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Electron capture and excitation in collisions of $O^+(^4S, ^2D, ^2P)$ ions with He atoms and He^+ ions with O atoms at energies below 10 keV

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Electron capture and excitation in $O^+(^4S,^2D,^2P)+He$ collisions above 100 eV are studied theoretically by using a semiclassical molecular representation and electron capture in $He^+ + O(^3P)$ collisions; excitation and deexcitation in $O^+(^4S)+He \leftrightarrow O^+(^2D)+He$ collisions at lower energies are studied by using a fully-quantum-mechanical molecular representation. At higher energies, nonadiabatic couplings are the driving forces that cause transitions. At collision energies below 10 eV, transitions are driven by spin-orbit couplings. At kilo-electron-volt energies, the contribution from metastable $O^+(^2D,^2P)$ ions to electron capture is much larger than that from the ground $O^+(^4S)$ ions. At energies below 1 eV, the cross section for electron capture in $He^+ + O$ collisions is very small, with a magnitude of less than 10^{-20} cm^2. The cross sections for the excitation-deexcitation of metastable O^+ ions are larger, with values near 10^{-18} cm^2.

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I. INTRODUCTION

Electron capture from oxygen atoms by helium ions at thermal energies is an important process in laboratory, atmospheric, and astrophysical plasmas. In particular, this process may contribute to the escape of helium from the terrestrial atmosphere [1] and to the removal of He^+ in the ejecta of supernova 1987A [2]. The reverse process is important at higher energies. Metastable $O^+(^2P)$ and $O^+(^2D)$ ions may be present in plasmas, and their reactions with He, including quenching reactions, are potentially significant [3].

Measurements of electron capture in kilo-electron-volt (keV) beams of O^+ ions in mixtures of ground $O^+(^4S)$ and metastable $O^+(^2D,^2P)$ states in helium have been carried out [4] with the unexpected conclusion that capture by $O^+(^2D,^2P)$ ions is much less efficient than capture by $O^+(^4S)$ ions. We previously reported the calculations of capture cross sections at keV energies, which are in disagreement with this conclusion [5].

We present here an extension of the calculations to lower energies and give detailed results for an extended energy range of cross sections for the reactions

$$O^+(^4S,^2P,^2D)+He \rightarrow O(^3P)+He^+ + (10.97, 7.64, 5.95)\ \text{eV}\ , \quad (1)$$

$$He^+ + O(^3P) \rightarrow He + O^+(^2P) + 5.95\ \text{eV}\ , \quad (2)$$

$$He + O^+(^2D) \leftrightarrow He + O^+(^4S) + 3.33\ \text{eV}\ . \quad (3)$$

Because of the open-shell, multielectron nature of oxygen, the electronic structure of the collision system is complicated and provides an interesting challenge.

II. THEORETICAL MODEL

Since some of the details of the application to HeO^+ [5] have been given [6], only a very brief summary is provided here.

A. Molecular states and couplings

The adiabatic electronic states of HeO^+ were described by the multireference single- and double-excitation configuration-interaction (CI) method [7,8]. The helium atom (Gaussian) basis set is the same as in our previous study, with a slight modification characterized as $(9s4p1d)/[7s3p1d]$. The oxygen atom basis set is of the double-ζ plus polarization type $(9s5p1d)/[5s3p1d]$, with added diffuse s, p, and d orbitals with exponents $\alpha_s=0.032$, $\alpha_p=0.028$, and $\alpha_d=0.015$ to yield correct descriptions of the excited states. The adiabatic potential curves obtained are presented in Fig. 1. The lowest level corresponds to a separation into the ground $O^+(^4S)+He$,

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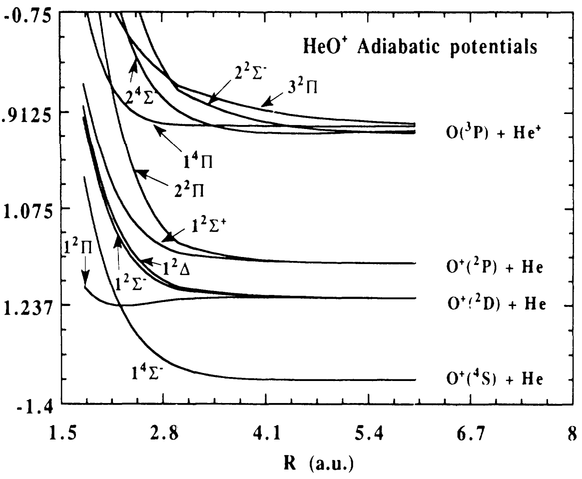

FIG. 1. Adiabatic potentials of the HeO^+ system. The energy is given relative to -76.0 a.u.

followed by several states separating to metastable $O^+(^2D,^2P)+He$. The metastable $O(^1D)+He^+$ state lies about 2 eV above the ground state separating to $O(^3P)+He^+$. Augustin *et al.* [9] reported adiabatic potentials of the HeO^+ system. Because of the larger basis size and CI's in conjunction with the methodology used in our study, the present adiabatic potentials are of higher precision.

The nonadiabatic coupling matrix elements were calculated by using a finite-difference method [10]. Representative results are illustrated in Fig. 2(a). The $2\,^2\Pi$ and $3\,^2\Pi$ potential curves possess a sharp avoided crossing at $R=1.9$ a_0, where the radial coupling between these curves has a sharp peak. The strong coupling, which has a maximum value of about 20 a.u., is a dominant mechanism for electron capture from the metastable $O^+(^2P)+He$ channel at higher energies, above 100 eV. The coupling connecting the ground $O^+(^4S)+He$ and the electron capture $O(^3P)+He^+$ channels is weak and will result in a small cross section.

Spin-orbit couplings may also drive transitions. For our calculation, the slightly different atomic orbital basis employed for oxygen consisted of four *s*-type and four *p*-type primitives augmented by a single *d* function with exponent $\alpha=1.33$, a Rydberg *s* function with $\alpha=0.032$, and a Rydberg *p* function with $\alpha=0.028$, in conjunction with a relativistic-effective core potential given by Pacios and Christiansen [11]. The relativistic CI with inclusion of spin-orbit effects was described in a recent publication on the BiO molecule [12]. The technical details of the present work on both spin-orbit and nonadiabatic couplings in HeO^+ are given in Table I.

In the study by Augustin *et al.* [9], no attempt was made to calculate directly the spin-orbit coupling between the $[O^+(^4S)+He]$ and $[O^+(^2D)+He]$ channels, but an estimate of 106 cm^{-1}, independent of R, was made from the atomic spin-orbit splittings. We obtained for the corresponding molecular states a maximum value of 72 cm^{-1} at $R=2.05$ a_0, falling sharply beyond the curve crossing, as shown in Fig. 2(b). This difference of about 32% in the magnitude of the spin-orbit coupling matrix element and its R dependence cause a significant change in the cross section for excitation.

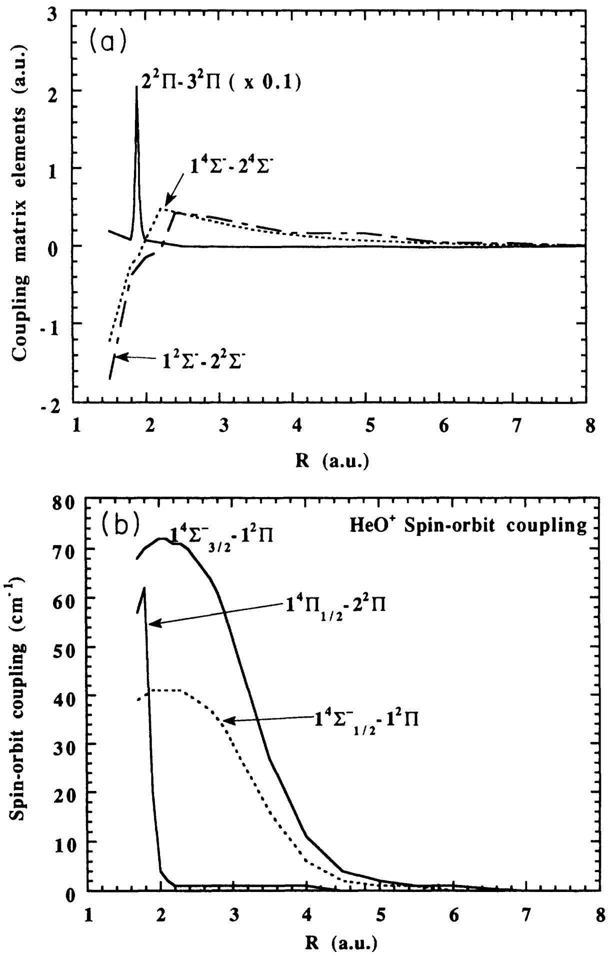

FIG. 2. (a) Representative nonadiabatic coupling matrix elements. (b) Spin-orbit coupling matrix elements.

B. Collision dynamics

1. *Semiclassical approach*

A semiclassical molecular orbital expansion method with a straightline trajectory was employed to study the

TABLE I. Number of reference configurations (N_{ref}) and number of roots (N_{root}) treated in each irreducible representation, with the corresponding numbers of generated ($N^{\mathrm{tot}}_{\mathrm{SAF}}$) and selected ($N^{\mathrm{sel}}_{\mathrm{SAF}}$) symmetry-adapted functions for a threshold of $T=3\mu E_h$ at a bond distance of 2.4 a_0. The first set of data refers to the spin-orbit calculations, the second (in parentheses) to the nonadiabatic treatment.

States	$N_{\mathrm{ref}}/N_{\mathrm{root}}$	$N^{\mathrm{tot}}_{\mathrm{SAF}}$	$N^{\mathrm{sel}}_{\mathrm{SAF}}$
$^2A_1$	64/4	393 707	9950
$^2B_{1,2}$	44/3 (65/3)	332 577 (513 048)	8701 (12 149)
$^2A_2$	34/4 (50/3)	371 949 (504 383)	7722 (13 387)
$^4B_{1,2}$	21/1	199 984	3973
$^4A_2$	26/3 (61/2)	242 036 (554 781)	8980 (17 556)

collision dynamics above 100 eV [6]. Transitions are driven by nonadiabatic couplings. The total scattering wave function was expanded in terms of products of a molecular electronic state and atomic-type electron translation factors (ETF's). Substituting the total wave function into the time-dependent Schrödinger equation and retaining the ETF correction up to the first order of relative velocity yields a set of first-order coupled equations. By solving the coupled equations numerically, we obtain the scattering amplitudes for transitions: the square of the amplitude gives the transition probability, and integration of the probability over impact parameter gives the cross section. The molecular states included in the dynamical calculations are the ten states shown in Fig. 1, separating to $O^+(^4S)+He$; $1\,^4\Sigma^-$, $O^+(^2D)+He$; $1\,^2\Sigma^-$, $1\,^2\Pi$, $1\,^2\Delta$, $O^+(^2P)+He$; $1\,^2\Sigma^+$, $2\,^2\Pi$, and $O^+(^3P)+He^+$; $2\,^4\Sigma^-$, $1\,^4\Pi$, $2\,^2\Sigma^-$, $3\,^2\Pi$.

2. *Quantum approach*

A fully-quantum-mechanical representation of a molecular orbital expansion method was employed for the study of electron capture and excitation-deexcitation processes below 10 eV. In this energy region, transitions are driven primarily by off-diagonal elements of the spin-orbit coupling [13,14]. The total scattering wave function is expanded as a sum of products of molecular electronic wave functions and nuclear wave functions. The coupled equations that the nuclear wave functions satisfy can be obtained from the time-independent Schrödinger equation [6]. The coupled equations are solved numerically, after partial wave decomposition, to obtain the scattering matrix. The molecular states included are two sets of two channels: (i) $O^+(^4S)+He$; $1\,^4\Sigma^-$ and $O^+(^2D)+He$; $1\,^2\Pi$ for excitation (deexcitation) and (ii) $O(^3P)+He^+$; $1\,^4\Pi$ and $O^+(^2P)+He$; $2\,^2\Pi$ for electron capture.

III. RESULTS

A. Electron capture by $O^+(^4S,^2D,^2P)$ ions above 100 eV

The calculated cross sections for capture by ground-state $O^+(^4S)$ ions and metastable $O^+(^2D)$ and $O^+(^2P)$ ions colliding with helium at impact energies from 160 eV to 9 keV are shown graphically in Fig. 3 and given numerically in Table II. As noted earlier [5], the metastable ion cross sections exceed the ground-state ion cross sections by an order of magnitude or more. At high energies, the cross sections for capture by $O^+(^2D)$ and $O^+(^2P)$ are comparable. At energies below about 1 keV, the $O^+(^2D)$ cross sections decrease rapidly, but the $O^+(^2P)$ cross sections pass through a minimum value of 1×10^{-16} cm^2 at about 1.2 keV and then increase slowly. The increase at lower energies is a consequence of the avoided crossing of the $2\,^2\Pi$ and $3\,^2\Pi$ states of HeO^+. Comparison with measurements is confused by the uncertain composition of the ion beam, which depends on the method used to generate the beams and is difficult to determine with precision [15–19].

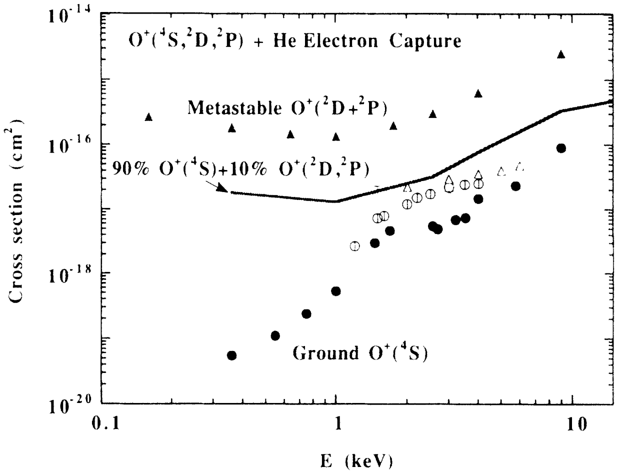

FIG. 3. Electron capture cross section above 100 eV. Present work: ●, $O^+(^4S)$; ▲, $O^+(^2D,^2P)$. Experiment: ○, $O^+(^4S)$; □, capture by mixed ground and metastable $O^+(^4S,^2D,^2P)$, Kusakabe *et al.* [20] and Wolfrum, Schweinzer, and Winter [4].

Kusakabe *et al.* [20] found that with ion beams containing an unknown mixture of the ground-state and metastable ions, the cross section increases by more than 80% above the cross section for pure ground-state ions below 1 keV. Wolfrum, Schweinzer, and Winter [4] carried out a similar experiment but found no increase in the cross section from the metastable ions to electron capture. The present capture results for the ground-state ion agree reasonably well with those of Kusakabe *et al.*, both in magnitude and energy dependence. By combining 90% of the cross section of the ground $O^+(^4S)$ state ion with 10% of that of the metastable $O^+(^2D,^2P)$ state ion, we can reproduce satisfactorily the experimental data of Kusakabe *et al.* for the mixed case below 2 keV.

The good agreement found between our [90% $O^+(^4S)$+10% $O^+(^2D,^2P)$] results and the experimental data of Kusakabe *et al.* and of Wolfrum, Schweinzer, and Winter in the same energy region suggest that metastable ions were present in the beams used by Wolfrum, Schweinzer, and Winter [4].

We studied the excitation-deexcitation process (3) and found that the cross section is 1×10^{-16} cm^2 at 0.4 keV, steadily increasing to 5×10^{-15} cm^2 at 10 keV. These cross sections are comparable in magnitude to those for

TABLE II. Electron capture cross sections for three initial channels. The numbers in brackets denote multiplicative powers of ten.

	Cross section (cm^2)		
E (keV)	$O^+(^4S)+He$	$O^+(^2D)+He$	$O^+(^2P)+He$
0.16	<10 [−20]	2.61 [−18]	2.58 [−16]
0.36	5.62 [−20]	6.62 [−18]	1.71 [−16]
0.64	1.44 [−19]	7.41 [−18]	1.55 [−16]
1.0	5.32 [−19]	1.19 [−17]	1.21 [−16]
1.44	2.88 [−18]	8.30 [−17]	1.15 [−16]
2.56	2.76 [−18]	1.07 [−16]	1.87 [−16]
4.0	1.27 [−17]	2.08 [−16]	3.95 [−16]
9.0	8.92 [−17]	2.68 [−16]	2.17 [−15]

electron capture, and they interfere with them in an out-of-phase manner.

B. Electron capture by He^+ ions below 20 eV

At low energies, in the meV to eV range, the strong radial coupling between $2\,^2\Pi$ and $3\,^2\Pi$ is not effective in causing the transition involved in reaction (2). Other possible mechanisms for the transition (while found to be extremely weak, as well as the spin-orbit coupling between the $1\,^4\Pi$ and $3\,^2\Pi$ states) have not been calculated. The $1\,^4\Pi$ and $2\,^2\Pi$ potentials cross each other near $R \simeq 2.1\ a_0$. This curve crossing lies approximately 1.6 eV above the asymptotic energy limit that is the barrier for the process. The spin-orbit coupling matrix has a large value inside the curve crossing [see Fig. 2(b)], but outside it drops sharply and is nearly zero. These features are reflected in the shape of the cross section for electron capture, as illustrated in Fig. 4. The cross section increases rather sharply above the threshold of 1 eV and quickly reaches its maximum value of 1.5×10^{-21} cm^2 at 8 eV. The cross section decreases gradually as the energy increases further. However, at energies higher than 20 eV, nonadiabatic couplings that form connections to other channels may become dominant for electron capture. Because of the small value of the cross section at thermal energies, process (2) is not significant in the He^+ ion balance in supernova 1987A [3].

C. Excitation of $\mathrm{O}^+(^4S)$ and deexcitation of $\mathrm{O}^+(^2D)$

The excitation process (3) was studied by Augustin *et al.* [9] who used the Landau-Zener theory with an approximate spin-orbit coupling matrix. They found that the cross section has a maximum of 8.6×10^{-19} cm^2 at 6 eV. The $1\,^2\Pi$ potential of $\mathrm{O}^+(^2D)+\mathrm{He}$ is slightly attractive at $R < 3.5\ a_0$ and crosses the $1\,^4\Sigma^-$ potential, corresponding to $\mathrm{O}^+(^4S)+\mathrm{He}$, at $R \simeq 2.2\ a_0$. The asymptotic energy defect is about 3.3 eV, which is the threshold for excitation. The spin-orbit couplings have maxima of 72 and 41 cm^{-1}, respectively, for $^4\Sigma^-_{3/2}$–$1\,^2\Pi$ and $^4\Sigma^-_{1/2}$–$1\,^2\Pi$ at 2.1 a_0, and they drop sharply at larger R values. The calculated cross sections for excitation and deexcitation are included in Fig. 4. The excitation cross section increases rapidly above its threshold of 3.3 eV and quickly reaches its maximum value of 3.7×10^{-19} cm^2 at 15 eV. At 6 eV, the present value is approximately 10^{-21} cm^2. The cross sections show a rather different energy dependence from those of Augustin *et al.* [9]. The deexcitation cross section has a broad peak around 0.1–1 eV, with a much larger value of 7×10^{-17} cm^2, and decreases slowly at lower and higher energies. Even at 10^{-4} eV collision energy, its value is $\sim10^{-21}$ cm^2. The cross section for excitation decreases gradually with weak oscillatory structures below 5 eV, because of a small residual spin-orbit coupling at $R \geq 2.5\ a_0$.

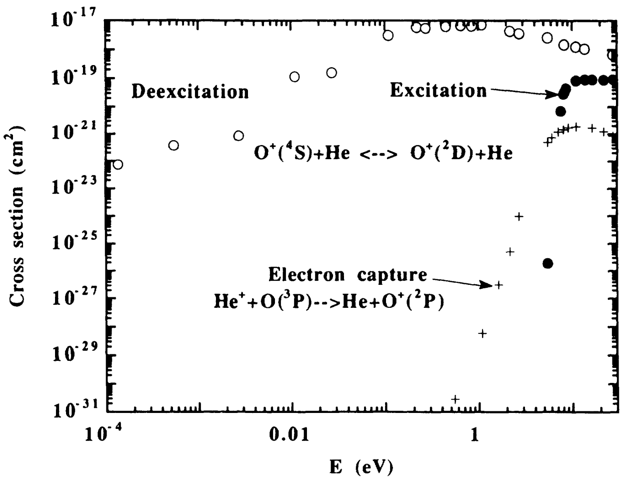

FIG. 4. Electron capture and excitation and deexcitation cross sections below 20 eV. Present work: ○, deexcitation; ●, excitation; +, electron capture.

IV. CONCLUSION

We have studied electron capture in collisions of $\mathrm{O}^+(^4S,{}^2D,{}^2P)$ with He above 100 eV and found a significant contribution from metastable $\mathrm{O}^+(^2D,{}^2P)$ ions. Below 20 eV, we investigated electron capture in collisions of He^+ with O and excitation-deexcitation in collisions of $\mathrm{O}^+(^4S)$ with He. These processes are driven by spin-orbit coupling. The excitation cross section is much smaller than that previously obtained in a less sophisticated calculation.

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