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Selective-state charge transfer in a collision between an α particle and ground-state Na: A molecular-states approach

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The semiclassical impact-parameter method, based on a 14-state molecular expansion, is employed to calculate the charge-transfer cross sections for He^{2+}-Na(3s) collisions. Electron translation effects have been taken into account. Selective capture into the $n=3$ manifold of He^+ is found to occur in the low kilo-electron-volt energy region. The total capture cross section also exhibits an oscillatory energy dependence in the low-energy region.

I. INTRODUCTION

Experimental[1-7] and theoretical[8-12] studies have established that charge-transfer reactions involving α particles and alkali-metal atoms provide a good mechanism for achieving population inversion, which may in turn be used for the production of soft x-ray lasers. The He^+ ions formed in this way tend to be preferentially populated in particular excited states at low energies. However, with increasing collision velocity this selective population washes out and the electron-capture probability tends to be distributed over a number of neighboring states. Extensive studies of electron capture by α particles from Li atoms, which have been carried out both experimentally[1-5] and theoretically,[8-11] are consistent with this observation. We expect similar behavior for electron capture by an α particle from a ground-state Na atom, a collision system that has not yet been studied in detail. DuBois and Toburen[6] have measured the cross sections for single charge transfer in the case of $He^{2+}+Na$; but they have not reported the individual cross sections for population of particular final states of He^+. Shingal, Noble, and Brandsen,[12] in a theoretical study, have complemented this measurement by calculating partial as well as total capture cross sections. They employed a coupled-state impact-parameter method in which the total wave function was expanded in terms of atomic states on both centers. Both of these studies, however, are in a comparatively high-energy region: beyond 2 keV amu^{-1}, where capture is known to be less selective. This gap has recently been bridged by Schweinzer and co-workers[7] through their measurement of electron-capture cross sections in the energy range 0.1–1.5 keV amu^{-1}. To the best of our knowledge there still exists no other theoretical calculation which extends to such low energies. Moreover, the measured cross sections of Schweinzer[7] are appreciably larger than those reported by DuBois and Toburen[6] and the theoretical results of Shingal, Noble, and Brandsen[12] in the energy range beyond 2 keV amu^{-1}. This discrepancy warrants a detailed investigation of low-energy electron capture by α particles colliding with ground-state Na, in part due to its possible use in a soft x-ray laser system. Another motivation for this study arises from recent molecular-orbital (MO) calculations[13,14] carried out for electron capture by Li^{3+} in a collision with ground-state Li, where the presence of a number of closely coupled output capture channels gives rise to oscillations in the capture cross section at low impact energies. We have therefore attempted to investigate the selective excitation of He^+ resulting from $He^{2+}+Na$ collisions by employing a molecular expansion in the semiclassical impact-parameter method, which is known to suitably incorporate the effect of molecular binding that is important at low impact energies.

II. THEORETICAL METHOD

In the present study we have used the standard semiclassical MO expansion method. Since the collision under consideration constitutes a pseudo-one-electron system, an atomic (plane-wave) form of the electron translation factor (ETF), up to first order in v (the collision velocity), has been used to account for the motion of the electron translating along with the nuclei. As pointed out by Kimura and Thorson,[15] the neglect of higher-order terms is not expected to cause any significant error in the calculated cross sections at low to intermediate energies. Also, we find that the probability at all contributing impact parameters is conserved to within $\pm 5\%$ in the present case. The molecular electronic energies and wave functions are calculated by using a modified valence-bond configuration-interaction (CI) method (see, for example, Ref. 15) with the Na^+ core represented by a pseudopotential, with parameters given by Bardsley.[16] Only one electron is taken to be active. The basis set for He^+ is assumed to be hydrogenic, and has been given by Sato and Kimura.[11] A straight-line trajectory is used to describe the relative motion of the nuclei in light of the fact that important couplings occur at large internuclear separa-

TABLE I. Various atomic states correlating to Σ and Π states used in the calculation.

$He^+(2s)+Na^+$	$2s\Sigma$	
$He^+(2p)+Na^+$	$2p\Sigma$	$2p\Pi$
$He^+(3s)+Na^+$	$3s\Sigma$	
$He^+(3p)+Na^+$	$3p\Sigma$	$3p\Pi$
$He^+(3d)+Na^+$	$3d\Sigma$	$3d\Pi$
$He^{2+}+Na(3s)$	Na $3s\Sigma$ (initial channel)	
$He^{2+}+Na(3p)$	Na $3p\Sigma$	Na $3p\Pi$
$He^+(4s)+Na^+$	$4s\Sigma$	
$He^+(4p)+Na^+$	$4p\Sigma$	$4p\Pi$
$He^+(4d)+Na^+$	$4d\Sigma$	$4d\Pi$

tions. Even at the largest impact energy investigated here, no significant contribution comes from impact parameters below $b=4a_0$. It is also worth mentioning at this point that the pseudopotential approach fails at small internuclear separations due to core-core overlap. The use of a cutoff for $R\leq 2a_0$ therefore ensures that unphysical couplings at small R values, due to the unsuitability of the pseudopotential technique, are not included in the present calculation. Also, since the important couplings are in the large-R region, the exclusion of very small internuclear separations from the collision dynamics is not expected to change the calculated cross sections by more then 5%.

In the molecular structure calculation, we have used 23 and 12 configurations, respectively, to obtain the Σ and Π molecular states. Several 14-state (8Σ and 6Π; see Table I for state designation) semiclassical calculations have been performed to obtain the capture cross sections for energy values up to 10 keV amu^{-1}. At low impact energies (below 1 keV amu^{-1}) we have performed a number of two- as well as four-state calculations to investigate the low-energy dependence of these cross sections.

III. RESULTS AND DISCUSSION

The adiabatic molecular potential curves are presented in Figs. 1 and 2, where only Σ states have been shown for clarity. In Fig. 2 we see that the initial channel (Na $3s\Sigma$) has a very close avoided crossing around $R=35a_0$, with the neighboring state $3d\Sigma$, which represents one of the capture channels. Similarly, $3d\Sigma$ and $3p\Sigma$ exhibit an equally strong coupling (and avoided crossing) in the neighborhood of $R=34a_0$. To examine the possibility of these couplings being diabatic, we reduced our step size considerably and repeated our MO calculations in the vicinity of these avoided crossings. The relevant adiabatic potentials are presented in Fig. 2. Since the energy differences between the above-mentioned states are found to be of the order of 10^{-5} a.u., these avoided crossings will be passed through diabatically even in the low-keV-energy range. This permits a simplification in that we are able to reduce the number of states in the coupled-states equation. Thus we construct a diabatic state, which serves as the initial channel for the present reaction. This diabatic state, asymptotically correlating to He^{2+}-Na(3s), is constructed by smoothly joining the Na $3s\Sigma$ state with the molecular states $3d\Sigma$ and $3p\Sigma$:

$$\Sigma_{\text{diab}}=3p\Sigma(R\leq 30.6)+3d\Sigma(30.6\leq R\leq 33.6)$$
$$+\text{Na } 3s\Sigma(R\geq 33.6)\ .$$

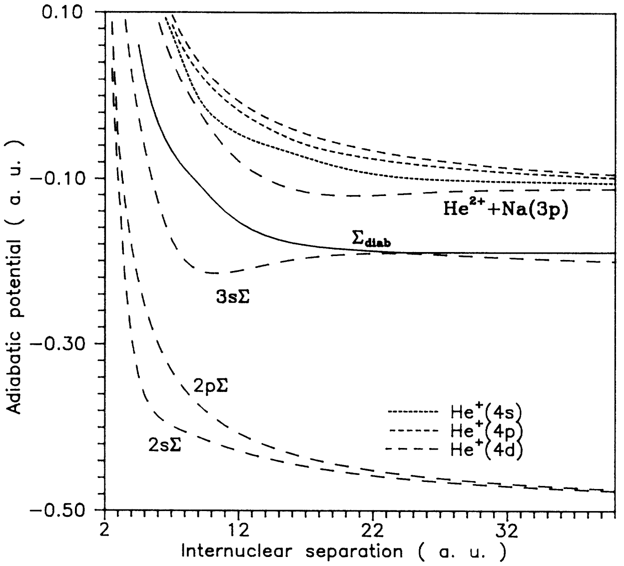

FIG. 1. Adiabatic potential energies for the reaction $He^{2+}+Na(3s)\rightarrow He^+(nl)+Na^+$. Different curves are labeled by their correlating atomic states. [States correlating to $He^+(n=3)$ are shown in Fig. 2.]

A similar approach has been used by Opradolce, Casaubon, and Piacentini[13] to calculate the charge-transfer cross sections for Li^{3+}-Li collisions.

The mechanism responsible for the charge transfer is the radial coupling that exists between the initial channel (Σ_{diab}) and the state $3s\Sigma$ in the vicinity of $R=24a_0$. This radial coupling matrix element has a sharp peak (of magnitude $\cong 0.75$) in the region where these two states exhib-

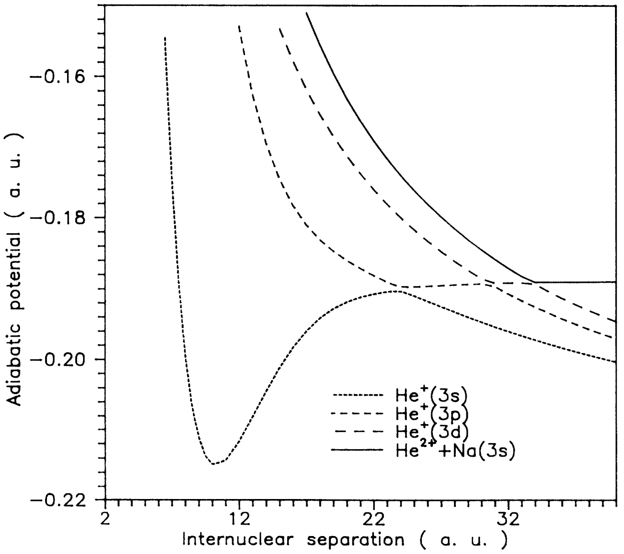

FIG. 2. Adiabatic potential energies for the reaction $He^{2+}+Na(3s)\rightarrow He^+(nl)+Na^+$. Different Σ states correlating to $He^+(n=3$ manifold) are labeled.

it a close avoided crossing (see Fig. 1). These states again couple at smaller-R values and it is in that region where these also couple strongly with the lower states $2s\Sigma$ and $2p\Sigma$, which correlate with the $n=2$ manifold of He^+. Since several states ($3s\Sigma$, $3p\Pi$, and $3d\Pi$) correlating with atomic states of the $n=3$ manifold of He^+ and the initial state (Σ_{diab}) are asymptotically close to one another, long-range angular Σ-Π couplings are important. At small R, the initial channel (Σ_{diab}) couples with $2s\Sigma$ and $2p\Sigma$, correlating with the $n=2$ manifold of He^+. Also, the initial channel is coupled with the higher excited states correlating to $He^+(n=4$ manifold) through the molecular states (both Σ and Π) correlating to Na($3p$).

The calculated cross sections are compared in Fig. 3 with those measured by DuBois and Toburen,[6] Schweinzer,[7] and the theoretical results of Shingal, Noble, and Brandsen.[12] It is worth mentioning here that the measurements of single-electron-capture cross section carried out by Schweinzer is based on the same approach as that described by Aumayr, Lakits, and Winter.[17(a)] The Na($3s$) target thickness in the experiment was calibrated by comparison with the absolute single-electron-capture cross sections obtained for H^+-Na($3s$) collisions by Aumayr, Lakits, and Winter[17(b)]. In addition to the present calculated total charge-transfer cross sections, calculated partial cross sections for capture into the $n=3$ manifold are also shown. We find that in the lower-energy region the major contribution to charge transfer corresponds to population of He^+ in the $n=3$ manifold. The cross section for this selective charge transfer into the $n=3$ manifold exhibits an oscillatory energy dependence in the low-energy region, similar to that of the total cross section. The large magnitude of the charge-transfer cross section and the resulting selective population of the $n=3$ manifold of He^+ make this process an excellent candidate for population inversion. Preferential population of the $n=3$ manifold of He^+ can result in the emission of either a 256-Å (48.4-eV) photon due to the process of direct decay to the ground state or a photon of 304 Å (40.8 eV) due to cascading via the $He^+(n=2)$ level. The degree of selective population decreases with increasing impact energy. But even at 10 keV amu^{-1}, nearly 65% of the total charge-transfer cross section corresponds to population of the $n=3$ manifold. It is interesting to note here that, according to Shingal, Noble, and Brandsen,[12] capture into the $n=3$ manifold of He^+ accounts for nearly 82% of the total charge transfer at 3.3 keV amu^{-1}, and that fraction is found to be close to 90% in our calculation at an impact energy of 3 keV amu^{-1}. It is also worth mentioning that unlike Shingal, Noble, and Brandsen,[12] we do not include higher excited states of Na (beyond $3p$) as well as those of $He^+(n \geq 5)$ in the basis set we use to generate the molecular states for the present calculation. The fact that these states are populated mainly at high impact energies is consistent with the fact that their calculated cross sections[12] are slightly larger than ours at impact energies beyond 5 keV amu^{-1}. The exclusion of these states, however, is not expected to have any significant effect on our calculated results at low impact energies where the selective capture takes place.

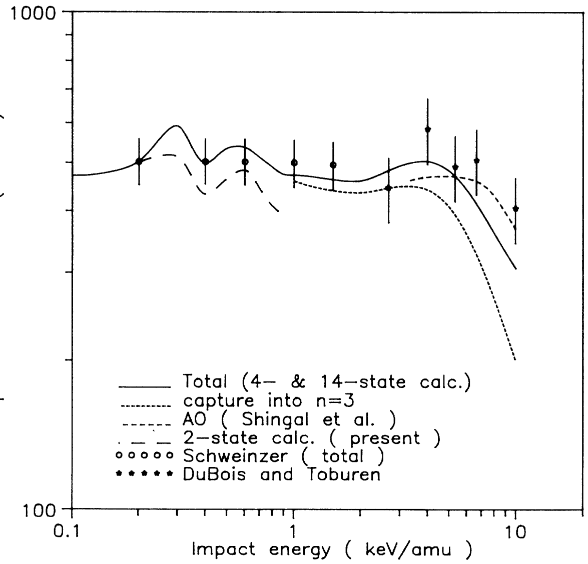

FIG. 3. Cross sections for electron capture by He^{2+} from Na($3s$). Error bars represent the uncertainty in the absolute values of the measured cross sections.

Since capture into the $n=3$ manifold of He^+ at 1 keV amu^{-1} accounts for more than 97% of the total electron capture, we can expect that even a smaller calculation will give a reliable estimate of these cross sections in the low-energy region. We therefore consider the molecular states correlating to the atomic states of $He^+(n=3)$ along with the ground state of Na in a four-state (2Σ and 2Π) calculation. By reducing the size of the problem we are able to investigate the low-energy region in some detail by calculating cross sections at a large number of impact energies between 0.1 and 1 keV amu^{-1} (see Fig. 3). (Test calculations at an impact energy of 1 keV amu^{-1}, corresponding to 14- and 4-coupled molecular states show that use of a smaller calculation at low impact energies is fully justified, the total electron-capture cross section for the two agreeing to within 2%.) In addition to two peaks around 0.2 and 0.6 keV amu^{-1} (see Fig. 3) in the low energy region, we also get a less pronounced peak around 4 keV amu^{-1}. To further investigate the oscillatory nature of the capture cross section in the low-energy region, we also carried out at two-state calculation, where the diabatic state represents the initial channel (Σ_{diab}) and the final capture channel is taken to be $3s\Sigma$. The two-state calculation exhibits the same low-energy dependence as has been obtained from the larger calculations except that the magnitudes of the two-state cross sections are smaller by about 13% at lower impact energies. This difference increases to 17% at collision energy of 1 keV amu^{-1}. This result suggests that the low-energy oscillation in the calculated cross sections is a Stuckelberg-Landau-Zener (see Ref. 18) oscillation that arises from an extremum in the energy difference between the two coupled electronic states involved in the reaction.

Our calculated cross sections are in good agreement with the theoretical results of Shingal, Noble, and Brandsen,[12] except in the high-energy region where the present calculation seems to underestimate the capture cross section. However, both theoretical results lie within the ±11% uncertainty quoted for the recent experimental measurements of Schweinzer[7] in the low-energy region. Similarly, both theoretical results are in satisfactory agreement with the experimental measurements of DuBois and Toburen,[6] which have an accuracy of approximately ±15%. These authors did not consider oscillations in their measured cross section to be significant since the magnitudes of the oscillations lie within the uncertainty of their measurements. The present calculations, however, indicate that Stuckelberg-Landau-Zener oscillations are expected to appear in the low-energy region as has also been observed in two recent MO calculations[13,14] carried out for the colliding system Li^{3+}-Li. As we pointed out earlier, in the present study, higher states of $He^{+}(n \geq 5)$ have not been included. Thus the calculated cross sections are expected to be too small at high energies. However, selective population is more probable at lower energies, where our results should be more reliable.

Finally, it is perhaps worth emphasizing that charge transfer in the case of α particles colliding with alkali-metal atoms occurs mainly due to the strong localized coupling at avoided crossings between the energy curves of the incoming and outgoing channels at finite-R values (in the vicinity of $R = 24a_0$ for the present case). It is the energy differences between the molecular electronic energies of course, not the asymptotic (atomic) values, that determine the magnitudes of the charge-transfer cross sections for these systems. This observation also applies to the cases of α particles colliding with ground-state K and Rb atoms. Although asymptotically the ground states of K and Rb ($E = -0.1595$ and -0.1535 a.u., respectively, relative to the first ionization threshold; the same for Na being equal to -0.1889 a.u.) are not very close to the $n = 3$ manifold of He^{+} ($E = -0.2222$ a.u.), the existence of strong coupling between the incoming and the outgoing channels at finite-R values may lead to significant state-selective capture. We are currently looking into this possibility.

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