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Charge transfer between O^+ ions and helium

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The charge-transfer processes $O^+(^4S^0, ^2D^0, ^2P^0) + He \rightarrow O(^3P) + He^+$ have been investigated by using a fully quantal molecular-orbital close-coupling (QMOCC) approach. Cross sections are presented for ion energies from 0.5 to 10 keV and compared with those from recent experiments and semiclassical theory. Good agreement is found between the QMOCC results and the measurements. Particular attention is given to addressing the metastable component of the experimental ion beams. We further argue that the so-called "suppressed electron-capture effect" for metastable ions proposed by Wolfrum *et al.* is not a viable mechanism to explain their measurements. However, the current QMOCC calculations were found to reproduce neither the ground-state nor metastable-state cross sections predicted by the semiclassical method.

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Charge transfer has been recognized to be an important atomic process in laboratory and astronomical plasmas for many decades. Diagnostics of plasma temperature and density and inference of atomic abundances in stars, the solar system, and the interstellar medium may depend on the accuracy of charge-transfer cross sections. A number of theoretical methods and experimental techniques have been developed to investigate charge-transfer processes for various systems. Good agreement between experiment and theory has been obtained for many ion-atom and ion-molecule systems (see, e.g., [1]). However, several recent experimental and theoretical studies on charge transfer for $O^+(^4S^0, ^2D^0, ^2P^0)$ and He collisions arrived at very discrepant conclusions.

Kusakabe *et al.* [2] showed that the total cross section for capture from He by metastable $O^+(^2D^0, ^2P^0)$ ions at keV energies is similar to or even greater than that for the ground-state $O^+(^4S^0)$. This conclusion was supported by Kimura *et al.*'s semiclassical calculation [3]. Kimura *et al.* found that the metastable cross sections are an order of magnitude larger than those for the ground state for ion energies between 1 and 10 keV. However, their results clearly contradicted another experiment [4] in which the metastable cross sections were found to be too small to be measureable. Wolfrum *et al.* [4] suggested that this unexpected behavior was caused by efficient suppression of electron capture by one of the metastable ions due to a competing, collisionally induced inelastic transition into the companion metastable state. More recently, Lindsay and Stebbings [5] carried out an experiment to comprehend the marked differences among these results. In their experiment, absolute differential cross sections were measured for charge-transfer scattering of 1–5 keV O^+ by He atoms at angles between 0.2° and 6.3° in the laboratory frame, and then integral cross sections were derived from these measurements. The experimental results showed that the metastable state cross sections are of the same order of magnitude as those for the ground state. This conclusion differs from that of Kimura *et al.* [3].

In an effort to resolve these discrepancies, we investigate charge transfer for $O^+(^4S^0, ^2D^0, ^2P^0)$ and He collisions by using a fully quantal molecular-orbital close-coupling (QMOCC) approach. As it is expected that the contribution from electron capture into excited states of O is small, we only consider charge-transfer processes into the ground state,

$$O^+(^4S^0, ^2D^0, ^2P^0) + He \rightarrow O(^3P) + He^+ - \Delta E. \qquad (1)$$

We adopted the multireference single- and double-excitation configuration-interaction (MRD-CI) [6] adiabatic potentials and nonadiabatic radial and rotational couplings for the OHe^+ system [3].

The QMOCC calculations begin with the solution of the molecular-orbital close-coupling equations in the diabatic representation

$$-\frac{1}{2\mu}\nabla^2 G(\mathbf{R}) + U(R)G(\mathbf{R}) = EG(\mathbf{R}), \qquad (2)$$

where μ is the nuclear reduced mass of the ion-atom pair, E is the relative collision energy in the center-of-mass frame, $\mathbf{R}$ is the coordinate of the relative nuclear motion, $G(\mathbf{R})$ is the scattering amplitude describing relative motion of the nuclei, and $U(R)$ is the diabatic potential matrix obtained from the adiabatic potential and nonadiabatic coupling matrices by a unitary transformation [7]. The unitary matrix W is defined by

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$$\frac{dW(R)}{dR} + iW(R)A^{\mathrm{rad}}(R) = 0, \tag{3}$$

where A^{rad} is the radial coupling matrix [8]. From the numerical results of the close-coupling equations and asymptotic expressions of the radial wave functions, the K matrix may be extracted and thus the radial scattering matrix S is obtained,

$$S_J = \frac{I + iK_J}{I - iK_J}. \tag{4}$$

The charge-tranfer cross sections from channel α to channel β is expressed in terms of the scattering matrix elements

$$\sigma_{\alpha\to\beta} = \frac{\pi g_\alpha}{k_\alpha^2}\sum_J (2J+1)|S_J|^2_{\alpha\beta}, \tag{5}$$

where k_α denotes the wave number for center-of-mass motion of the initial ion-atom channel, g_α is an approach probability factor in channel α, and J is the total angular momentum.

The potentials of ten molecular states evaluated in the MRD-CI method have been reported in our previous paper [9]. Detailed information on the potentials, such as the comparison of the asymptotic separated-atom energies with the experimental and other theoretical energies, can be found therein and therefore is omitted in the present work. Four of these ten electronic states, $2\ ^2\Sigma^-$, $3\ ^2\Pi$, $2\ ^4\Sigma^-$, and $1\ ^4\Pi$, are formed in the approach of $O(^3P)$ with He^+, the two states $1\ ^2\Sigma^+$ and $2\ ^2\Pi$ by $O^+(^2P^0)$ with He, the three states $1\ ^2\Delta$, $1\ ^2\Pi$, and $1\ ^2\Sigma^-$ by $O^+(^2D^0)$ with He, and the state $1\ ^4\Sigma^-$ by $O^+(^4S^0)$ with He. All 19 radial and rotational couplings between the ten states were evaluated from internuclear distance $R=1.5-8.0a_0$ [3]. In Fig. 1, representative coupling matrix elements are illustrated as a function of R. Electron capture into the state $O(^3P)$ is driven directly by the $1\ ^4\Sigma^- - 2\ ^4\Sigma^-$ and $1\ ^4\Sigma^- - 1\ ^4\Pi$ couplings [see Fig. 1(a)]. The strongest of all 16 doublet-state couplings is the $2\ ^2\Pi - 3\ ^2\Pi$ with a peak at about $1.88a_0$, as displayed in Fig. 1(b), corresponding to an avoided crossing between the $2\ ^2\Pi$ and $3\ ^2\Pi$ potentials. This coupling is expected to significantly contribute to electron capture for the metastable states.

The current cross sections for electron capture by $O^+(^4S^0)$ and $O^+(^2D^0, ^2P^0)$ are plotted as a function of projectile energy in Fig. 2, together with the available experimental results [2,4,5]. Values at four energy points are tabulated for detailed comparison in Table I. Fig. 2(a) displays the theoretical charge-transfer cross sections along with the $O^+(^2D^0) \leftrightarrow O^+(^2P^0)$ excitation-deexcitation cross sections due to He collisions, while Fig. 2(b) displays only the $O^+(^4S^0)$ ground state charge-transfer cross sections from the current work and the semiclassical MOCC (SCMOCC) results of Kimura *et al.* [3]. The experimental results shown in Fig. 2(b) are from measurements presumed to be for pure $O^+(^4S^0)$ beams or beams with small metastable contamination. The QMOCC results are shown to be in good agreement with most of the measured data. This is in relatively stark contrast with the SCMOCC results which are smaller

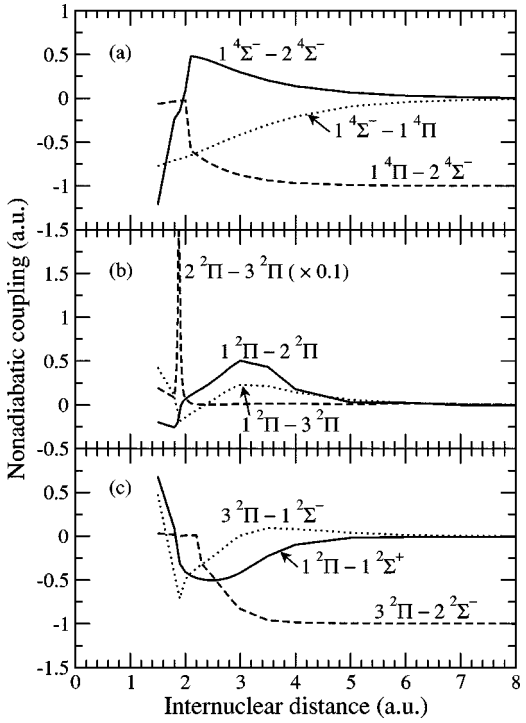

FIG. 1. The nonadiabatic radial and rotational couplings (a) between quartet states, and (b) and (c) between doublet states of the OHe^+ system as a function of internuclear distance R.

than all of the available experiments. However, the data of Kusakabe *et al.* [2] are smaller than the other measurements and our calculations below 2 keV. Lindsay and Stebbings [5] suggest that the discrepancy may be a consequence of the fact that the cross section *is* small, and therefore difficult to measure, and that the energy is the lowest point at which the apparatus is capable of operating. Below about 5 keV, our ground-state cross sections are consistent with those of Wolfrum *et al.* [4]. However, above 5 keV the ground-state QMOCC cross sections are larger than the Ref. [4] and Ref. [5] measurements. In the latter case, this is not surprising in view of the fact that the differential cross sections, which are integrated to obtain the total cross sections, are lacking from 0° to 0.1° in the experiment. From Fig. 2 of Ref. [5] the contribution from laboratory angles below 0.1° is not negligible for $E=5$ keV. Thus their integral cross sections may be underestimated. Furthermore, it may be inferred from Kusakabe *et al.*'s measurements that capture cross sections for the metastable states are similar to those for the ground state above about 3 keV. This is easily understood from our QMOCC calculations [see Fig. 2(a)].

The QMOCC cross sections for capture by $O^+(^2D^0)$ and $O^+(^2P^0)$ are plotted and compared with the measurements of Lindsay and Stebbings [5] in Fig. 2(c). We reproduce the experimental data, except at $E=5.0$ keV, by taking the ratio of $O^+(^2P^0)$ to $O^+(^2D^0)$ to be 1:4 as the experiment was made with an unspecified mixture of metastable ions. The difference at $E=5$ keV may also be due to omission of contributions from 0° to 0.1° in the differential cross-section measurement, as was the case for the ground state.

In Figs. 2(b) and 2(c) the QMOCC results are compared with the SCMOCC cross sections [3]. The discrepancies be-

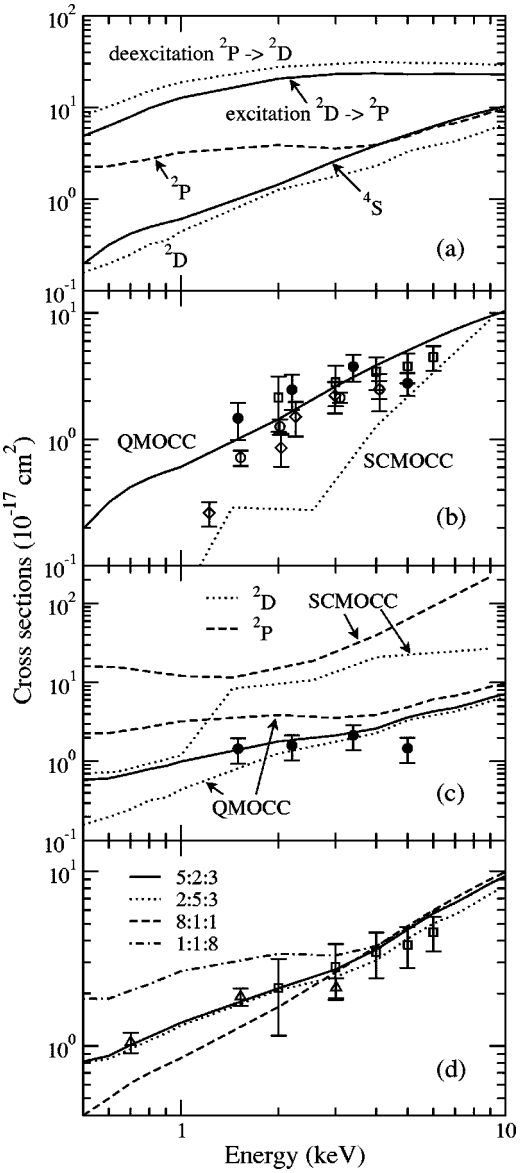

FIG. 2. Cross sections for O^+ collisions with He. (a) The current QMOCC charge-transfer results for the ground $^4S^0$ and $^2D^0$ and $^2P^0$ metastable states. Also shown are the metastable excitation and deexcitation cross sections. (b) Ground-state charge transfer. Experiment: (○) Kusakabe *et al.* [2]; (◇), Kusakabe *et al.*, mostly ground state but small metastable contamination [2]; (□) Wolfrum *et al.* [4]; (●) Lindsay and Stebbings [5]. Theory: (—) QMOCC; (----) SCMOCC. (c) Metastable-state charge transfer. Experiment: (●) Lindsay and Stebbings [5]. Theory: QMOCC and SCMOCC as indicated; (—) QMOCC with 80% $O^+(^2D^0)+20\%O^+(^2P^0)$. (d) Mixed-state charge transfer. Experiment: (△) Kusakabe *et al.*; (□) Wolfrum *et al.* Theory: QMOCC with indicated $^4S^0:^2D^0:^2P^0$ ratios.

tween the two approaches vary from a factor of a few to more than one order of magnitude. This is surprising as the two approaches are expected to give consistent results at intermediate energies (see, e.g., [10]). We emphasize that the potentials and couplings should not be responsible for the differences, because we used the *same* potential and coupling data obtained with the MRD-CI method. It should be mentioned that the QMOCC calculations do not include electron translation factors (ETFs), but the neglect of ETFs should not result in an error larger than about 50% in the concerned energy region. The differences between the SCMOCC and QMOCC remain to be explained.

TABLE I. Comparison of cross sections between this work and experiment for electron capture into the ground-state $^4S^0$ and the metastable-mixed states $^2D^0$ and $^2P^0$ in 10^{-17} cm^2. The fraction ratio of $O^+(^2P^0)$ and $O^+(^2D^0)$ is assumed to be 1:4.

	$O^+(^4S^0)$		$O^+(^2D^0, ^2P^0)$	
Energy (keV)	Theory[a]	Expt[b]	Theory[a]	Expt[b]
1.5	0.950	1.47±0.48	1.350	1.45±0.51
2.2	1.664	2.48±0.77	1.905	1.59±0.56
3.4	3.120	3.78±0.91	2.309	2.14±0.75
5.0	5.046	2.78±0.57	3.616	1.47±0.51

[a]This work.
[b]Lindsay and Stebbings [5].

Returning to Fig. 2(a), the QMOCC calculations show that electron capture from the ground and metastable states is dominated by the $^2P^0$ state below 3 keV; the cross sections for capture for the $^4S^0$ and $^2D^0$ increase with increasing energy and the importance of capture for these two states becomes comparable with that from the $^2P^0$ above about 3 keV. It is interesting, therefore, to compare the QMOCC calculations with the measured results for the mixed ground and metastable states by Kusakabe *et al.* [2]. In Fig. 2(d) we plot various assumed mixing ratios for the ground and metastable ions using the QMOCC results. It is clear that the mixed beam results of Kusakabe *et al.* can be reproduced at 0.7 and 1.5 keV if the beam is assumed to contain about 30% $^2P^0$, but with nearly any fraction of the other two states. At 3 keV, this constraint is relaxed as all of the QMOCC cross sections are similar, but a significant $^2D^0$ fraction is implied. Furthermore, we also plot in Fig. 2(d) the measurements from Ref. [4] which are claimed to be for a pure $O^+(^4S^0)$ beam. However, due to the fact that all of the QMOCC cross sections have similar magnitude over the measured energy range, the Wolfrum *et al.* results are consistent with any level of metastable mixing up to about 80%. Above about 5 keV, however, there is a tendency towards a significant $^2D^0$ contribution which can explain the discrepancy noted for Fig. 2(b). We therefore find, similar to the conclusions of Kimura *et al.* [3], that the reported measurements of Wolfrum *et al.* correspond to a beam of mixed composition. Further, the metastable fraction is likely to be larger than 20%, a value larger than the 10% estimate of Ref. [3] due to our smaller metastable cross sections. Further evidence comes from the $O^+(^2D^0)$ and $O^+(^2P^0)$ appearance potential measurements of Hughes and Tiernan [11] which found values of 26.5 and 28.3 eV, respectively, for electron collisions with water. The ion beam in Ref. [4] was obtained with 30-eV electrons.

Finally, the QMOCC calculations do not support the so-called suppressed electron-capture mechanism proposed by Wolfrum *et al.* [4]. They found that when the electron beam

energy was increased above 40 eV, the measured electron-capture cross section became unexpectedly smaller. They suggested that either the metastable cross sections were small or that the competing process of collisional excitation was suppressing electron capture. We find that they are incorrect on both accounts. Figure 2(a) shows that the metastable and ground-state cross sections are of the same magnitude. Further, the excitation cross sections, also displayed in Fig. 2(a), are not significantly larger and excitation results only in a redistribution of the $^2D^0/^2P^0$ ratio.

In order to explain the differences among various results of experiment and theory, we have investigated charge transfer for O^+ and He collisions using a fully quantal molecular-orbital close-coupling approach. The cross sections for capture from the ground-state $O^+(^4S^0)$ ions and metastable-state $O^+(^2D^0, ^2P^0)$ ions are computed and compared with both theoretical and measured results. The QMOCC calculations are found to be in good agreement with the measurements when the issue of metastable contamination is taken into account. We argue that the so-called suppressed electron-capture mechanism is not valid. However, the current QMOCC calculations were found to reproduce neither the ground-state nor metastable-state cross sections predicted by the semiclassical method. The discrepancy between the QMOCC and SCMOCC results varies from a factor of a few to more than one order of magnitude. It remains to be explained.

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