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Electron capture in collisions of $O^{2+}(^3P)$ ions with He atoms at energies below 10 keV: The effect of metastable $O^{2+}(^1D)$ ions

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Electron capture in $O^{2+}(^3P,^1D)+\mathrm{He}$ collisions is studied theoretically by using a semiclassical molecular representation with six molecular channels at collision energies above 50 eV and by using a fully quantum-mechanical molecular representation with three Π channels below these energies. The *ab initio* potential curves and nonadiabatic coupling matrix elements for the HeO^{2+} system are obtained from multireference single- and double-excitation configuration-interaction calculations employing a relatively large basis set. The present total cross sections for electron capture by the ground-state O^{2+} ions are found to be in reasonable accord with those calculated by Gargaud, Bacchus-Montabonel, and McCarroll [J. Chem. Phys. **99**, 4495 (1993)] below 30 eV/u but are slightly larger above this energy. Partial cross sections for the l distribution are also slightly different. Cross sections for electron capture by the metastable O^{2+} ions decrease much more sharply than those for the ground-state ion as the energy is lowered, reaching a difference between them approximately as large as one to two orders of magnitude below 100 eV. The present rate coefficient for the reaction is approximately 10^{-9} cm^3/s above 10 000 K, suggesting that the small rate coefficient of about 10^{-12} cm^3/s at 20 000 K observed by Kwang and Fang [Phys. Rev. Lett. **71**, 4127 (1993)] for electron capture by the ground-state ion might be caused, in part, by a mixture of ground and metastable ions in their experiment. [S1050-2947(96)01906-3]

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I. INTRODUCTION

Recent measurements of electron capture for thermal energies of ground-state O^{2+} ions in helium have been carried out [1,2], and a rate coefficient of 10^{-12} cm^3/s at 20 000 K was obtained. This result is in serious disagreement with theoretical findings, in which much larger values from 10^{-9} to 10^{-10} cm^3/s were calculated in a similar temperature region [3–6].

The theoretical studies were based on a molecular-orbital (MO) expansion method within a semiclassical or fully quantal formalism. Butler, Heil, and Dalgarno [3] and Bienstock, Heil, and Dalgarno [4] studied electron-capture processes by the ground-state $O^{2+}(^3P)$ ion from He atoms at energies below 600 eV using a fully quantal MO method with three Π states, corresponding to the initial and electron capture to $O^+(^2P,^2D)$ states only. Bacchus-Montabonel, Courbin, and McCarroll [5] employed six (Σ and Π) MO states from the initial and electron-capture channels to $O^+(^2P,^2D)$ with a semiclassical approach, and Gargaud, Bacchus-Montabonel, and McCarroll [6] used a fully quantal approach with inclusion of two channels corresponding to the initial and final Π states. In all cases, the molecular states were described by using a configuration-interaction (CI) method with large basis sets, and hence, the quality of the different molecular structure calculations is similar. The theoretical rate coefficients were found to be large and to vary from 1×10^{-9} [5] to 3×10^{-10} cm^3/s [3] at 20 000 K. The difference between the two theoretical results has been attributed to a combination of the quality of MOs and the number of channels included in the calculation [6]; the much larger discrepancy between theory and experiment was not understood.

We present here a theoretical study which is intended to shed some light on this controversy. We wish in particular to assess the role of metastable O^{2+} ions in electron capture. The processes we have studied are as follows, with corresponding asymptotic energy defects: (i) ground-state ions:

$$O^{2+}(^3P)+\mathrm{He}\rightarrow O^{+}(^2P)+\mathrm{He}^{+}+5.55\ \mathrm{eV} \tag{1a}$$

$$\rightarrow O^{+}(^2D)+\mathrm{He}^{+}+7.24\ \mathrm{eV}, \tag{1b}$$

and (ii) metastable ions:

$$O^{2+}(^1D)+\mathrm{He}\rightarrow O^{+}(^2P)+\mathrm{He}^{+}+8.06\ \mathrm{eV} \tag{2a}$$

$$\rightarrow O^{+}(^2D)+\mathrm{He}^{+}+9.76\ \mathrm{eV}. \tag{2b}$$

The metastable ^1D states, which separate with 2.51-eV higher energy than the ground states, are considered to compete in collision dynamics with the ground state. Hence it is important to understand the electron-capture mechanisms of both the ground and metastable states and to determine each cross section accurately. Furthermore, experimental ion beams produced by an electron-impact ionization technique are often a mixture of a ground and metastable states when open-shell ions are involved; knowledge of the collision dynamics may be helpful for experimental analysis [7,8].

The present theoretical approach is basically the same as that used in earlier studies, being based on the MO expansion method within a semiclassical formalism for collision energies above 50 eV and a fully quantal formalism below 50 eV.

TABLE I. Number of reference configurations (NREF) and number of roots (NROOT) treated in each irreducible representation, with the corresponding numbers of generated (SAFTOT) and selected (SAFSEL) symmetry-adapted functions for a threshold of $(5\times10^{-6})E_h$ at a bond distance of $2.4a_0$.

States	NREF, NROOT	SAFTOT	SAFSEL
$^1A_1$	99,6	727 385	9 442
$^1B_1$	74,4	750 475	8 452
$^1A_2$	57,4	680 651	7 738
$^3A_1$	103,3	1 307 275	6 855
$^3B_1$	86,5	1 452 964	10 965
$^3A_2$	69,6	1 384 627	9 679
$^5B_1$	45,2	772 649	4 745
$^5A_2$	49,3	696 950	6 069

II. THEORETICAL MODEL

Because the present HeO^{2+} calculations are similar to earlier work on the HeO^+ system reported [7,9], only a brief summary is provided here.

A. Molecular states and couplings

The adiabatic potential curves of HeO^{2+} are obtained by employing the *ab initio* multireference single- and double-excitation configuration-interaction (MRD-CI) method [10–12], with configuration selection at a threshold of $(5.0\times10^{-6})E_h$ and energy extrapolation, using the Table CI algorithm [13–15]. The nonadiabatic coupling elements are calculated by using a finite-difference method [16]. In these calculations, we have employed the same atomic orbital basis set for the helium atom $(9s4p1d)/[7s3p1d]$ as we did in earlier work for HeN^+ [17]. For the oxygen atom we used the $(13s8p2d)$ basis contracted to $[7s4p2d]$ of van Duijneveldt [18]. Because the present basis set is larger than that used in previous calculations [3–6], the asymptotic energies are more accurate by a few %. Further details of our *ab initio* MRD-CI calculations are presented in Tables I and II. Figure 1 displays the adiabatic potential curves for the ground and metastable initial $(O^{2+}+He)$ states and the electron-capture channels that lie closest to the initial channels.

Representative results for the nonadiabatic coupling matrix elements are illustrated in Fig. 2(a). The $2\,^3\Pi$ and $3\,^3\Pi$ potential curves undergo a sharply avoided crossing at $R=5.4a_0$, at which point the radial coupling between these states has a strong peak. This strong coupling, which has a maximum value of about 2.3 a.u., is the dominant mechanism for electron capture from the ground $O^{2+}(^3P)$ + He channel at higher energies above 100 eV. The coupling between the metastable $[O^{2+}(^1D)+He]$ and the electron-capture $[O^+(^2P)+He^+]$ channels does not possess a strong peak [Fig. 2(b)] and hence is relatively weak, suggesting a less efficient process at lower energies.

B. Collision dynamics

1. Semiclassical approach

A semiclassical MO expansion method with a straight-line trajectory was employed to study the collision dynamics above 100 eV [8]. 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 (ETFs). Substituting the total wave function into the time-dependent Schrödinger equation and retaining ETF correction up to the first order of

TABLE II. Leading configuration for each of the eigenfunctions in energetically increasing order at an internuclear distance of $2.4a_0$. For the A_1 and A_2 irreducible representations in the C_{2v} point group, the corresponding $C_{\infty v}$ states (Σ^+,Δ and Σ^-,Δ, respectively) are also indicated. All B_1 states correspond to Π states.

States	Configurations		States	Configurations	
$^1A_1$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	$(\Delta+\Sigma)$	$^3A_1$	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^2$	$(\Delta+\Sigma)$
	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2$	(Σ)		$1\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1 1\pi^2$	(Δ)
	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^2$	$(\Delta+\Sigma)$			
	$1\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1 1\pi^2$	(Δ)			
$^1B_1$	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^1$				
	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^3$		$^3B_1$	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^1$	
	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^2 1\pi^1$			$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^3$	
	$1\sigma^2 2\sigma^1 3\sigma^2 1\pi^3$			$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^2 1\pi^1$	
				$1\sigma^2 2\sigma^1 3\sigma^2 1\pi^3$	
				$1\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1 1\pi^3$	
$^1A_2$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	(Δ)			
	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^2$	$(\Sigma+\Delta)$	$^3A_2$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	Σ
	$1\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1 1\pi^2$	(Δ)		$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^2$	$(\Sigma+\Delta+\Sigma)$
				$1\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1 1\pi^2$	$(\Delta+\Sigma)$
$^5B_1$	$1\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1 1\pi^3$				
	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2 2\pi^1$				
$^5A_2$	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^2$	(Σ)			
	$1\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1 1\pi^2$	(Σ)			
	$1\sigma^2 2\sigma^1 3\sigma^1 4\sigma^2 1\pi^2$	(Σ)			

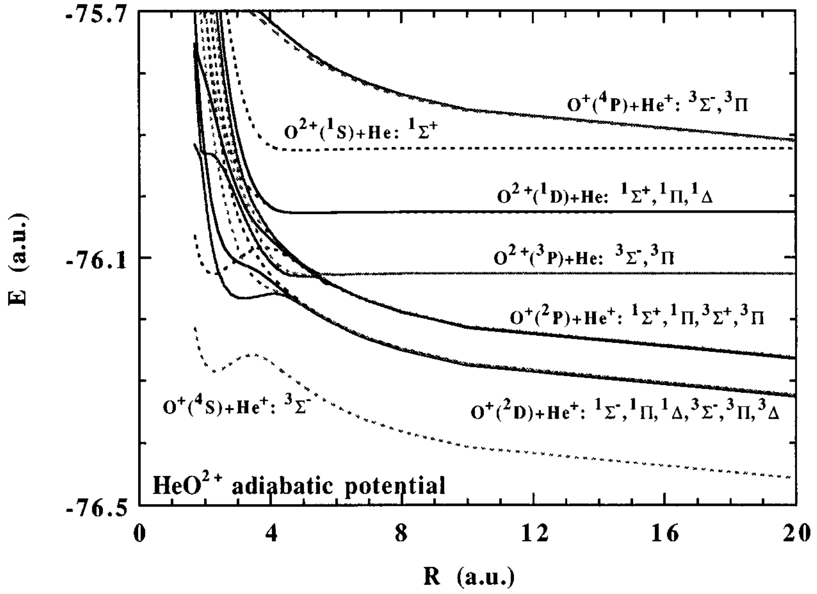

FIG. 1. Adiabatic potentials of the HeO^{2+} system.

relative velocity, we obtain 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 the impact parameter gives the cross section. The molecular states included in the dynamical calculations are the two sets of states, shown in Fig. 1, separating to $[O^{2+}(^3P)+He]$; $3\,^3\Sigma^-$, $3\,^3\Pi$, $[O^+(^2D)+He^+]$; $2^3\Sigma^-$, $1\,^3\Pi$, $1\,^3\Delta$, $[O^+(^2P)+He^+]$; $1\,^3\Sigma^+$, $2\,^3\Pi$ for the ground channel, and $[O^{2+}(^1D)+He]$; $2\,^1\Sigma^+$, $3\,^1\Pi$, $[O^+(^2P)+He^+]$; $1\,^1\Sigma^+$, $2\,^1\Pi$, $[O^+(^2D)+He^+]$; $1\,^1\Sigma^-$, $1\,^1\Pi$ for the metastable channel.

2. Quantum approach

A fully quantum-mechanical representation of the MO expansion method was employed for collision energies below 10 eV. In this energy region, transitions are also driven by nonadiabatic coupling. 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 are obtained from the time-independent Schrödinger equation [8]. 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: (1) $O^{2+}(^3P)+He$; $3\,^3\Pi$ and $O^+(^2P)+He^+$: $2\,^3\Pi$ and (2) $O^{2+}(^1D)+He$; $3\,^1\Pi$ and $O^+(^2P)+He^+$: $2\,^1\Pi$.

III. RESULTS

A. Electron capture by the ground-state O^{2+} ions

The calculated cross sections are illustrated in Fig. 3 along with the earlier results by Bienstock, Heil, and Dal-

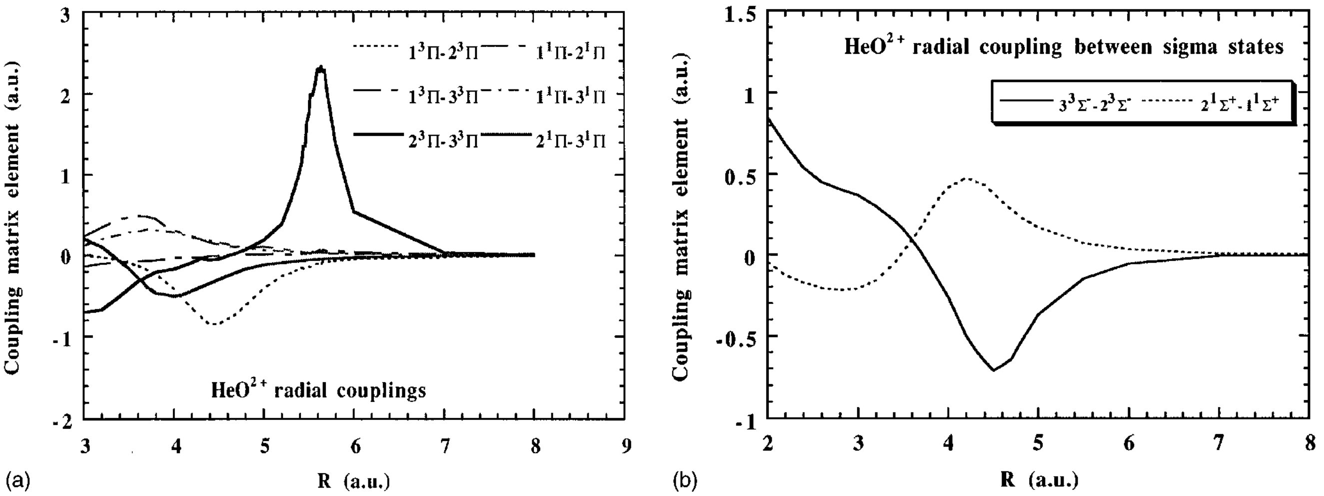

FIG. 2. (a) Representative nonadiabatic coupling matrix elements for the ground system. (b) Nonadiabatic coupling matrix elements for the metastable system.

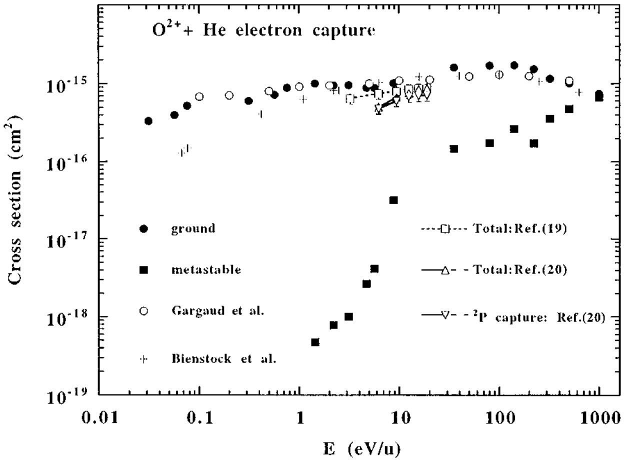

FIG. 3. Electron-capture cross section below 1 keV/u. Present work: ●, $O^{2+}(^3P)$; ■, $O^{2+}(^1D)$; theoretical work [4]: +, $O^{2+}(^3P)$; theoretical work [6]: ○, $O^{2+}(^3P)$; experimental data [19] -□-, total; experimental data [20]- △-, total; -▽-, $O^{+}(^2P)$ formation.

garno [4], Gargaud, Bacchus-Montabonel, and McCarroll [6], and experimental measurements [19,20]. The present results are found to be 20% larger than those experimental results of Huq, Champion, and Doverspike [19] in most energy regions, but the energy dependence is similar. The experimental data of Bangsgaard *et al.* [20] agree well with those of Huq, Champion, and Doverspike at 19 eV/u, but drop sharply at lower energies, hence widening the deviation from the present results. Experimental results on single-electron-capture spectra based on high-resolution translational energy-loss measurement by Lee *et al.* [21] suggest that $O^{2+}(^3P)$ ions dominate the spectrum, which is consistent with the present theory. The present results are in reasonably good accord with those of Gargaud, Bacchus-Montabonel, and McCarroll [6] in all energies, but the result becomes slightly larger at energies from 30 to 300 eV/u. Because the magnitude and position of the dominant radial coupling between the 2 $^3\Pi$ and 3 $^3\Pi$ states are comparable to that of Gargaud, Bacchus-Montabonel, and McCarroll [6], a close agreement between the two cross sections is expected, particularly at lower energies. Because of the strong coupling, the cross section is nearly constant over a wide range of energy. The cross sections of Bienstock, Heil, and Dalgarno [4] drop rather sharply below an energy of 10 eV. The origin of this discrepancy was discussed in Ref. 6. The present results show somewhat different oscillatory patterns below 1 eV/u than those of Gargaud, Bacchus-Montabonel, and McCarroll [6], and this difference is a reflection of the different partial cross sections for ^2P and ^2D capture. Strong resonancelike peaks in the cross section are found below 0.1 eV/u. In earlier work for [N^{5+}+H] [22], we observed similar peaks arising as a result of the contribution of a single partial wave to the cross section. These peaks contribute structure in the rate coefficient.

B. Electron capture by the metastable $O^{2+}(^1D)$ ions

Electron-capture cross sections by the metastable $O^{2+}(^1D)$ ions are included in Fig. 3. The cross sections decrease rapidly as the energy is lowered below 100 eV/u, with a value of less than 10^{-18} cm^2 at a few eV. The size of the cross section becomes comparable to that of the ground-state ion, of the order 10^{-16} cm^2, above 200 eV/u. Oscillatory structures in the cross section due to a multichannel interference effect are clearly seen below 100 eV/u. Because of the strong rotational coupling between the 2 $^1\Sigma^+$ and 3 $^1\Pi$ states, resulting in an effective sharing of the initial flux, the contributions from the 2 $^1\Sigma^+$ and 2 $^1\Pi$ initial channels to electron capture are nearly equal in this energy region and these states must be considered simultaneously in the calculations.

TABLE III. Rate coefficients for electron capture.

	Rate coefficient (cm^3/s)	
	Initial channel	
Temperature (K)	$O^{2+}(^3P)$+He	$O^{2+}(^1D)$+He
1 000	1.1×10^{-10}	4.0×10^{-16}
2 000	2.3×10^{-10}	3.1×10^{-15}
4 000	3.2×10^{-10}	4.6×10^{-14}
6 000	4.5×10^{-10}	1.5×10^{-13}
8 000	5.6×10^{-10}	2.9×10^{-13}
10 000	6.5×10^{-10}	5.2×10^{-13}
20 000	1.0×10^{-9}	4.7×10^{-12}
40 000	1.7×10^{-9}	3.2×10^{-11}
60 000	2.7×10^{-9}	7.5×10^{-11}
80 000	2.8×10^{-9}	1.2×10^{-10}
100 000	3.3×10^{-9}	1.7×10^{-10}

C. Rate coefficients

The rate coefficients for electron capture by the ground-state $O^{2+}(^3P)$ and metastable $O^{2+}(^1D)$ ions are listed in Table III. The values for the ground-state ions increase from 10^{-10} cm^3/s at 1000 K to 10^{-9} cm^3/s at 20 000 K while those for the metastable ions vary from 10^{-16} to 10^{-12} cm^3/s. The present rate coefficient for the ground-state ion at 20 000 K is in excellent agreement with that of Gargaud, Bacchus-Montabonel, and McCarroll [6], who reported a value of 1.01×10^{-9} cm^3/s. The value obtained by Butler, Heil, and Dalgarno [3] is smaller by a factor of 2.5 (4×10^{-10} cm^3/s) at the same temperature. Kwang and Fang [1] obtained an experimental rate coefficient of 1.12×10^{-12} cm^3/s at 20 000 K. They claimed that the ion beams used contain only ground-state $O^{2+}(^3P)$ ions. Although the source of this discrepancy is not clear, it could, in part, be the use of the beam contained a larger fraction of metastable ions.

IV. CONCLUSION

We have studied electron capture in collisions of $O^{2+}(^3P,^1D)$ with He below 1 keV/u and found good agreement for cross sections involving the ground-state ion with those obtained by Gargaud, Bacchus-Montabonel, and McCarroll [6]. We also investigated electron capture by metastable $O^{2+}(^1D)$ ions from He in the same energy range and found that although the magnitude of the cross section is comparable to that for the ground-state ion at 1 keV/u, it rapidly decreases as the energy is lowered and becomes less than 10^{-18} cm^2 below 10 eV/u. Our rate coefficient for electron capture by the ground-state ion is approximately 10^{-9} cm^3/s above 10 000 K, in good agreement with the rate constant obtained by Gargaud, Bacchus-Montabonel, and McCarroll [6]. By combining the present rate constants for capture by the ground- and metastable-state ions, our value varies from 10^{-13} to 10^{-9} cm^3/s depending upon the fraction of the metastable contribution. We suspect that the rate coefficient measured by Kwang and Fang [1] may be due, in part, to an admixture of metastable ions in their experimental beam.

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