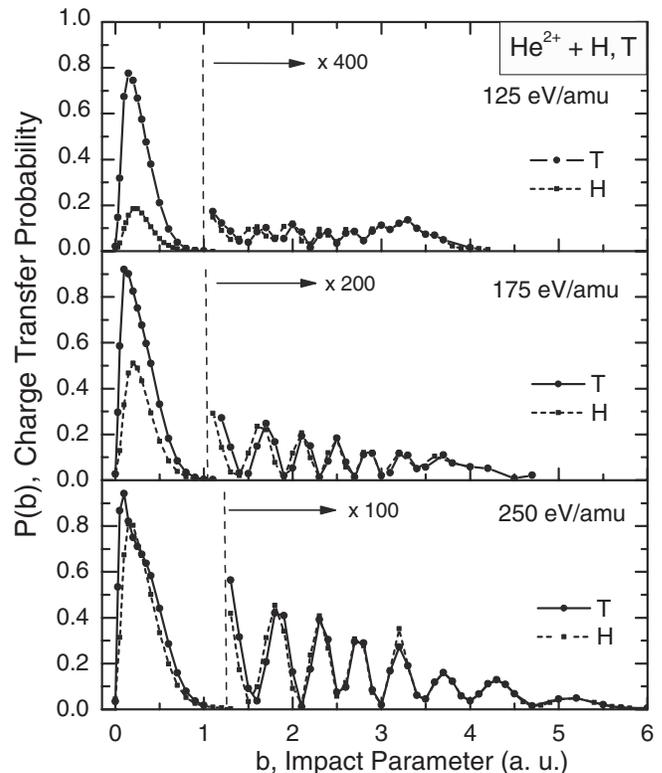
FIG. 2. Probabilities $P(b)$ for charge transfer in collisions of He^{2+} with hydrogen (H) and tritium (T). The impact energies are 125, 175, and 250 eV/amu as indicated in the graphs. For H similar results are obtained by Krstić [6].

amplitudes, associated with the double passage of the radial coupling regions of the incoming and outgoing branch of the collision, add coherently giving rise to sinusoidal interferences. From Fig. 2 it is seen that, apart from a small phase shift, the charge-transfer probabilities for the H and T atoms agree within the outer region which is dominated by radial coupling. On the other hand, large differences are observed within the inner region which is governed by rotational coupling. These differences are expected to be also visible in the corresponding cross sections.

The cross section for charge transfer, σ, was determined by integration of the charge-transfer probability

$$\sigma = 2\pi \int_0^\infty b P(b) db. \qquad (1)$$

In Fig. 3(a), the cross sections for H, D, and T are shown as a function of the He^{2+} projectile energy. It is seen that cross sections for H compare well with the calculations of Krstić [6] and Le *et al.* [5], whose results are represented by one unique line (since they agree within the line thickness). Except for the lowest energy (75 eV/amu) the present and previous cross sections differ by less than 15%. The cross sections for all target atoms H, D, and T coincide above 500 eV/amu. However, with decreasing energy the cross sections are strongly enhanced for D and, even more so for T, as compared to those for H. Figure 3(b) depicts cross section ratios obtained for D and H (labeled D/H) as well as for T and H (labeled T/H). At energies below 80 eV/amu the theoretical H data [5,6] are used for normalization. We note that the D/H cross section ratio reaches a value of ~ 100 and the T/H ratio increases to a factor of ~ 1000.

For the analysis of the enormous differences in the cross sections, we first estimate the contribution of the radial coupling. Following the analysis of Crothers [14] the charge-transfer probability for the double passage of the transition region at $R_c \approx 6$ a.u. is obtained as

$$P(b) = 4p(1-p)\sin^2\left(\frac{1}{2v}\int_{-z_c}^{z_c} \Delta\varepsilon \, dz\right), \qquad (2)$$

where p is the single-passage probability and $\Delta\varepsilon$ is the energy difference between the $2p\sigma$ and $3d\sigma$ orbitals (Fig. 1). For a straight line trajectory it follows that $z = vt = \sqrt{R^2 - b^2}$, where t is time, v is the projectile velocity, and R is the internuclear distance. The integration limits are given by $z_c = \sqrt{R_c^2 - b^2}$.

It can readily be shown that Eq. (2) reproduces well the Stueckelberg oscillations observed in the outer region of impact parameters. In particular, it explains the increase of the oscillation frequency with decreasing projectile velocity v. Hence, we used Eq. (2) to perform an extrapolation of the radial coupling contribution into the inner region. The extrapolation involves uncertainties which, however, are small due to the weighting of the transfer probability by the impact parameter. The charge-transfer cross sections,
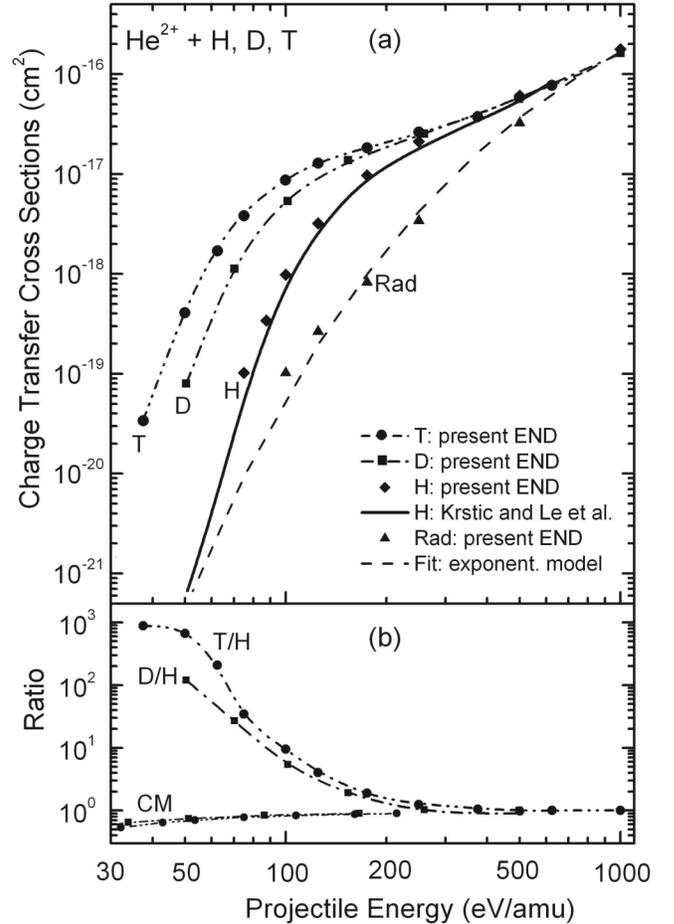
FIG. 3. Upper graph (a) END results for charge transfer cross sections in collisions of He^{2+} with H ($\blacklozenge$), D ($\blacksquare$), and T ($\bullet$) as a function of the projectile energy. The solid line represents the data by Le *et al.* [5] and Krstić [6]. The dashed curve and the triangles are estimates for the radial coupling contribution. The lower graph (b) shows the cross section ratios T/H ($\bullet$) and D/H ($\blacksquare$). The curves labeled CM display ratios of the rotational coupling contributions as a function of the center-of-mass energy (see text).

caused exclusively by radial coupling, are depicted in Fig. 3(a) as triangles labeled "Rad".

The radial coupling contribution can also be estimated from Eq. (2) by assuming in a rough approximation that $p(b) \approx p(0)$ for $b \leq R_c$ and $p(b) = 0$ otherwise. Then, the integration can be performed analytically yielding

$$\sigma = 2p(1-p)\pi R_c^2, \qquad (3)$$

where the $\sin^2$ function was replaced by its average value $1/2$. The single-passage transition probability p is given by an exponential expression derived by Demkov [7] and on more accurate grounds by Solov'ev [8]

$$p = [1 + \exp(a/v)]^{-1} \approx \exp(-a/v), \qquad (4)$$

where a is a model parameter, for which different values are obtained by the previous theories [7,8]. Therefore, we treated a, as well as R_c, as adjustable parameters, to

interpolate the END results (triangles) and perform a smooth transition to the RC-HCCC results [5,6]. The fit yields $a = 0.524$ a.u. and $R_c = 6.6$ a.u. In Fig. 3(a), the results of the exponential model are given by the dashed curve, which compares well with the triangles (END results) representing the radial coupling contribution. In fact, the model calculations provide also an excellent fit to the RC-HCCC [5,6] results within the energy range from 10–50 eV/amu, where the cross sections vary by 10 orders of magnitude (not shown here).

In the collision, the recoiling H, D, and T atoms produce certain differences in the particle trajectories and relative projectile-target velocities. Since the radial coupling occurs at large distances, these isotope effects are weak within the coupling region. Nevertheless, isotope effects are observed by small phase shifts between the oscillatory structures for H and T (Fig. 2). However, they do not change the absolute values of the charge-transfer probability and, thus, do not affect the corresponding cross sections.

To obtain the contributions for rotational coupling, the cross section for radial coupling was subtracted from the charge-transfer cross section. For higher impact energies, from about 250–1000 eV/amu, the subtraction yields rotational coupling contributions, which are essentially constant. Within the intermediate energy region, from about 35–250 eV/amu, the charge-transfer cross sections are not much affected by the subtraction, since in this range the radial coupling contributions are negligible. Hence, we conclude that the large differences in the charge-transfer cross sections observed for the target atoms H, D, and T are essentially produced by isotope effects in the rotational coupling mechanism.

For low collision energies, the recoiling target atoms limit the distance of closest approach, R_{min}, between the collisions partners so that the rotational coupling region can no longer be reached. In particular, the distances of closest approach for H, D, and T differ significantly. For impact parameters close to zero the distance of closest approach can readily be estimated from $R_{min} = Z_1 Z_2 / E_p^c$, where Z_1 and Z_2 are the (screened) nuclear charges of the collision partners and E_p^c is the center-of-mass energy. For 100 eV/amu, the distances of closest approach for H, D, and T amount to $R_{min} = 0.65$, 0.4, and 0.3 a.u., respectively. Thus, the rotational coupling region is barely reached for H, whereas for D, and even more so for T, the coupling regions are accessed. Accordingly, at 100 eV/amu the cross section for H is an order of magnitude lower than that for T (Fig. 3).

In accordance with the present consideration, a two-state model for rotational coupling at the united atom limit predicts a scaling of the charge-transfer cross sections in terms of the center-of-mass energy E_p^c. Indeed, when the rotational coupling contributions are plotted as a function of E_p^c, the differences between the results for H, D, and T are drastically reduced. In Fig. 3(b) the cross section ratios T/H (dots) and D/H (squares) are given by curves labeled CM. The ratios approach unity at higher energies ($E_p^c \approx$ 250 eV/amu) and decrease to values of 0.33 (D/H) and 0.18 (T/H) at lower energies ($E_p^c \approx 15$ eV/amu). Hence, there remain differences as large as a factor of 5.5 between the results of the isotopes. This dependence is consistent with the two-state model involving a dependence of the rotational coupling on the velocity $v = \sqrt{2 E_p^c / \mu}$, where μ is the reduced mass of the collision system, as will be discussed in a forthcoming paper.

In conclusion, we have calculated capture cross sections for collision systems, which are of fundamental importance for fusion reactors. The contributions due to radial and rotational coupling were separated. The contributions due to rotational coupling are found to differ by orders of magnitude which is attributed to isotope effects influencing the distance of closest approach. The differences can be reduced strongly when the rotational coupling contribution is scaled by the center-of-mass energy. However, this procedure is inapplicable to the full charge-transfer cross sections, as they contain the radial coupling contribution which scales with the laboratory energy. Hence, the scaling laws can be used for fair estimates of the radial and rotational coupling contributions. However, for an accurate determination of the charge-transfer cross sections, an *ab initio* theory is required.

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