The Chemiionization Reactions Ce + O and Ce + O₂: Assignment of the Observed Chemielectron Bands

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ABSTRACT: Multiconfigurational quantum chemical methods (CASSCF/CASPT2) have been used to study the chemiionization reactions Ce + O → CeO⁺ + e⁻ and Ce + O₂ → CeO₂⁺ + e⁻. Selected spectroscopic constants for CeOₙ and CeOₙ⁺ (n = 1, 2), as well as reaction enthalpies of the chemiionization reactions of interest, have been computed and compared with experimental values. In contrast to the lanthanum case, for both Ce + O₂(X³Σ⁺) and Ce + O₂(a¹Σ⁺), the Ce + O₂ → CeO₂⁺ + e⁻ reaction is shown to be exothermic, and thus, contributes to the experimental chemielectron spectra. The apparent discrepancy between the computed reaction enthalpies and the high kinetic energy offset values measured in the chemielectron spectra is rationalized by arguing that chemielectrons are produced mainly via two sequential reactions (Ce + O₂(X³Σ⁺) → CeO + O(¹Σ⁺), followed by Ce + O → CeO⁺ + e⁻) as in the case of lanthanum. For Ce + O₂(a¹Σ⁺), a chemielectron band with higher kinetic energy than that recorded for Ce + O₂(X³Σ⁺) is obtained. This is attributed to production of O(¹D) from the reaction Ce + O₂(a¹Σ⁺) → CeO + O(¹D), followed by chemiionization via the reaction Ce + O(¹D) → CeO⁺ + e⁻. Accurate potential energy curves for the ground and a number of excited states of CeO and CeO⁺ have been computed, and a mechanism for the chemiionization reactions investigated experimentally was proposed. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2068–2079, 2009

Key words: cerium oxides; multiconfigurational methods; chemiionization reactions; spin-orbit coupling
CHEMIIONIZATION REACTIONS Ce + O AND Ce + O₂

Introduction

In a recent publication, the chemiionization reactions that occur for the La + O(⁹P), La + O₂(X³Σ⁻), and La + O₂(a¹Δg) reaction conditions have been established by quantum chemical methods [1]. It has been shown that for La + O₂(X³Σ⁻) and La + O₂(a¹Δg), the chemiionization reaction La + O₂ → LaO₂⁺ + e⁻ is endothermic and does not contribute to the experimental chemielectron spectrum. Instead, chemiionization occurs via a two-step process, a rapid first step La + O₂ → LaO + O, followed by LaO + O → LaO⁺ + e⁻. For all reaction conditions studied, (i.e., La + O₂(X³Σ⁻), La + O₂(a¹Δg), and La + O(⁹P)), production of LaO⁺ was attributed to the primary chemiionization reaction (LaO + O → LaO⁺ + e⁻), whereas LaO₂⁺, observed in the mass spectra, does not arise from a chemiionization process, but from ion-molecule reactions involving LaO⁺. This work is now extended to the Ce + O and Ce + O₂ chemiionization reactions. Experimentally, electron spectroscopy was employed to study the chemiionization reactions of cerium with the oxidants O(⁹P), O₂(X³Σ⁻), and O₂(a¹Δg) [2, 3]. As in the study on lanthanum [1], an effusive beam of cerium was crossed with an effusive beam of oxygen which contains O₂(X³Σ⁻), O₂(a¹Δg), and O(⁹P). For all reaction conditions studied, the above microwave discharge conditions but with O(⁹P) deactivated, or (C) pure O₂(X³Σ⁻). The Ce + O₂(X³Σ⁻) reaction gave a chemiionization band, which showed resolved vibrational structure, with a most probable kinetic energy (MPKE) (band maximum) of (0.90 ± 0.04) eV and a high kinetic energy offset (HKEO) of (2.4 ± 0.1) eV. For the Ce + O₂(a¹Δg) reaction, these values were (1.83 ± 0.10) and (3.1 ± 0.3) eV, whereas for the Ce + O(⁹P) reaction, they were (0.13 ± 0.06) and (0.9 ± 0.1) eV.

In the experimental work [2, 3], although assignment of a chemiion electron band to a particular chemiionization reaction was made, the measured HKEO values showed large differences with reaction enthalpies derived from available thermodynamic values (shown in Table I for cerium). This was partly because available thermodynamic values for CeO, CeO⁺, CeO₂, and CeO₂⁺ are not sufficiently well determined to allow reaction enthalpies for the chemiionization reactions to be reliably estimated. For example, for Ce + O₂(X³Σ⁻) → CeO₂⁺ + e⁻ and Ce + O₂(a¹Δg) → CeO₂⁺ + e⁻, the heats of reaction were calculated as (−(0.2 ± 1.0) and (−(1.2 ± 1.0) eV compared to HKEO values of (2.4 ± 0.1) and (3.1 ± 0.3) eV. Hence, although the chemiion bands observed under the Ce + O₂(X³Σ⁻) and the Ce + O₂(a¹Δg) reaction conditions were assigned to the above chemiionization reactions, the discrepancy between the HKEO values and the available reaction enthalpies was large. The objective of this work, therefore, is to compute selected spectroscopic constants for CeO, CeO⁺, CeO₂, and CeO₂⁺, to make a comparison with available experimental values, and to compute the standard reaction enthalpies for Ce + O and Ce + O₂ chemiionization reactions, shown in Table I, in order to assign the experimental chemiion bands. Also, by computing relevant parts of the potential energy curves for the relevant neutral and cationic states, we hope to propose a mechanism for the Ce + O → CeO⁺ + e⁻ and Ce + O₂ → CeO₂⁺ + e⁻ chemiionization reactions investigated experimentally. Comparison with the lanthanum case can then be made.

Computational Details

The study was performed using the complete active space (CAS) SCF method [4] followed by multiconfigurational second-order perturbation theory (CASPT2) [5]. Scalar relativistic effects were included using the Douglas-Kroll-Hess Hamiltonian [6, 7] and the relativistic ANO-RCC basis set [8, 9], where the primitive set of 25s22p15d11f4g2h functions was contracted to 9s8p5d4f3g2h for cerium and the primitive set of 14s9p4d3f2g basis functions was contracted to 5s4p3d2f for oxygen. Spin-orbit coupling effects were computed using the complete active space state interaction (CASSI) method [10, 11], in which an effective one-electron spin-orbit Hamiltonian, based on the atomic mean field approximation of the two-electron part, was employed. This approach has been shown to work successfully in a number of earlier applications [12–23]. All calculations were performed using the MOLCAS 7.0 program package [24]. In the CASSCF treatment, the molecular orbitals formed by linear combinations of 6s, 5d, and 4f orbitals of Ce with 2p orbitals of O were included in the active space, resulting in an active space of eight electrons (four from Ce and four from O) in 16 orbitals for CeO. The complete valence active space in the case of CeO₂ would consist of 19 orbitals with 12 electrons. Such an active space, however, is unaffordable with nowadays technology. Thus, we used the space constructed of the six bonding and six antibonding
TABLE I
Experimental and computed reaction enthalpies (eV) for possible reactions (see text).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction enthalpy from Ref. [2]</th>
<th>Computed values w.r.t. O(<em>2)(X(^3\text{S}</em>\text{g}))</th>
<th>Computed values w.r.t. O(<em>2)(a(^1\text{Δ}</em>{\text{g}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Ce + O(_2) → CeO(_2)(^+) + e(^-)</td>
<td>−0.2 ± 1.0</td>
<td>−0.76</td>
<td>−1.72</td>
</tr>
<tr>
<td>(2) Ce + O(_2) → CeO(_2)(^+) + O</td>
<td>0.6 ± 1.0</td>
<td>1.42</td>
<td>0.46</td>
</tr>
<tr>
<td>(3) Ce + O(_2) → CeO(_2)(^+) + O + e(^-)</td>
<td>2.1 ± 1.0</td>
<td>2.79</td>
<td>1.83</td>
</tr>
<tr>
<td>(4) Ce + O(_2) → Ce(^+) + O(_2)(^-)</td>
<td>5.1 ± 0.1</td>
<td>5.23</td>
<td>4.27</td>
</tr>
<tr>
<td>(5) Ce + O(_2) → CeO + O</td>
<td>−3.1 ± 0.2</td>
<td>−2.47</td>
<td>−3.43</td>
</tr>
<tr>
<td>(6) Ce + O → CeO(_2)(^+) + e(^-)</td>
<td>−3.0 ± 0.7</td>
<td>−2.45</td>
<td>−4.38</td>
</tr>
<tr>
<td>(7) CeO(_2)(^+) + O → CeO(_2)(^+) + O</td>
<td>2.8 ± 1.7</td>
<td>1.69</td>
<td>0.73</td>
</tr>
<tr>
<td>(8) CeO(_2)(^+) + Ce → CeO(_2)(^+) + CeO</td>
<td>−5.9 ± 1.9</td>
<td>−4.16</td>
<td></td>
</tr>
<tr>
<td>(9) CeO(_2)(^+) + M → CeO(_2)(^+) + O + M</td>
<td>2.9 ± 1.7</td>
<td>3.55</td>
<td></td>
</tr>
<tr>
<td>(10) CeO + O → CeO(_2)(^+) + e</td>
<td>2.9 ± 1.2</td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>(11) CeO(_2)(^+) + O + M → CeO(_2)(^+) + M</td>
<td>−3.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that the first four reactions (1)–(4) are primary ionization reactions, whereas reactions (5)–(11) are neutral or ion-molecule processes. The separation of the reactions in this way follows the approach used in the previous experimental paper (Ref. [2]).

Ce–O orbitals, 12 electrons in 12 orbitals in total. In the subsequent CASPT2 calculations, the [Kr] 4d orbitals of Ce and 1s orbitals of O were kept frozen. In total, 18 electrons were correlated for CeO, and 24 electrons were correlated for CeO\(_2\). C\(_{2\text{v}}\) symmetry was imposed for all the species considered. In addition, density functional theory (DFT) calculations were performed with the hybrid B3LYP functional [25] using the same basis sets for Ce and O. The potential energy curves for several electronic states of CeO and CeO\(_2\) were calculated at the CASPT2 level of theory. The spectroscopic constants for their ground states were determined by using the program VIBROT in the MOLCAS 7.0 package. The equilibrium structures of CeO and CeO\(_2\) were obtained by geometry optimizations followed by numerical vibrational frequency calculations at both CASPT2 and DFT levels.

To ensure consistency of the results, we also performed calculations with the relativistic four-component Dirac-Coulomb (DC) Hamiltonian as implemented in the DIRAC code [26], which includes spin-orbit coupling effects from the outset, so that mixing of orbitals with different orbital angular momenta is included already at the Hartree-Fock (HF) level. To facilitate analysis, and for comparison with results from other methods, DC-Coupled Cluster calculations, DC-CCSD and DC-CCSD(T) [27], which employed the same active space as in the CASPT2 calculations, were performed with 18 electrons correlated for CeO and 24 electrons correlated for CeO\(_2\). The Dyall uncontracted double-zeta basis set consisting of 24s19p13d8f2g basis functions was used for Ce (Gomes, A. S. P., Private Communication) and the cc-pVDZ basis set was used for O [28]. This basis-set size has already been shown to be sufficiently large to predict with high accuracy excited states of metal oxide species [29]. The ionization energies were computed at the geometries optimized at the CASPT2 level of theory.

Results and Discussion

CeO AND CeO\(_2\)

The computed equilibrium spectroscopic constants (equilibrium bond distance \(R_{\text{e}}\), dissociation energy \(D_{\text{e}}\), and harmonic vibrational constant \(\omega_{\text{e}}\)) for the ground states of CeO and CeO\(_2\) are summarized in Table II, along with the computed first ionization energies of Ce and CeO. As the first 4f-element, cerium represents a bridge between the lanthanide and the 5d-block elements. It is worth-mentioning its unusual ground state, [Xe] 6s\(^2\)5d\(^4\)4f\(^1\), \(1G_{\text{g}}\), which violates Hund’s rules (the unnatural parity states) [30]. Moreover, the first ionization energy of Ce is also very unusual, that is, the ground state of the ion is [Xe] 5d\(^2\)4f\(^4\), \(4H_{\text{g}/2}\), which means that one 6s electron is removed, and the second 6s electron moves to the 5d shell. The ionization energy IE(Ce) is also influenced by spin-orbit coupling (SOC) effects. As evident from Table II, the IE value is 5.67 eV without SOC and 5.53 eV with SOC included (the experimental value is 5.54
eV [31]). The ground states of CeO and CeO$^+$ are $^3\Phi$ and $^3\Phi$, respectively. The CASPT2 computed equilibrium distance and vibrational constant of CeO are 1.821 Å and 825 cm$^{-1}$, respectively, in good agreement with the experimental values of 1.82009 Å and 829 cm$^{-1}$ [32]. The $^3\Phi$ ground state has one electron in the $6s$ and one electron in the $4f$ orbital of cerium. The spin-orbit calculation shows that it is a $^3\Phi_2$ state. It is composed of 93% $^3\Phi$, 6% $^3\Delta$, and 1% $^1\Delta$. The first ionization energy of CeO computed at the CASPT2 level of theory is 5.26 eV, which agrees well with the DC-CCSD(T) value of 5.53 eV as well as the experimentally obtained values as evident from Table II. The minor SOC influence on the IE(CeO) is because the $6s$ electron does not couple strongly with the other valence electrons. The spin-free dissociation energy ($D_0$) of CeO is 8.13 eV which changes slightly to 8.18 eV due to spin-orbit interactions, in good agreement with the experimental data obtained from electronic absorption and emission spectroscopic studies [47] as well as that from semiempirical ligand field [39] and quasirelativistic pseudopotential CI [35] calculations. The computed equilibrium distance of CeO$^+$ is 1.776 Å; experimental information on the equilibrium bond length of CeO$^+$ is not available. The vibrational wavenumber $\omega_e$ is computed as 888 cm$^{-1}$, ~40 cm$^{-1}$ higher than the reported experimental value measured in an argon matrix [43]. The $^2\Phi$ ground state arises from removal of an electron from the $6s$ orbital of the $^3\Phi$ state of neutral CeO, and thus the single unpaired electron is left in a nonbonding $4f$ orbital of cerium. The spin-orbit calculation reveals that it is a $^2\Phi$ state with $\Omega = 2.5$. Table V summarizes the computed spectroscopic constants (equilibrium bond distance $R_e$ and harmonic vibrational constant $\omega_e$) for the ground state and the low-lying excited states of CeO$^+$, along with the spin-free vertical excitation energies (in cm$^{-1}$) evaluated at the ground-state equilibrium bond length (1.776 Å). The corresponding excitation energies obtained by including spin-orbit coupling effects and the total angular momentum quantum number ($\Omega$) of each state are given in Table VI. The first electronically excited state of CeO$^+$ has $^2\Delta$ symmetry and is only 0.07 eV higher in energy than the ground state. In this state, the equilibrium cerium-oxygen bond distance is 1.771 Å and the harmonic vibrational frequency is 882 cm$^{-1}$. It should be noted that the $^2\Delta$ state has been found to be the ground state for CeO$^+$ within the DFT scheme [48]. The second excited state has $^2\Sigma^+$ symmetry and is only 0.19 eV higher than the $^2\Phi$ state. For this $^2\Sigma^+$ state, the equilibrium bond distance is 1.767 Å and the harmonic vibrational frequency is 886 cm$^{-1}$. Finally, very close in energy there is a $^2\Pi$ state (0.21 eV higher than the $^2\Phi$ state), for which the $R_e$(Ce−O) is 1.771 Å and $\omega_e$ is 882 cm$^{-1}$. The computed dissociation energy of CeO$^+$ is 8.54 eV which changes slightly to 8.45 eV on including SOC effects. It agrees well with the experimentally reported values collected in Table II.

**CeO$_2$ AND CeO$_2^+$**

From the observed deflection of a molecular beam of CeO$_2$ in an electric quadrupole field [49] and infrared spectroscopic data [50], the neutral CeO$_2$ molecule is known to have a bent geometry. The angle $\theta$(O−Ce−O) = 146 ± 2° has been derived from the infrared spectrum of CeO$_2$ in an Ar matrix [50]. This value does not include corrections for anharmonicity effects which are estimated to reduce $\theta$(O−Ce−O) by 5 ± 10°[50]. Experimental information on the structure of CeO$_2^+$ is not available. Previous nonrelativistic DFT calculations performed by Heinemann et al. [48] reported a linear geometry of CeO$_2$, which on including a scalar quasirelativistic treatment adopts a bent structure with a cerium-oxygen bond length of 1.843 Å and bond angle (O−Ce−O) of 131.5°. The optimized geometries for CeO$_2$ and CeO$_2^+$, their computed bond dissociation energies with respect to Ce + O$_2$ and Ce$^+$ + O$_2$, respectively, and the first ionization energy of CeO$_2$ as obtained in this work are given in Table VII. At a CASPT2 level, neutral CeO$_2$ molecule is computed to have a bent C$_2v$ structure with a cerium-oxygen bond length of 1.816 Å and bond angle (O−Ce−O) of 126°. The Ce−O equilibrium bond lengths are virtually the same as the equilibrium bond distance in CeO (1.821 Å). The geometry is in good agreement with MRCI ($R_e = 1.813$ Å; $\theta$(O−Ce−O) = 115°) and ACPF ($R_e = 1.838$ Å; $\theta$(O−Ce−O) = 118°) results reported in Ref. [48]. A bent geometry is also obtained at the DFT/B3LYP level of theory, with a bond angle of 140° and a cerium-oxygen bond length of 1.822 Å. Energetically, the optimized linear structure is only 0.18 eV less stable than the bent geometry. According to our
The CASPT2 computed harmonic vibrational wave-numbers for the ground state of CeO$_2$ are 102, 784, and 822 cm$^{-1}$. The 102 cm$^{-1}$ value corresponds to the deformation mode ($\nu_2$), and the latter two values correspond to the antisymmetric ($\nu_3$) and symmetric stretching ($\nu_1$) modes involving the Ce–O bonds, respectively. The DFT frequencies are 59($\nu_2$), 790($\nu_3$), and 794($\nu_1$) cm$^{-1}$, in relatively good agreement with the CASPT2 frequencies. Neutral CeO$_2$ has been observed in argon matrices and fundamental absorptions have been measured at 737 cm$^{-1}$, the $\nu_3$ stretch and 757 cm$^{-1}$, the $\nu_1$ stretch [43].

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>$R_e$ (Å)</th>
<th>$D_e$ (eV)</th>
<th>$\omega_i$ (cm$^{-1}$)</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>CASPT2</td>
<td>1.821</td>
<td>8.13</td>
<td>825</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>SO-CASPT2</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>ACPF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO-ACPF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO</td>
<td>CASPT2</td>
<td>1.819c</td>
<td>8.26c</td>
<td>849c</td>
<td>5.26</td>
</tr>
<tr>
<td></td>
<td>SO-CASPT2</td>
<td>1.800c/1.827d</td>
<td>6.74c/7.28d</td>
<td>891c/838d</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>1.809c/1.815ae</td>
<td>7.60c/7.91e</td>
<td>874c/854e</td>
<td></td>
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<tr>
<td></td>
<td>CISD</td>
<td>1.804c/1.806f</td>
<td>8.23c/8.23g</td>
<td>844c/821f</td>
<td>4.9 ± 0.1lo</td>
</tr>
<tr>
<td></td>
<td>CISD + Q</td>
<td>1.813/1.808f</td>
<td>8.23c/8.23g</td>
<td>862c/829c/808n</td>
<td>5.47/5.48f</td>
</tr>
<tr>
<td></td>
<td>DFT/B3LYP</td>
<td>1.767/1.759f</td>
<td>8.80 ± 0.16h/8.94 ± 0.17l</td>
<td>906/912c</td>
<td>4.90q</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>1.820g</td>
<td>8.19 ± 0.18h</td>
<td>5.2 ± 0.2p</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>8.22 ± 0.08i</td>
<td>5.2 ± 0.5i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.24 ± 0.08h</td>
<td>5.2 ± 0.5i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.30 ± 0.14i</td>
<td>4.90q</td>
<td></td>
</tr>
<tr>
<td>CeO$^+$</td>
<td>CASPT2</td>
<td>1.776</td>
<td>8.54</td>
<td>888</td>
<td>5.6</td>
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<tr>
<td></td>
<td>SO-CASPT2</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>DFT/B3LYP</td>
<td>1.767/1.759f</td>
<td>8.80 ± 0.16h</td>
<td>906/912c</td>
<td>4.90q</td>
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<tr>
<td></td>
<td>Expt.</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Equilibrium bond distances ($R_e$) in Å, dissociation energy ($D_e$) in eV, and harmonic vibrational constants ($\omega_i$) in cm$^{-1}$. First ionization energy (IE) for Ce and CeO is in eV. Previous calculations along with available experimental data are also listed. This work unless otherwise indicated.

a Ref. [33].
b Ref. [31].
c Ref. [34].
d Ref. [35].
e Ref. [36].
f Ref. [37].
g Ref. [32].
h Ref. [38].
i Ref. [2].
j Ref. [39].
k Ref. [40].
l Ref. [41].
m Ref. [42], taking $w_xs_a = 2.5$ cm$^{-1}$.
n Ref. [43], from measurements in an argon matrix.
o Ref. [44].
p Ref. [45].
q Ref. [46].

Calculations, CeO$_2$ has a $^1A_1$ electronic ground state. The CASPT2 computed harmonic vibrational wave-numbers for the ground state of CeO$_2$ are 102, 784, and 822 cm$^{-1}$. The 102 cm$^{-1}$ value corresponds to the deformation mode ($\nu_2$), and the latter two values correspond to the antisymmetric ($\nu_3$) and symmetric stretching ($\nu_1$) modes involving the Ce–O bonds, respectively. The DFT frequencies are 59($\nu_2$), 790($\nu_3$), and 794($\nu_1$) cm$^{-1}$, in relatively good agreement with the CASPT2 frequencies. Neutral CeO$_2$ has been observed in argon matrices and fundamental absorptions have been measured at 737 cm$^{-1}$, the $\nu_3$ stretch and 757 cm$^{-1}$, the $\nu_1$ stretch [43].
TABLE III
Spin-free vertical excitation energies (cm$^{-1}$) for CeO and the electronic configuration for each spin-free state.

<table>
<thead>
<tr>
<th>State</th>
<th>Composition</th>
<th>$E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Phi$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>0</td>
</tr>
<tr>
<td>$^1\Phi$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>340</td>
</tr>
<tr>
<td>$^3\Delta$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>1,092</td>
</tr>
<tr>
<td>$^1\Delta$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>1,546</td>
</tr>
<tr>
<td>$^3\Sigma$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>1,872</td>
</tr>
<tr>
<td>$^3\Pi$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>1,926</td>
</tr>
<tr>
<td>$^1\Pi$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>2,754</td>
</tr>
<tr>
<td>$^1\Sigma$</td>
<td>(6s)$^1$(4f$^6$)$^1$</td>
<td>2,869</td>
</tr>
</tbody>
</table>

The computed energies are evaluated at the equilibrium bond distance (1.821 Å).

CeO$_2^+$ is formed by removal of an electron from one of the bonding orbitals with concomitant relaxation of the O–Ce–O angle to 180° and shortening of the cerium-oxygen bond length to 1.765 Å (CASPT2) and 1.758 Å (DFT/B3LYP). Quasirelativistic DFT and ACPF calculations [48] give a bond length of CeO$_2^+$ of 1.784 and 1.789 Å, respectively, whereas the bond length computed at the MRCI level of theory is 1.756 Å [48], very close to our values. The ground state of CeO$_2^+$ is a $^2\Sigma^+$ state. The first excited state ($^2\Pi_u$) is computed to be 2.19 eV higher in energy, followed by a $^2\Sigma^+_g$ state (2.64 eV) and $^2\Pi_g$ state (3.08 eV). The CASPT2 harmonic vibrational frequencies for linear CeO$_2^+$ are 141(ν$_2$), 748(ν$_3$), and 780(ν$_5$) cm$^{-1}$, in very good agreement with the DFT/B3LYP frequencies at 165(ν$_2$), 752(ν$_3$), and 772(ν$_5$) cm$^{-1}$. Experimental information on the vibrational wavenumbers of CeO$_2^+$ is not available.

The adiabatic ionization energy (AIE) of CeO$_2$ computed at the CASPT2 and DFT/B3LYP levels of theory is 8.43 and 8.58 eV, respectively, in very good agreement with the DC-CCSD(T) value of 8.50 eV. They are all below the experimentally reported IE(CeO$_2$) of 9.7 ± 0.5 eV as derived in Ref. [2]. Nevertheless, the results are very similar to the adiabatic ionization energies computed at CISD (8.52 eV) and ACPF (8.57 eV) levels of theory published in Ref. [48]. Spin-orbit effects on the AIE have been found to be of minor importance. As far as the dissociation energy of CeO$_2$ is concerned, the calculated CASPT2 $D_e$ values, relative to Ce and O$_2$(X$^3\Sigma^-$), are 9.28 eV (spin-free) and 9.19 eV (spin-orbit). The DC-CCSD value is 9.34 eV, which increases to 9.96 eV upon including the perturbative

TABLE IV
Spin-orbit vertical excitation energies (cm$^{-1}$) for CeO and composition of each spin-state in terms of spin-free states.

<table>
<thead>
<tr>
<th>Ω value</th>
<th>Composition (%)</th>
<th>$\sigma_0^a$ (cm$^{-1}$)</th>
<th>$\sigma_0^b$ (cm$^{-1}$)</th>
<th>$\sigma_0^c$ (cm$^{-1}$)</th>
<th>$\sigma_0^d$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$^3\Phi$(93), $^3\Delta$(6), $^1\Delta$(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$^3\Phi$(53), $^1\Phi$(39), $^3\Delta$(8)</td>
<td>129</td>
<td>80</td>
<td>121</td>
<td>119</td>
</tr>
<tr>
<td>1</td>
<td>$^3\Delta$(84), $^1\Pi$(12), $^1\Pi$(3)</td>
<td>1,212</td>
<td>812</td>
<td>806</td>
<td>913</td>
</tr>
<tr>
<td>2</td>
<td>$^3\Delta$(50), $^1\Delta$(31), $^3\Pi$(19)</td>
<td>1,337</td>
<td>912</td>
<td>911</td>
<td>1,045</td>
</tr>
<tr>
<td>0</td>
<td>$^3\Pi$(56), $^3\Sigma$(44)</td>
<td>1,739</td>
<td>1,679</td>
<td>1,778</td>
<td>1,396</td>
</tr>
<tr>
<td>1</td>
<td>$^3\Sigma$(50), $^3\Pi$(35), $^3\Pi$(15)</td>
<td>1,941</td>
<td>1,870</td>
<td>1,878</td>
<td>1,476</td>
</tr>
<tr>
<td>0</td>
<td>$^3\Pi$(74), $^3\Sigma$(26)</td>
<td>1,994</td>
<td>1,932</td>
<td>1,866</td>
<td>1,715</td>
</tr>
<tr>
<td>4</td>
<td>$^3\Phi$(97), $^3\Pi$(3)</td>
<td>2,233</td>
<td>2,040</td>
<td>2,022</td>
<td>2,139</td>
</tr>
<tr>
<td>3</td>
<td>$^1\Phi$(54), $^3\Phi$(44)</td>
<td>2,406</td>
<td>2,141</td>
<td>2,185</td>
<td>2,286</td>
</tr>
<tr>
<td>3</td>
<td>$^3\Delta$(91), $^1\Phi$(6), $^3\Phi$(3)</td>
<td>3,179</td>
<td>2,617</td>
<td>2,632</td>
<td>2,872</td>
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<tr>
<td>2</td>
<td>$^3\Delta$(43), $^1\Delta$(41), $^3\Pi$(9), $^3\Phi$(3)</td>
<td>3,372</td>
<td>2,772</td>
<td>2,763</td>
<td>3,039</td>
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<td>2</td>
<td>$^3\Pi$(80), $^1\Delta$(10), $^3\Delta$(9)</td>
<td>3,957</td>
<td>3,463</td>
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<td>$^3\Pi$(59), $^3\Sigma$(31), $^3\Delta$(8), $^1\Pi$(1)</td>
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<td>3,642</td>
<td>3,601</td>
<td>3,391</td>
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<td>0</td>
<td>$^3\Sigma$(56), $^3\Pi$(44)</td>
<td>4,068</td>
<td>3,822</td>
<td>4,035</td>
<td>3,476</td>
</tr>
<tr>
<td>1</td>
<td>$^3\Pi$(76), $^3\Sigma$(17), $^3\Delta$(6)</td>
<td>4,571</td>
<td>4,133</td>
<td>4,102</td>
<td>3,605</td>
</tr>
<tr>
<td>0</td>
<td>$^1\Sigma$(74), $^3\Pi$(26)</td>
<td>4,729</td>
<td>4,458</td>
<td>4,263</td>
<td>4,234</td>
</tr>
</tbody>
</table>

$^a$ This work.
$^b$ Experimental values [47].
$^c$ Energies obtained from semi-empirical ligand field calculations [39].
$^d$ Quasirelativistic pseudopotential CI calculations [35].
energy with respect to O\textsubscript{2}(a\textsubscript{1}) electron in a
(DC-CCSD) and 6.77 eV (DC-CCSD(T)). The exper-
mentally derived value is 10.39 and 10.89 eV, re-
spectively. The experimentally derived value is
(10.9 \pm 0.5) eV [2]. The energy to dissociate CeO\textsubscript{2}\textsuperscript{+}
to Ce\textsuperscript{+} and O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsubscript{g}\textsuperscript{−}) is 6.52 eV (spin-free) and 6.28 eV
(spin-orbit), compared to the values of 6.39 eV
(DC-CCSD) and 6.77 eV (DC-CCSD(T)). The experi-
mental value is (5.7 \pm 0.5) eV [46]. The dissociation
energy with respect to O\textsubscript{2}(a\textsubscript{1}) computed at the
CASPT2 level of theory is 7.48 eV which decreases
to 7.24 eV upon including spin-orbit effects. The
experimentally available values with DC-CCSD and
DC-CCSD(T) are 7.52 and 7.83 eV, respectively. The
experimental value is (6.7 \pm 0.5) eV [32, 46]. On
comparison with LaO\textsubscript{2}\textsuperscript{2+}, which has a closed-shell
ground state (\Sigma\textsuperscript{g}\textsuperscript{+}), CeO\textsubscript{2}\textsuperscript{2+}(\Sigma\textsuperscript{g}\textsuperscript{+}) has the additional
electron in a \pi bonding orbital. This results in a
more strongly bound complex whose dissociation
energy D\textsubscript{a}(CeO\textsubscript{2}\textsuperscript{+}) of 6.28 eV is much higher than the
corresponding value D\textsubscript{a}(LaO\textsubscript{2}\textsuperscript{2+}) of 3.99 eV [1]. In
contrast, the additional electron in CeO\textsubscript{2}\textsuperscript{+}(\Phi\textsuperscript{2}) when
compared with LaO\textsubscript{2}\textsuperscript{2+}(\Sigma\textsuperscript{+}) occupies a nonbonding f
orbital, hence their dissociation energies are similar.

### ASSIGNMENT OF THE EXPERIMENTAL
CHEMIELECTRON SPECTRA

On the basis of the experimentally available values
for CeO\textsubscript{2} (D\textsubscript{a}(CeO\textsubscript{2}) = (9.9 \pm 0.5) eV and IE-
(CeO\textsubscript{2}) = (9.7 \pm 0.5) eV [2, 3]), it is not possible to
establish if the chemiionization reaction Ce + O\textsubscript{2} \rightarrow
CeO\textsubscript{2}\textsuperscript{+} + e\textsuperscript{−} is exothermic. However, the CASPT2 results
(D\textsubscript{a}(CeO\textsubscript{2}) = 9.19 eV and IE(CeO\textsubscript{2}) = 8.43 eV)
clearly indicate that this chemiionization reaction is exothermic. Similarly, D\textsubscript{a}(CeO) > IE(CeO)
from both experiment and theory, indicating that the
Ce + O \rightarrow CeO\textsuperscript{+} + e\textsuperscript{−} reaction is also exothermic (see Table I). However, the computed enthalpy
for the Ce + O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{−}) \rightarrow CeO\textsubscript{2}\textsuperscript{+} + e\textsuperscript{−} reaction is
= 0.76 eV (the corresponding experimental value is
−0.2 \pm 1.0 eV), which does not fit the high kinetic energy
offset of (2.4 \pm 0.1) eV measured under the
Ce + O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{−}) reaction conditions. Under these
conditions the observed chemielectron band is too
high in electron kinetic energy to be attributed to Ce
+ O\textsubscript{2} \rightarrow CeO\textsubscript{2}\textsuperscript{+} + e\textsuperscript{−}, although the low kinetic
energy part will have a contribution from this reaction.
Hence, the original assignment of the chemi-
electron bands in Refs. (2) and (3) for the Ce +
O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{−}) and Ce + O\textsubscript{2}(a\textsubscript{1}\Delta\textsubscript{g}) reaction conditions to
reaction (1) for O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{−}), and the corresponding
reaction for O\textsubscript{2}(a\textsubscript{1}\Delta\textsubscript{g}), respectively, cannot be
Correct. Instead, as in the La case (see Ref. [1]), it is
likely that the following reactions take place under the
Ce + O\textsubscript{2}(X\textsuperscript{3}\Sigma\textsuperscript{g}\textsuperscript{−}) reaction conditions

\[
\text{Ce} + \text{O}_2(X^3\Sigma_g^-) \rightarrow \text{CeO} + \text{O}(^3\Pi) (5), \Delta H = -2.47 \text{ eV}
\]

then

\[
\text{Ce} + \text{O}(^3\Pi) \rightarrow \text{CeO}^+ + e^- (6), \Delta H = -2.45 \text{ eV}
\]
the chemiellectron band observed under the Ce/O(3P) reaction. Therefore, it appears that the Ce + O reaction is contributing to the Ce + O(3P) experimental band and significantly affecting the shape of the high kinetic energy side. Unfortunately, the experimental values for the chemiellectron band from Ce + O(3P) (MPKE = (0.13 ± 0.06) eV and HKEO = (0.90 ± 0.1) eV) differ significantly from the Ce + O(3P) values. However, the signal-to-noise obtained for the Ce + O reaction conditions is much lower than that obtained from the Ce + O(3P) reaction conditions (and from the Ce + O(3P) reaction conditions), and it is clear now that these Ce + O spectra are not good enough to be taken as representative of the Ce + O → CeO(e) + e− chemionization reaction.

For the Ce + O(3P) reaction, as for the La + O(3P) reaction, a more intense chemiellectron band is observed at higher electron kinetic energy than under the Ce + O(3P) reaction conditions. It has a MPKE value of (1.83 ± 0.10) eV and a HKEO value of (3.1 ± 0.3) eV. The chemionization reaction Ce + O2(a1Δg) → CeO2+ + e− is exothermic with a computed reaction enthalpy of −1.72 eV obtained from CASPT2 calculations. The only possible explanation for the significantly higher HKEO value when compared with the calculated enthalpy of the Ce + O2(a1Δg) → CeO2+ + e− reaction, is that reaction (5)

### TABLE VII
Spectroscopic constants for the ground state of CeO2 and CeO2+.  

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>R_e</th>
<th>∠(O−Ce−O)</th>
<th>O2(X3Σ_g−) D_e</th>
<th>O2(a1Δg) D_e</th>
<th>ω_e</th>
<th>IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO2</td>
<td>CASPT2</td>
<td>1.816</td>
<td>126</td>
<td>9.28</td>
<td>10.24</td>
<td>102(v2), 784(v3), 822(v1)</td>
<td>8.43</td>
</tr>
<tr>
<td>CeO2</td>
<td>CASPT2-SO</td>
<td>1.816</td>
<td>126</td>
<td>9.19</td>
<td>10.15</td>
<td>8.15</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DC-CCSD</td>
<td>1.816</td>
<td>126</td>
<td>9.34</td>
<td>10.39</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DC-CCSD(T)</td>
<td>1.816</td>
<td>126</td>
<td>9.96</td>
<td>10.89</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DFT/B3LYP</td>
<td>1.822</td>
<td>140</td>
<td>59(v2), 790(v3), 794(v1)</td>
<td>8.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>Expt.</td>
<td>1.88a</td>
<td>146 ± 2a</td>
<td>10.07 ± 0.65b</td>
<td>264(v2), 737(v3), 757(v1)a,e</td>
<td>9.7 ± 0.5b,d</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td></td>
<td>9.81 ± 0.22c</td>
<td>9.9 ± 0.5d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td></td>
<td>9.1 ± 0.3f</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>CASPT2</td>
<td>1.765</td>
<td>180</td>
<td>6.52</td>
<td>7.48</td>
<td>141(v2), 748(v1), 780(v3)</td>
<td>9.1</td>
</tr>
<tr>
<td>CeO2</td>
<td>Linear</td>
<td>1.765</td>
<td>180</td>
<td>6.28</td>
<td>7.24</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DC-CCSD</td>
<td>1.765</td>
<td>180</td>
<td>6.39</td>
<td>7.52</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DC-CCSD(T)</td>
<td>1.765</td>
<td>180</td>
<td>6.77</td>
<td>7.83</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>DFT/B3LYP</td>
<td>1.758</td>
<td>180</td>
<td>165(v2), 752(v1), 772(v3)</td>
<td>9.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>Expt.</td>
<td>5.7 ± 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equilibrium bond distance (R_e) in Å, angles in (deg), dissociation energy (D_e) and ionization energy (IE) in eV, and harmonic vibrational constant (ω_e) in cm⁻¹. The dissociation energies of CeO2 and CeO2+ are given with respect to Ce + O2 and Ce+ + O2, respectively. The available experimental data are also listed.

This work unless otherwise indicated.

The equation numbering follows that in Table I, and the ΔH values are the computed values in this work, also shown in Table I.

### CHEMIIONIZATION REACTIONS Ce + O AND Ce + O2

- a Ref. [50].
- b Ref. [51].
- c Ref. [52].
- d Ref. [2].
- * Ref. [43].
- f Ref. [41].
- g Ref. [53].
- h Ref. [46].
- i Ref. [48].

(The equation numbering follows that in Table I, and the ΔH values are the computed values in this work, also shown in Table I.)
Ce + O_2(a^1\Delta_g) \rightarrow CeO + O(^1D, ^3P) \ (5), \ \Delta H = -3.43 \ eV

is again followed by

Ce + O(^1D) \rightarrow CeO^+ + e^- \ \ 
\text{(6),} \ \ \Delta H = -4.38 \ eV

Again as in the La case, for the HKEO value from the Ce + O_2(a^1\Delta_g) reaction conditions to be higher than for the Ce + O_2(X^3\Sigma_g^-) reaction conditions, some of the excess energy from reaction (5) must be available for reaction (6). It is proposed that, as in the La + O_2(a^1\Delta_g) case, this is achieved by O(^1D) production. O(^1D) is known to be long-lived with respect to the O(^3P) ground state. The reaction enthalpy of -4.38 eV of reaction (6) compares with the observed HKEO value of (3.1 \pm 0.30) eV implying that the chemielectron onset has not been observed because of unfavorable Franck-Condon factors in the band onset region.

Hence, the results from our calculations indicate the same overall interpretation of the chemionization reactions as we put forward for the La case. The potentials of the CeO* curve and the CeO^+ curve at the CeO* classical turning point.

A number of excited states of CeO and CeO^+ were investigated to understand the chemionization mechanisms of the Ce + O \rightarrow CeO^+ + e^- reaction. Singlets, triplets, and quintets have been computed for CeO, and doublets and quartets have been computed for CeO^+. As discussed above, CeO and CeO^+ have many low-lying excited states of the \Sigma, \Pi, \Delta, \Phi types. For CeO, 24 singlets, 20 triplets and 2 quintets were computed for each of the above irreducible representations and were included in the spin-orbit calculations. So, many states had to be included because of the need to describe the chemionization region occurring at about 6.5 eV above the CeO ground state. The potential energy curves of the ground states of CeO and CeO^+ are shown in Figure 1, and an enlarged region of this figure of particular interest (the region where the chemionization occurs) is given in Figure 2. The reactants Ce and O approach each other (the horizontal lines shown for the Ce and O(^3P) reagents (solid line) and the Ce and O(^1D) reagents (dotted line)) until the left-hand turning point of a CeO^+ curve is reached. Autoionization then occurs in accordance with the Franck-Condon principle and the most intense transition from the left-hand turning point of the CeO^+ curve is the vertical transition onto the CeO^+ ground state curve where the overlap of the initial and final vibrational wavefunctions is largest. Thus, the maximum intensity of the chemielectron band will occur at an energy corresponding to the vertical energy difference between the CeO^+ curve and the CeO^+ curve at the CeO^+ classical turning point. From spin conservation, reaction between Ce(^1G) + O(^1D) can only give singlet CeO^+ excited states for chemionization, whereas Ce(^1G) and O(^3P) can give rise to triplet CeO^+ states. The autoionization process CeO^+ \rightarrow CeO^+(2\Phi) + e^- is a spin-allowed process if \Delta S between the initial (CeO excited state) and final (ion plus electron) state is zero. Moreover, the \Delta \Omega = 0 selection rule has to be fulfilled between the initial and the final state.

For the Ce + O(^3P) chemiionization reaction, the horizontal (solid) line from the reactants crosses CeO^+ states at internuclear distances at about 1.62

\text{2\Phi state, is 888 \ cm}^{-1} \text{and the separation between the vibrational levels of CeO^+ must be reduced to (790 \pm 30) \ cm}^{-1} \text{by anharmonicity in the region of the chemiclelectron band maximum.}
Å. These are quintet states of CeO located about 1.66 eV vertically above the CeO$^+$ ground state. However, the autoionization process $^5$CeO$^+$ → CeO$^+_0(2^3\Phi)$ + e$^-$ is spin-forbidden as the $\Delta S = 0$ selection rule is not satisfied. The first triplet CeO$^+$ state that fulfills both selection rules is encountered at about 1.52 Å and is located ca. 0.93 eV above the CeO$^+$ ground state, in excellent agreement with the experimental MPKE value of (0.90 ± 0.04) eV. For the Ce + O(1D) chemiionization reaction, the horizontal (dotted) Ce + O(1D) line crosses singlet CeO excited states at internuclear distances at ca. 1.47 Å and at this distance the CeO$^+$ state is located 1.47 eV vertically above the CeO$^+$ ground state. The computed chemielectron band of 1.47 eV is in a reasonable agreement with the experimental MPKE value of 1.83 ± 0.10 eV (HKEO value (3.1 ± 0.3) eV). It is important to note that, in agreement with the experimental observations, the chemielectron band maximum for Ce + O(1D) → CeO$^+$ + e$^-$ is higher than that for Ce + O(3P) → CeO$^+$ + e$^-$. The chemiionization reaction Ce + O$_2$(a$^1\Sigma_g^+$) → CeO$_2$(X$^2\Sigma_g^+$) + e$^-$ is calculated to have a reaction enthalpy of −1.72 eV (see Table I). This must therefore be contributing to the low kinetic energy side of the band observed with a maximum (MPKE) value of 1.83 ± 0.10 eV.

Finally, the calculations show that the reaction Ce(1G) + O$_2$(X$^3\Sigma_g^+$) → CeO(X$^2\Phi$) + O is sufficiently exothermic to produce O(3P) and O(1D), with O(3P) being the dominant product. Chemiionization occurs via Ce(1G) + O(3P) → CeO$^+_0(2^3\Phi)$ + e$^-$ to give a chemielectron band with a MPKE value of 0.90 ± 0.04 eV. In contrast, Ce(1G) + O$_2$(a$^1\Delta_g$) → CeO(X$^2\Phi$) + O produces a significant amount of O(1D) as indicated by the higher energy chemielectron band from the reaction Ce(1G) + O(1D) → CeO(X$^2\Phi$) + e$^-$, with an experimental MPKE value of 1.83 ± 0.10 eV.

**Conclusions**

Multiconfigurational quantum chemical methods (CASSCF/CASPT2) have been used to establish the chemiionization reactions that occur for the Ce + O(3P), Ce + O$_2$(X$^3\Sigma_g^-$), and Ce + O$_2$(a$^1\Delta_g$) reaction conditions. As was found for the U + O$_2$ reaction [54] and the La + O$_2$ reaction [1], chemiioniza-
tion for Ce + O₂(X³Σ⁻) occurs predominantly via a two-step process, a rapid first step Ce + O₂ → CeO + O(³P) (reaction (5)) followed by Ce + O(³P) → CeO⁺ + e⁻ (reaction (6)). For Ce + O₂(a¹Δg), chemiionization occurs via the same two-step mechanism. In this case, the experimental chemielectron spectra can be explained by production of O(1D) from reaction (5) followed by formation of chemielectrons via CeO⁺ + e⁻. For all reaction conditions studied, the primary chemiionization reaction is Ce + O → CeO⁺ + e⁻. However, in contrast to the La case, the reaction Ce + O₂ → CeO₂ + e⁻ is exothermic for both O₂(X³Σ⁻) and O₂(a¹Δg), and therefore contributes in the lower kinetic energy regions of the chemielectron spectra recorded for the Ce + O → CeO⁺ + e⁻ reactions considered provide strong support for the chemiionization mechanisms proposed.

ACKNOWLEDGMENT

The theoretical chemiionization project started during the stay of L. G. in the laboratory of Professor Kimihiko Hirao in 2003. The authors thus dedicate this article to their friend, Kimihiko who has been very inspiring and encouraging in this research.

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