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Systematic theoretical investigation of charge exchange in He$^+$-alkali-atom collisions

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A comprehensive systematic study of near-resonant charge exchange into He*($n = 2$) levels in He$^+$–alkali-atom collisions is reported. The relevant quasimolecular properties of the (He-alkali)$^+$ systems are obtained within the one-electron projected-valence-bond method of Kubach and Sidis. The detailed investigation of the considered systems enables one to assess the relevance of the two-state Demkov model for near-resonant charge exchange and the role of rotational coupling. The present multistate close-coupling treatment considerably improves upon the previous simplified theory of Olson and Smith and nicely reproduces the measured relative abundance of the specific He*($2\,^{3,1}S$, $2\,^{3,1}P$) states formed by charge exchange. The calculated summed total charge-exchange cross sections generally agree with experiment for He$^+$-Cs, -Rb, and -K, whereas problems remain for He$^+$-Na.

I. INTRODUCTION

The ionization potential of ground-state alkali atoms is nearly equal to the binding energy of an electron in excited states (radiative or metastable) of most other atoms (see, e.g., Fig. 1 for the He case). This property is expected and indeed found to favor near-resonant charge-exchange excitation processes in low- and medium-energy collisions of a number of ions with alkali atoms. Moreover, these reactions provide an efficient method for producing intense neutral metastable beams that can be used in a variety of further applications.

In previous papers[1,2] we reported on a theoretical investigation of near-resonant charge exchange into $n = 2$ levels of H in H$^+$-alkali-atom collisions. This study is extended herein to the He$^+$–alkali-atom systems. Referring to the H$^+$–alkali-atom cases, the presently considered systems offer a few interesting new features, namely, the $n = 2$ shell splitting and its effect on the He* polarizability (quadratic Stark effect) together with the possibility of having the entrance channel squeezed between two outgoing channels in one or both spin multiplicity sequences (see Fig. 1). These features should dramatically influence the primary charge-exchange transitions and the secondary He* ($2s$-$2p$) sharing processes. Another particular interest in the He$^+$–alkali systems, especially those involving K, Rb, and Cs, arose from the disagreement between the theoretical predictions of Olson and Smith[3] and the recent experimental data of Reynaud *et al.*[4] concerning the relative population of excited He*($2\,^{3,1}S$, $2\,^{3,1}P$) states formed in these collisions. One of our objectives was to understand the reasons of this unsuccess by carefully analyzing the previous theoretical work[3] (Sec II). To go beyond this previous theory we had to evaluate the relevant interactions between the collision partners. For the cases of major interest here (He$^+$-K, -Rb, -Cs) *ab initio* all-electron calculations would have been rather costly. This problem has been overcome by using simple one-electron Hamiltonians involving effective two-center screened Coulomb potentials. The procedure to be discussed in Sec. III stems from and extends the approximations discussed in our previous work.[2] In Sec. IV are reported the results of cross section calculations and their comparison with available experiments.

II. ANALYSIS OF THE PREVIOUS THEORETICAL INVESTIGATION OF He$^+$-ALKALI-ATOM COLLISIONS

The principal aim of the work of Olson and Smith[3] was to provide a simple quantitative treatment of charge transfer processes in He$^+$-alkali collisions by making use of a "modified two-state Demkov theory"[5,6] involving known or estimated properties of the separated collision partners (i.e., ionization potentials, dipole polarizabilities, and quadrupole moments). Following these authors[3] the problem can be split into two independent problems according to the spin multiplicity (triplet and singlet subspaces) of the reactants and products (Wigner spin conservation rule). Indeed, even for the heaviest alkali atoms the spin-orbit interaction is negligible as can be estimated from the atomic J-energy intervals,[7] e.g., for Cs the $6\,^2P_{3/2}$-$6^2P_{1/2}$ splitting amounts to ~0.7 eV. Although this is an important simplification of the problem it does not imply that simple *independent two-state approximations* in each subspace are generally valid since for each entrance channel two closely lying outgoing channels [He*($2S$ and $2P$) + alkali$^+$] are involved. This is especially true in the He$^+$-Cs, -Rb, -K systems where an entrance channel lies between the two outgoing channels (Fig. 1). Therefore, consider-

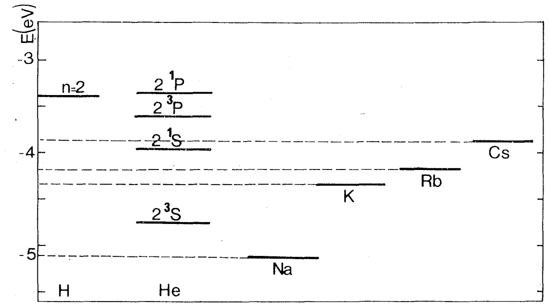

FIG. 1. Atomic energy levels for the considered He^+ + alkali → $He^*(n=2)$+ alkali$^+$ charge-exchange processes. The hydrogen case is shown for comparison on the left-hand side of the figure. The ordinates correspond to the binding energy of the active outer electron in the initial and final states.

ation of independent two-state models, as done in Ref. 3, may violate flux conservation. As a consequence the cross sections calculated by Olson and Smith can only represent an estimate of an upper bound.

Among the important parameters involved in the theory of Olson and Smith are the unknown static dipole polarizabilities of the excited radiating $He^*(2\,^{3,1}P)$ states. These parameters were estimated in that work by scaling the known dipole polarizabilities of the $He^*(2\,^{3,1}S)$ states to the ionization potentials of the $2\,^{3,1}P$ states. Although intuitively sound, this assumption has to be further analyzed. Let us first consider the dipole polarizability of the $2^{3,1}S$ states. When a metastable $He^*(2^{3,1}S)$ state is placed in the field of a positive charge at large distance R it mainly mixes with the closely lying $He^*(2\,^{3,1}P)$ state. This mixing accounts for about 95% of the dipole polarizability of $He^*(2\,^{3,1}S)$ (Ref. 8). Accordingly, by using the asymptotic form of the Wigner multipole expansion in powers of R^{-1} the S and P energy levels of Σ symmetry split for large R values as

$$E_- \approx E_S - \frac{h^2}{R^4(E_P - E_S)} , \tag{1}$$

$$E_+ \approx E_P - \frac{\beta}{R^3} + \frac{h^2}{R^4(E_P - E_S)} , \tag{2}$$

where β is the quadrupole moment of the P state and h is the $\langle 2s|z|2p\rangle$ transition moment. These equations show that contrary to the assumption made by Olson and Smith[3] [in their Eq. (2)], the adiabatic energy level correlated to the P state is *repelled* as $\alpha/2R^4$ where α has the same size as the dipole polarizability of the S state. This repulsion even compensates the charge quadrupole interaction for $R \leq 15a_0$, so that the polarized Σ (P) states can hardly couple in a favorable way with the Σ entrance channel. Yet, the above discussion has involved only two states ($2S$, $2P$). As shown in Sec. III the cumulative interactions of the $2P$ state with higher excited states, (e.g., $He^*(nL,\ n \geq 3)$ still cannot yield the behavior assumed by Olson and Smith. We thus conclude that *their calculated He*(2P) cross sections are certainly overestimated.*

Another point subject to criticism is the inclusion of polarization contributions to the (diagonal) energy terms without taking into account corresponding effects in the interactions. More precisely the effect of a distant charge B^+ on atom A is to mix its initial wave function $|\phi_A^0\rangle$ with other states on the same atom $|\phi_A^i\rangle$:

$$|\phi_A^{\text{pol}}\rangle = \alpha_0|\phi_A^0\rangle + \sum_i \alpha_i|\phi_A^i\rangle , \tag{3}$$

and similarly for atom B polarized by a distant charge A^+. The corresponding charge-exchange interaction between the polarized states then writes

$$\begin{aligned}\langle\phi_A^{\text{pol}}|H|\phi_B^{\text{pol}}\rangle = {} & \alpha_0\beta_0\langle\phi_A^0|H|\phi_B^0\rangle + \alpha_0\sum_j \beta_j\langle\phi_A^0|H|\phi_B^j\rangle \\ & + \beta_0\sum_i \alpha_i\langle\phi_A^i|H|\phi_B^0\rangle \\ & + \sum_{i,j}\alpha_i\beta_j\langle\phi_A^i|H|\phi_B^j\rangle .\end{aligned} \tag{4}$$

For near lying He^* ($2S$, $2P$) states and for alkali (nS, nP) states the charge-exchange interaction involves not only the interaction between the unperturbed states[3] but at least also the second and third cross terms (first-order terms) of Eq. (4). Disregarding this correction certainly affects the determination of the critical transition region R_c and thereby also the cross section. The failure of Olson and Smith to account for an important $He^*(2\,^1S)$ cross section in He^+-Cs as observed by Reynaud *et al.*[4] is a typical illustration of the discussed inconsistency. Indeed, in the early stages of the present investigation, modified Demkov-model calculations[6] were carried out in this case using Eq. (4) along with an improved Smirnov formula for the exchange interaction (see, e.g., Ref. 10) and the resulting $He^*(2\,^1S)$ cross section reproduced quite nicely the present multistate close-coupling result of Sec. IV.

In several places of their paper, Olson and Smith[3] invoke rotational coupling as a possible cause of uncertainty in their predictions. However, within the framework of their simplified theory the importance of this effect and its relevance to the considered charge-exchange processes could not be precisely assessed. Since, as discussed above, the He*($2^{3,1}P$) cross sections resulting from only Σ-Σ interactions should be much smaller than predicted in Ref. 3, one readily suspects, in view of the results of Reynaud *et al.*[4] that rotational coupling must play a major role as already pointed out by Melius and Goddard[11] for the alkali$^+$-alkali systems.

From the above analysis it is seen that a multistate close-coupling treatment involving *improved estimates of the molecular properties* of the considered collision systems is generally required to treat the competitive effects of charge exchange and polarization interactions together with rotational coupling.

III. MOLECULAR CALCULATIONS

A. Model Hamiltonian and practical considerations

The model calculations we have performed to evaluate the electronic interactions in the (He-alkali)$^+$ systems are based on two fundamental *assumptions.*

(i) The charge-exchange transitions have to take place at relatively large internuclear distances ($R > 7a_0$) to yield as large cross sections as determined experimentally.[12]

(ii) Only the single outermost electron participates in the transition mechanisms. Arguments supporting this assumption have been given by Olson and Smith[3] for keV collision energies and it has recently been confirmed experimentally[13] down to collision energies of 500 eV. At lower energies some problems arise, the discussion of which is deferred to Sec. IV B.

In view of assumption (i), an essentially atomic description of the problem is most appropriate. Accordingly, we have chosen a projected-valence-bond (PVB) representation.[1a,14] The second assumption (ii) enables the use of an effective one-electron potential model.

Referring to our previous work on (H-alkali)$^+$ systems[2] the effect of the alkali ion core can be simulated in a PVB approach, by the screened Coulomb potential,

$$V_A(r_A) = -\frac{1 + Ae^{-ar_A}}{r_A} \quad . \tag{5}$$

Proceeding in the same way for He (Ref. 15) the effective Hamiltonian acting on the outer orbital then writes

$$\mathcal{H} = E_{A^+} + E_{\mathrm{He}^+} + (P^0_{\tilde{A}} + P^0_{\tilde{\mathrm{He}}})\, h (P^0_{\tilde{A}} + P^0_{\tilde{\mathrm{He}}}) + 1/R, \tag{6}$$

where

$$h = -\tfrac{1}{2}\Delta + V_A(r_A) + V^{S,T}_{\mathrm{He}}(r_{\mathrm{He}}) \ , \tag{7}$$

and where $P^0_{\tilde{A},\tilde{\mathrm{He}}}$ are the projectors onto the active outer electron space orthogonal to the cores, and

$$V^{S,T}_{\mathrm{He}} = -\frac{1 + B^{S,T} e^{-b^{S,T} r_{\mathrm{He}}}}{r_{\mathrm{He}}} \tag{8}$$

(S and T stand for singlet and triplet respectively). The parameters A, a [Eq. (5)] and the Slater-type (STO) expansion bases for the alkali atoms are the same as in the work of Kubach and Sidis.[2] The parameters $B^{S,T}$ and $b^{S,T}$ determined in a similar way as in this previous work are given in Table I. The STO basis set for the He triplets is that of Krauss *et al.*[16]; for the singlets the diffuse STO exponents $\zeta^T_{2s} = 0.615$ and $\zeta^T_{2p} = 0.518$, are replaced by $\zeta^S_{2s} = 0.540$ and $\zeta^T_{2p} = 0.498$. These exponent variations were found to improve the calculated dipole polarizability of He* ($1s2s\,^1S$). To be in a position to correctly account for the He* ($2^{1,3}P$) polarizabilities we have included in our PVB bases $3s$, $3p$, and $3d$ polarization STO. The exponents of these additional orbitals were obtained by requiring maximum energy lowering of the adiabatic $^{1,3}\Sigma(2P_{\mathrm{He}})$ level issued from He* ($2^{1,3}P$) when this state is placed in the field of a distant ($R \gtrsim 30\ a_0$) bare positive charge. The results were not significantly modified when the basis was extended to include twice as many polarization functions encompassing the optimum ones. These calculations did not confirm the behavior assumed by Olson and Smith[3]: Neither the charge quadrupole term nor the $2p_{\mathrm{He}}$ - ($3d_{\mathrm{He}}$, $3s_{\mathrm{He}}$) (and higher order $2p_{\mathrm{He}}$-$3p_{\mathrm{He}}$) interactions could efficiently compensate for the repulsive effect of the $2s_{\mathrm{He}}$-$2p_{\mathrm{He}}$ interaction on the $2^{3,1}P$ state [see Eq. (2)]. In the final He basis set used in the systematic (He-alkali)$^+$ calculations we retained only the $3d$ and $3p$ polarization STO with exponents 0.35 and 0.45, respectively. The calculated ionization potentials and dipole polarizabilities of He($n = 2$) are given in Tables II and III respectively. All other computational details are the same as described by Kubach and Sidis.[2]

The accuracy of the model one-electron Hamiltonian [Eq. (6)] was tested on the (He-Na)$^+$ system by comparing its results with all electron PVB calculations. For all internuclear distances $R > 5a_0$ the deviations were less than 2.10^{-4} a.u. confirming the reliability of the method.

TABLE I. Parameters $B^{S,T}$ and $b^{S,T}$ of the effective potential [Eq. (8)] for He* ($n = 2$) in atomic units.

	B	b
Triplet	1.234	1.740
Singlet	0.401	2.650

TABLE II. Comparison between the theoretical (T) and experimental (E) binding energies and energy differences (Δ_{S-P}), in atomic units, for the $2S$ and $2P$ states of He.

	Triplets		Singlets	
	T	E	T	E
$2S$	0.174	0.175	0.152	0.146
$2P$	0.132	0.133	0.118	0.124
Δ_{S-P}	0.042	0.042	0.034	0.022

B. Results

In Figs. 2–5 are presented a few typical examples displaying the general trends of the *adiabatic* potential energy curves for the considered excited states[17] of the (He-alkali)$^+$ systems (other examples have been presented in Ref. 10). These energy curves are obtained by diagonalizing the model PVB Hamiltonian matrix in the following subspace. Σ: σns_{alk}, σnp_{alk}, $\sigma 2s_{\text{He}}$, $\sigma 2p_{\text{He}}$, $\sigma 3p_{\text{He}}$(pol), $\sigma 3d_{\text{He}}$(pol); Π: πnp_{alk}, $\pi 2p_{\text{He}}$, $\pi 3p_{\text{He}}$(pol), $\pi 3d_{\text{He}}$(pol), the He$^+$-alk$^+$ core being implicit. The states listed above are those used in the collision calculations of Sec. IV. The behavior of the entrance energy curve correlated with He$^+$ + alkali depends on the specific relative position of the atomic energy levels (see Fig. 1). For (He-Na)$^+$ (singlets and triplets) and for (He-K, -Rb)$^+$ (singlets) the entrance channel is the lowest in energy[17] and the corresponding energy curve displays a potential well as in the case of the (H-alkali)$^+$ systems. For (He-K -Rb)$^+$ (triplets) and (He-Cs)$^+$ (triplets and singlets) the entrance channel lies between He*($2S$) + alkali$^+$ and He* ($2P$) + alkali$^+$, and except for a possible very shallow well at large distances the corresponding energy curve is repulsive. This behavior results from the opposite effects of the exchange interactions between the entrance channel and the two mentioned outgoing channels. As a consequence the entrance Σ energy curve undergoes a crossing with the lowest Π curve correlated with He*($2P$) + alkali$^+$. One can readily anticipate that *in addition to the expected near-resonant Demkov-type*[3, 5, 6] *Σ-Σ transitions, an alternative important route for charge exchange into He* (2P) might be provided by this Σ-Π crossing.* If this transition mechanism has a significant probability it will indeed yield large total cross sections since the corresponding geometrical estimate lies in the range 50 Å $\leq Q \leq$ 75 Å^2.

From the above description of the results it appears that the investigated systems can be divided into two classes according to the expected possibility of having a contribution of Σ-Π curve crossing to charge exchange.

(a) In the He$^+$-Na (triplet and singlet) and He$^+$-K, –Rb (singlet) systems rotational coupling only *shares* the initial Demkov-type population between the charge-exchange channels. (Fig. 2).

(b) In the He$^+$-K, -Rb (triplet) and He$^+$-Cs (triplet and singlet), both the Demkov-type Σ-Σ transition and rotational coupling participate in the *direct* population of the charge-exchange channels. (Figs. 3–5).

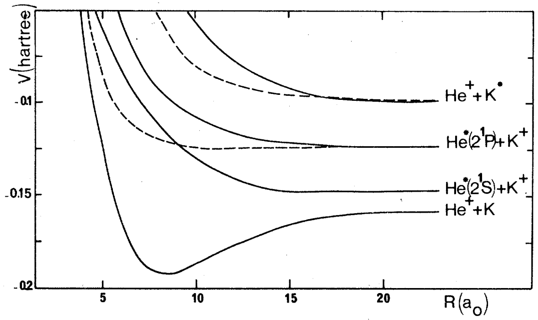

FIG. 2. Adiabatic potential energy curves of the (He-K)$^+$ system in the singlet sequence; full lines: Σ states; dashed lines: Π states. This figure samples the behavior of the adiabatic energy curves for systems belonging to class (a) (defined in text).

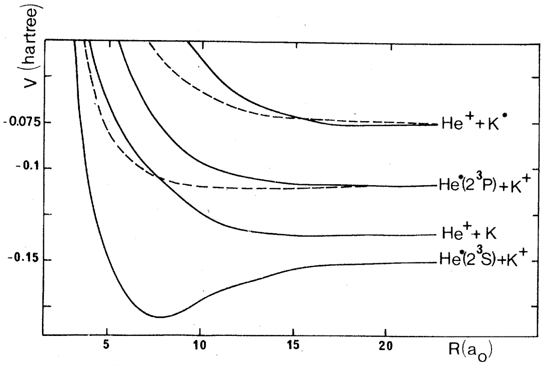

FIG. 3. Adiabatic potential energy curves of the (He-K)$^+$ system in the triplet sequence; full lines: Σ states; dashed lines: Π states. This figure illustrates the general behavior of the adiabatic energy curves for systems belonging to class (b) (defined in text).

TABLE III. Comparison of the currently calculated dipole polarizabilities α of the $2S$ states of He with results from Ref. 8. The present results are obtained with the STO basis sets including $3p$ and $3d$ polarization STO as discussed in text. The calculated quadrupole moments (β) of the He ($2P$) states are also displayed.

	Triplet	Singlet
α (a_0^3) Present	344	761
α (a_0^3) Ref. 8	316	803
β (a_0^2) Present	10.3	12.6

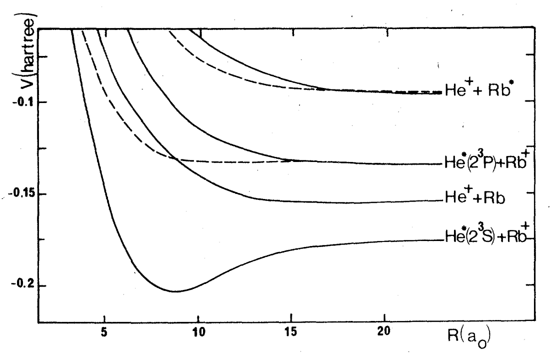

FIG. 4. Same caption as in Fig. 3 except for (He-Rb)$^+$.

We stress that the Σ-Π curve crossing and the related rotational coupling is a subtle effect occuring in a *molecular region* where the actual states are mixtures of individual atomic states. More precisely, when the exchange and polarization interactions become larger than the asymptotic energy level spacings the physical states of the system are

$$\Pi_{\text{adiab}} = a\Pi(nP_{\text{alk}}) + b\,\Pi(2P_{\text{He}})$$

$$\Sigma_{\text{adiab}} = \alpha\Sigma(nS_{\text{alk}}) + \alpha'\,\Sigma(nP_{\text{alk}}) + \beta\Sigma(2S_{\text{He}}) + \beta'\,\Sigma(2P_{\text{He}}) \tag{9}$$

(where we have restricted the expansion to the S and P states). From these equations it is seen that the Σ-Π rotational coupling is efficient when the quantity $\sim a\alpha' + b\beta'$ is important around the curve crossing which is actually the case in the investigated He$^+$-alkali systems.

It is to be noted that the systems in class (a) have the closest resemblance to the previously investigated (H-alkali)$^+$ systems. Nevertheless, the potential energy diagrams display no avoided crossing between the curves correlated with He$^*(2S)$ + alkali$^+$ and He$^*(2P)$ + alkali$^+$. This new feature is certainly connected with the relatively large He ($n = 2$) shell splitting at $R \to \infty$. In concluding this section it could be remarked that a modified two-state Demkov model[6] can only be justified for systems in class (a) and only when considering total charge exchange without attempts to predict populations of specific charge-exchange channels.

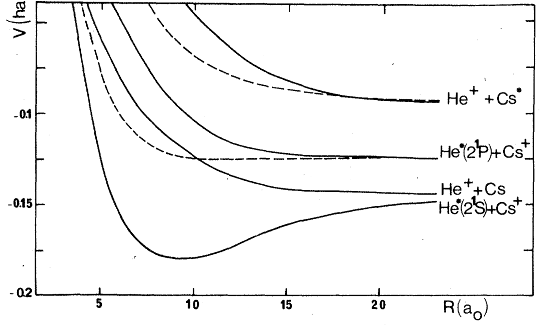

FIG. 5. Same caption as in Fig. 3 except for (He-CS)$^+$ singlet sequence.

IV. CROSS-SECTION CALCULATIONS

A. Close-coupling treatment

In order to obtain transition probabilities one generally needs dynamic (radial and rotational) couplings in addition to the electronic Hamiltonian matrix. However, when one is going to evaluate the dynamic couplings two major difficulties arise, namely, the nontranslational invariance of these couplings and their spurious long-range behavior at $R \to \infty$ for *nondegenerate* states satisfying the rule $\Delta L = \pm 1$ (Ref. 18). As is now well known these drawbacks result from the inability of the clamped nuclei electronic basis to represent electron clouds traveling with the nuclei, and electron translational factors have been proposed to handle this problem.[18] Here we will not attempt to solve this as yet open problem,[18c] but we admittedly circumvent it using an accepted method.[19] Explicitly the dynamic couplings are evaluated after the replacement[20]

$$\vec{\nabla}_R\big|_{\text{c.m.}} \to P^0_{\tilde{A}}\,\vec{\nabla}_R\big|_A P^0_{\tilde{A}} + P^0_{\tilde{\text{He}}}\,\vec{\nabla}_R\big|_{\text{He}} P^0_{\tilde{\text{He}}} + P^0_{\tilde{A}}\,\vec{\nabla}_R\big|_{\text{c.m.}} P^0_{\tilde{\text{He}}} + P^0_{\tilde{\text{He}}}\,\vec{\nabla}_R\big|_{\text{c.m.}} P^0_{\tilde{A}}\ , \tag{10}$$

where $\vec{\nabla}_R\big|_{\alpha = A,\,\text{He},\,\text{c.m.}}$ act holding fixed the electronic coordinates with respect to center A (alkali-atom), He, or the center of mass of the nuclei. The last two terms in Eq. (10) have negligible contributions to the transition processes (especially for the heaviest alkali atoms[1a,14]) and thus have always been set to zero.

The transition probabilities were calculated using the impact parameter method with a straight line trajectory.[21] The calculations involved all the Σ and Π PVB states (valence, Rydberg, and polarization) discussed in Sec. III A. Tests were also made using an additional alkali polarization state (nd_A) but the results were insensitive to this inclusion. In these calculations we have not concerned ourselves with possible oscillations in the total cross sections as a function of the reciprocal collision velocity,[11,22] the cross section are drawn as smooth curves connecting the calculated points.

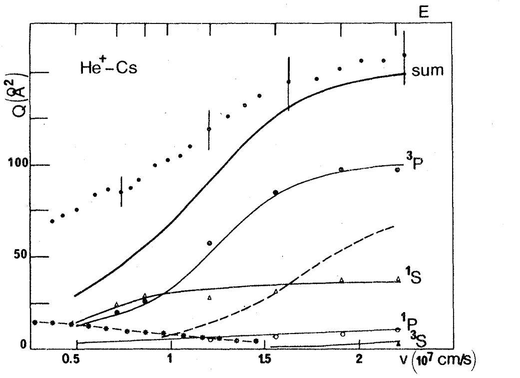

FIG. 6. Total charge-exchange cross sections for the He$^+$-Cs collision versus collision velocity. The upper scale gives corresponding He$^+$ laboratory collision energies in eV: 50, 100, 150, 200, 300, 500, 750, and 1000. The theoretical cross sections for the population of specific He*($2\,^{3,1}S$, $2\,^{3,1}P$) states and their sum are shown as full lines. The experimental data of Reynaud *et al.* (Ref. 4) normalized to the present theory are displayed as follows: △△ $2\,^1S$, ▲▲ $2\,^3S$, ○○ $2\,^1P$, ●● $2\,^3P$. The experimental data of Peterson and Lorents (Ref. 12) for total charge exchange irrespective of the final He state are displayed by dots. The dashed line shows the theoretical $2\,^3P$ cross section obtained by neglecting rotational coupling. The curve $*-*$ represents the cross section for charge exchange into a resonant He ($1s^2$) + Cs^{+}*($5p^5nl$) channel.

B. Results and discussion

We present in Figs. 6–9 both the individual cross sections for populating the He* ($2\,^3S$, $2\,^3P$; $2\,^1S$, $2\,^1P$) states and their sum. Note that the curves shown take into account the relevant statistical weights: $\frac{3}{4}$ for the triplets and $\frac{1}{4}$ for the singlets. The results are seen to account quite nicely for the experimental findings of Reynaud *et al.*[4] concerning the relative abundance of specific He* states formed by charge-exchange collisions of He$^+$ with alkali atoms. For the He$^+$-Cs case we also show as an example the He*($2\,^3P$) cross section calculated without inclusion of the Π states. This result clearly demonstrates the importance of rotational coupling in this system (see Sec. III B) down to the lowest considered collision energies. For the He$^+$-K and Rb systems (triplet sequence) the dominance of the He ($2\,^3P$) cross section over the He ($2\,^3S$) one, which might seem surprising in view of the involved resonance energy defects (Fig. 1), is again a remarkable effect of rotational coupling. This effect appears especially at low energy where the entrance channel (He$^+$ + alkali) is not too strongly depopulated in the incoming part of the collision (decreasing R) by the Σ-Σ Demkov-type transitions.

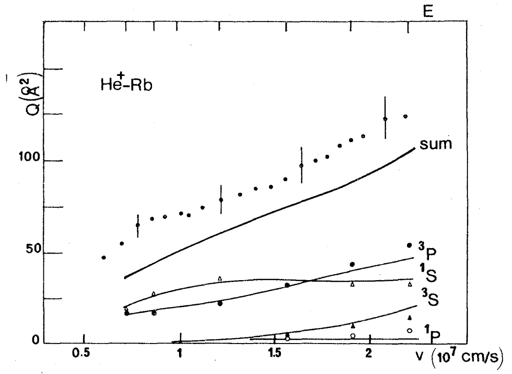

FIG. 7. Same caption and labeling as in Fig. 6 except for He$^+$-Rb.

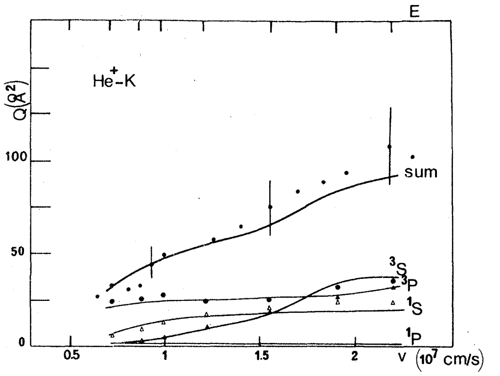

FIG. 8. Same caption and labeling as in Fig. 6 except for He$^+$-K.

Considering the summed total charge-exchange cross sections, good agreement is found for He$^+$-K, -Rb with the measurements of Peterson and Lorents[12] (Figs. 7 and 8). For He$^+$-Cs (Fig. 6) the present results significantly depart from the experimental curve[12] below a collision energy of about 300 eV. In view of the considered collision energy range and of the actual transition regions a Langevin-type[23] enhancement of our

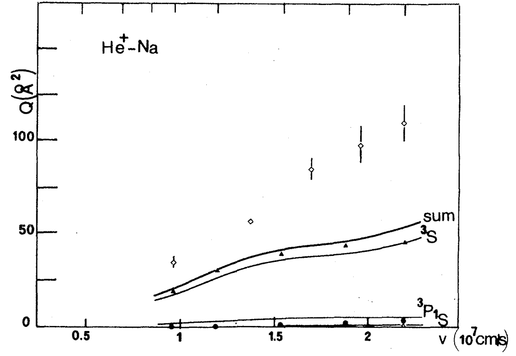

FIG. 9. Same caption and labeling as in Fig. 6 except for He$^+$-Na. Note also that in this figure the experimental points (◇◇) for total charge exchange irrespective of the final He state are data of McCullough (Ref. 27).

straight-line trajectory cross sections[24] is unlikely ($E_{\max}^{\mathrm{Lang}} \approx 0.1$ eV). On the other hand a more plausible source of error in our calculation could be the omission of He$(1s^2)$+Cs$^{+*}[5p^5nl,\ n=6,$ $7,\ 8,\ 9]$ charge-exchange channels forming a quasicontinuum in which the entrance channel is embedded.[24] This possibility is at variance with assumption (ii) of Sec. III A and should be kept in mind while considering the adiabatic energy curves of Sec. III B. Since accidental resonance and/or near resonance occur in this case we have estimated the *resonant* cross section Q_R for the exchange of one electron between the $5p_{\mathrm{Cs}}$ and $1s_{\mathrm{He}}$ core orbitals using the Firsov-Smirnov formula[25]:

$$Q_R = \pi\rho^2/2\ , \tag{11a}$$

$$\rho = \frac{1}{\lambda}\left[\ln\left(\frac{A\sqrt{\pi}}{0.28\sqrt{2}\lambda^{2\nu}}\right) - \ln v\right]\ , \tag{11b}$$

where $A = 7.44$ a.u., $v = 0.74$, $\lambda = 1.352\ a_0^{-1}$ are characteristic of the $5p_{\mathrm{Cs}}$-$1s_{\mathrm{He}}$ exchange interaction $[AR^{2\nu-1}\exp(-\lambda R)]$ obtained using the Smirnov asymptotic theory.[25] The result shown in Fig. 6 is clearly insufficient to account for the gap between theory and experiment. Still the question remains open since in the present state of art it is quite difficult to estimate how the large number of He$(1s^2)$+Cs^{+*} channels encompassing the entrance channel can contribute to the cross section. If the above tentative explanation turns out to be correct the reason why a similar effect is absent in the He$^+$-Rb, -K cases is most probably related to the much smaller number of He$(1s^2)$ +Rb^{+*}, K^{+*} states at resonance or near resonance with He$^+$+Rb, K. Yet the remaining question is why such charge-exchange channels do not show up in the time-of-flight spectra taken at zero scattering angle by Reynaud *et al.*[4] A possible answer could be the different response of the detectors for low-energy ground state and metastable neutrals. Checks of this suggestion are currently underway.[13]

As for the He$^+$-Na case (Fig. 9) the measurements of McCullough[26] yield a much larger cross section than the present calculations. The experimental cross section for He$^+$-Na is as large as that of the more resonant He$^+$-K system. Similar anomalies were pointed out and discussed in our investigation of the H$^+$-Na collision.[2] For the same arguments we again believe that this anomaly has an experimental origin.

V. CONCLUSION

The present work further confirms the efficiency of the PVB method as modified and improved in Ref. 2 to treat charge-exchange problems involving one active electron at large internuclear distances. This method was initially designed to properly account for the exchange interactions and has now been demonstrated to be flexible enough to include gradually polarization effects. This facility has enabled us to assess the relative role and competitive effects of exchange and polarization interactions in terms of which important features of the H$^+$ and He$^+$-alkali-atom systems can be understood. It has been shown that for charge-exchange collision systems involving small binding energies, high polarizabilities, and close lying states connected by dipole transitions ($\Delta L = \pm 1$), a multistate treatment is generally required to achieve quantitative predictions. This explains the unsuccess of previous simplified attempts.[3,12,27] An important outcome of the present investigation is the crucial role of rotational coupling requiring *a fortiori* multistate calculations as was stressed for other cases in the earlier work of Melius and Goddard.[11] From the comparison of the present theory with experiments it appears that open problems still remain for the He$^+$-Cs collision and more generally for collisions involving Na target. In the latter case we have pointed out that the discrepancy between experiment and theory has most probably an experimental origin.

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