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Charge transfer and excitation in slow proton collisions with sodium

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The charge transfer and excitation cross sections for protons colliding with Na(3*s*) atoms are calculated in the incident energy region from 1.7 eV to 5 keV by a quantum-mechanical molecular-orbital close-coupling (QMOCC) method and from 1 to 100 keV by a two-center atomic-orbital close-coupling method. The present QMOCC charge transfer cross section for low energy (<40 eV) is in agreement with some other calculations, but disagrees with the experimental measurements [Z. Phys. A **313**, 155, 1983]. For the higher energies, the cross sections calculated by the two methods are in harmony with the experimental and other theoretical data.

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I. INTRODUCTION

Heavy-particle collisions (including charge transfer, excitation, ionization, etc.) have been recognized as the important atomic processes in many applied fields, such as astrophysics, controlled fusion plasmas, radiology, and thin-film manufacture. The charge transfer can influence the ionization balance in astronomical and laboratory plasmas, and it can also significantly contribute to atomic emission spectra by populating excited states as well as the collision excitation. These characteristic spectra may be used for diagnosing the plasma temperature and density in the solar system and the interstellar medium. As an example, the produced line emission by charge transfer has been utilized to determine the composition and properties of particles in comets [1] and stellar wind [2,3].

A number of experimental techniques and theoretical methods (see reviews and books [4–7]) have been developed to investigate the heavy-particle collision processes for various systems. Good agreement between experiment and theory has been obtained for many ion-atom and ion-molecule systems. In the present work, we are interested in collisions involving protons and sodium atoms for charge transfer $H^+ + Na(3s) \to H(n=2) + Na^+$ and collision excitation $H^+ + Na(3s) \to H^+ + Na(3p)$, which are important in order to understand the ionization distribution of stellar winds [2]. In the higher-energy region, theoretical and experimental results for total charge transfer cross sections are in good agreement [8]. In the lower energy region, from 1.7 to about 40 eV (in the center-of-mass energies), controversy remains even for the total charge transfer cross sections [9–12]. In view of this controversy, we decided to reexamine the proton-sodium collision system. Firstly, an *ab initio* multireference configuration interaction (MRD-CI) package [13,14] is utilized to calculate the potential curves, radial and rotational coupling matrix elements, and then a quantum molecular-orbital close-coupling (QMOCC) calculation is carried out to obtain the charge transfer and collision excitation cross sections. For the higher-energy region (>1 keV/u), a two-center (TC) atomic-orbital close-coupling (AOCC) calculation is also performed to produce the cross sections and compare with MOCC calculations.

II. THEORETICAL METHOD

In the present study, an *ab initio* configuration interaction calculation is carried out for potential curves of four Σ^+ plus one Δ electronic states in A_1 symmetry and two electronic Π states in B_1 symmetry of $(NaH)^+$ system by using the MRD-CI package [13,14]. A basis set of $(6s,3p,2d,1f)$ contracted to $[4s,3p,2d,1f]$ [15] is employed for hydrogen; an effective core potential (ECP) adapted basis set $(4s,4p,2d,1f)$ [16] is used for the Na atom. A diffuse $(2s2p)$ basis set centered on the Na atom is employed to describe its Rydberg states, while a diffuse $(2s3p)$ set is used for H atom. The errors in calculated energy positions for the considered electronic states fall in the hundreds of cm^{-1} range in the asymptotic region. The resulting highly correlated electronic wave functions are then employed to calculate radial couplings among Σ^+ states and rotational couplings between Σ^+ and Π states by using finite differentiation and analytical approaches, respectively [17].

The computed adiabatic potentials are plotted in Fig. 1, in which $2\,^2\Sigma^+$, $3\,^2\Sigma^+$, $4\,^2\Sigma^+$, $5\,^2\Sigma^+$, $1\,^2\Pi$, and $2\,^2\Pi$ correspond to $Na(3s)+H^+$, $Na^+ + H(2p\sigma^+)$, $Na^+ + H(2p\sigma^-)$, $Na(3p\sigma)+H^+$, $Na^+ + H(2p\pi)$, and $Na(3p\pi)+H^+$ states in the asymptotic region, respectively. A strongly avoided crossing exists at about 5 a.u. between $3\,^2\Sigma^+$ and $4\,^2\Sigma^+$ states. More interestingly, when the internuclear distance $R<4$ a.u., the potentials for $2\,^2\Sigma^+$ and $1\,^2\Pi$ become very close with decreasing of R, which implies that the rotational coupling between them may be important [18]. No apparent differences are found with the molecular potential curves of Refs. [10–12]. For the radial coupling matrix elements, the positions for each peak are consistent with the positions of avoided crossings in Fig. 1.

The most important rotational couplings are between the $2\,^2\Sigma^+$ and $1\,^2\Pi$ channels [12]. Our results agree well with the two calculations [10,12], especially in the important region

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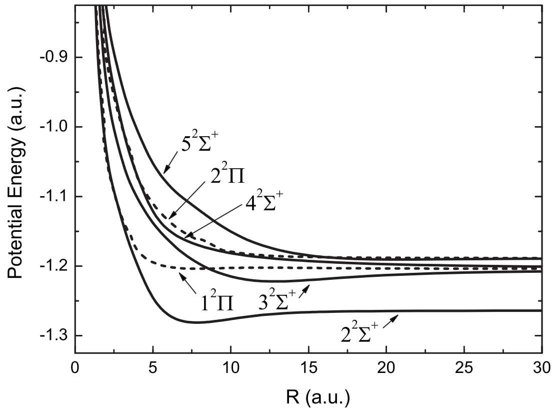

FIG. 1. Adiabatic potential curves for NaH$^+$. Solid lines for $^2\Sigma^+$ channels, dashed lines for $^2\Pi$ channels. The 2 $^2\Sigma^+$, 3 $^2\Sigma^+$, 4 $^2\Sigma^+$, 5 $^2\Sigma^+$, 1 $^2\Pi$, and 2 $^2\Pi$ correspond to Na(3s)+H$^+$, Na$^+$+H(2$p\sigma^+$), Na$^+$+H(2$p\sigma^-$), Na(3$p\sigma$)+H$^+$, Na$^+$+H(2$p\pi$), and Na(3$p\pi$)+H$^+$ states in the asymptotic regions, respectively.

of $R<5$ a.u.. But there exists a discrepancy with that of Dutta *et al.* [11]. It should be noted that in our calculations of nonadiabatic couplings, the origin of electronic coordinates is placed at the center-of-mass of the collisional system. Furthermore, as electron translation factors (ETFs) [5] are not included in our description of the collision, the validity of our calculations is restricted to the low impact energy region (typically $E<5$ keV/amu) [7,19,20].

The QMOCC approaches to describe charge transfer in ion-atom collisions have been formulated by Zygelman *et al.* [21]. The radial coupled equations are solved with the log-derivative method of Johnson [22]. When $E>1$ keV/u, the TC-AOCC approach [23,24] can be used for the change transfer and collisional excitation processes. The parameters of the effective potential used in the TC-AOCC are adopted from Ref. [25].

III. RESULTS AND DISCUSSION

In Fig. 2, we display the present QMOCC calculated total charge transfer cross sections for excitation to H(n=2) states in the energy region from 1.7 to 40 eV, and compare them with the experimental data [9] and other theoretical results [10–12]. Clearly, the results are catalogued into two groups, Dutta *et al.*'s theoretical work [11] are in good agreement with the measurements [9], while the other theoretical studies [10,12] and the present work find a much more rapid decrease as the collision energy drops below 10 eV. This supports our doubts regarding the experimental data of Kushawaha [9] and the scattering calculations of Dutta *et al.* [11]

Next, we examine the differences among the three theoretical results in the second group. With the same effective potential of Na$^+$ and the same set of molecular basis as that in Ref. [10], the results of Le *et al.* [12] agree with the calculations of Ref. [10] better than ours in the energy 3–40 eV. But at energies below about 3 eV, the cross section of Ref. [12] drops rapidly, while in Ref. [10], the cross section shows a kink at about 3 eV, as shown in Fig. 2. Although, Le *et al.* [12] argued that they do not expect the 3 $^3\Sigma^+$ channel to become dominant at energies below 4 eV, and in their HSCC calculation, the radial coupling was not calculated nor used. The explicit calculation shows that the partial cross sections to the 3 $^2\Sigma^+$ channel become dominant at energies below 3 eV. This can be interpreted from the potential curves in Fig. 1. For energy larger than 3 eV, the most efficient mechanism for populating the excited states is via the rotational coupling. The rotational coupling between 2 $^2\Sigma^+$ and 1 $^2\Pi$ can provide an effective mechanism in exciting the electron to the 1 $^2\Pi$ curve. In fact, despite that all the calculations were carried out using six channels, a two-channel calculation including only the 2 $^2\Sigma^+$ and 1 $^2\Pi$ channels can produce almost the same results, as shown in Fig. 2 (open circles). As the collision energies decrease, the classical turning point for each partial wave will move to larger R where the energy gap between the 2 $^2\Sigma^+$ curve and the 1 $^2\Pi$ curve becomes larger (see Fig. 1). Thus, this rotational coupling becomes inefficient and the partial charge-transfer cross section through 1 $^2\Pi$ drops rapidly. Then the cross sections to the 3 $^2\Sigma^+$ channel, which are nearly constant for the whole energy range, become dominant at energies below 3 eV.

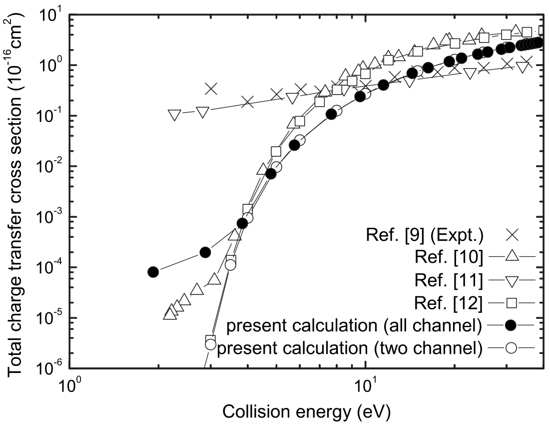

FIG. 2. Comparison of the total charge-transfer cross sections for Na(3s)+H$^+$$\rightarrow$Na$^+$+H($n$=2) reactions. Open circles, this work, only 2 $^2\Sigma^+$, 1 $^2\Pi$ included; full circles, this work, all channels are included. Other theoretical works, up-triangle, Ref. [10]; downward-triangle, Ref. [11]; squares, Ref. [12]. Experiments, crosses, Ref. [9].

To check the validity of the MRD-CI+QMOCC method, and also for the practical reasons, we also applied them to the middle and high energy region, where a number of experimental techniques [26,27] and theoretical methods [28–30] have been developed. Good agreement between experiment and theory, including our TC-AOCC results, has been obtained. The QMOCC results are in agreement with these results in the overlapping energy region of 1–5 keV/u within 50%, as shown in Fig. 3. Although, the QMOCC approach gives the correct turning point of the cross sections near E =5 keV, it is larger than other results for $E>5$ keV/u. The ETF is not included in our calculation, which may be important in this higher energy region. By using the same *ab initio* potentials and couplings, the semiclassical MOCC results should better merge with QMOCC ones than AOCC results

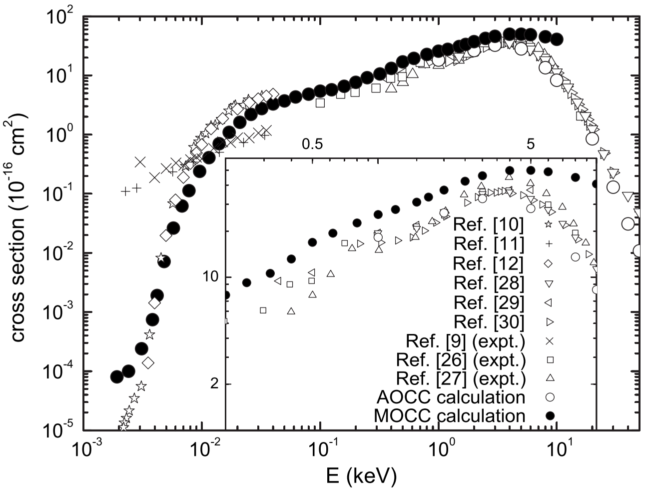

FIG. 3. Comparison of the total charge-transfer cross sections for $\mathrm{Na}(3s)+\mathrm{H}^{+}\rightarrow\mathrm{Na}^{+}+\mathrm{H}(n=2)$ in the whole energy region. Present result, MOCC calculation, full circles; AOCC calculations, open circles. The calculation of Ref. [10], stars; Ref. [11], plus; Ref. [12], diamond; Ref. [28], downward-triangle; Ref. [29], left-triangle; Ref. [30], right-triangle. Experiments, Ref. [9], crosses; Ref. [26], squares; Ref. [27], up-triangle.

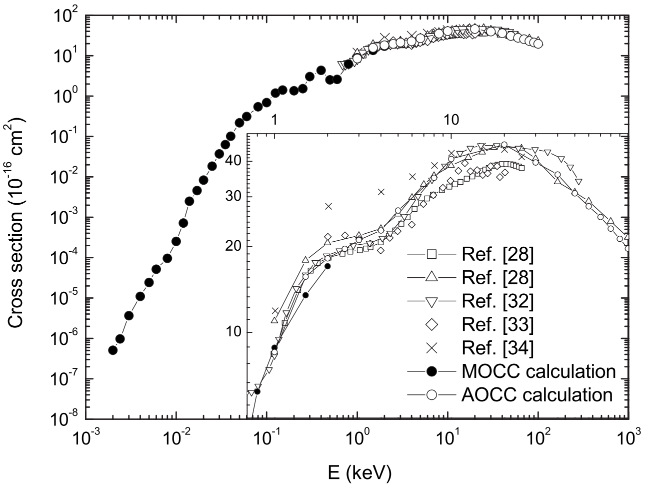

FIG. 4. Comparison of the collision excitation of $\mathrm{Na}(3s)\rightarrow\mathrm{Na}^{+}(3p)$ in the whole energy region. Present result, MOCC calculation, full circles; AOCC calculations, open circles. The calculation of Jain and Winter [28], squares (without cascade effects), up-triangle (with cascade effects); while the AO calculation of Fritsch [32], downward-triangle. Experiments, Ref. [33], diamond; Ref. [34], crosses.

with QMOCC ones in the overlapping energy region [31].

In Fig. 4, we consider the collision excitation of $\mathrm{Na}(3s)\rightarrow\mathrm{Na}^{+}(3p)$ in the whole energy region, and compare them with the AOCC calculation and other studies. The present MOCC calculation results (8.842 and 17.098 $\times 10^{-16}$ cm^2, at 1 and 2 keV impact energy) agree with the AOCC calculation ones (8.533 and 18.228×10^{-16} cm^2, respectively). They are in fair agreement with the two-center coupled-Sturmian-pseudostate approach of Jain and Winter [28] (without cascade effects) and the AO calculation of Fritsch [32]. All these calculations are in general agreement with the experiment results of Refs. [33,34], while all the measurements have absolute errors of the order of 40%.

IV. CONCLUSION

In the present study we have reexamined charge-transfer cross sections for protons colliding with $\mathrm{Na}(3s)$ atoms for collision energies from the threshold at 1.7 to 40 eV using the QMOCC method. The MOCC calculations utilize *ab initio* adiabatic potentials and nonadiabatic radial and rotational couplings obtained with the MRD-CI approach, while the effective potentials of Na^{+} are utilized in Refs. [10,12]. Our results are in agreement with the calculations of Refs. [10,12], but disagree with the calculations of Ref. [11], and raise doubts on the experimental data [9]. Furthermore, we extend our QMOCC calculations to keV/u energy region, while the TC-AOCC calculations are also carried out. By comparing with our AOCC results and other theoretical and experimental data, our work shows that the MRD-CI +QMOCC method can be applied up to 5 keV/u within 50% accuracy for the NaH^{+} system.

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