The gas-phase chemiionization reaction between samarium and oxygen atoms: A theoretical study

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The Sm+O chemiionization reaction has been investigated theoretically using a method that allows for correlation and relativistic effects. Potential energy curves have been calculated for several electronic states of SmO and SmO$^+$. Comparison with available spectroscopic and thermodynamic values for these species is reported and a mechanism for the chemiionization reaction Sm+O is proposed. The importance of spin–orbit coupling in the excited states of SmO, in allowing this chemiionization reaction to take place, has been revealed by these calculations. This paper shows the metal-plus-oxidant chemiionization reaction. © *2004 American Institute of Physics.*
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I. INTRODUCTION

Chemiionization is an intriguing form of ionization in the gas-phase, which can occur between ground state reagents. It has been observed to occur in metal-plus-oxidant reactions and hydrocarbon–oxygen reactions in flames.[1–4] The simplest case is the reaction between a metal, M, and an oxygen atom, O, to give MO$^+$ plus an electron. The reaction is exothermic, and can therefore be observed experimentally, if the dissociation energy of the metal oxide produced is greater than the adiabatic ionization energy of the neutral metal oxide. Unfortunately, although qualitative potential energy curves can be drawn to explain the production of ions and electrons for an M+O chemiionizatiion reaction,[5–7] no electronic structure calculations have yet been made for the states involved for any M+O reactions studied experimentally. This is almost certainly because most of the metals (M) for which this form of ionization has been observed are lanthanides and actinides, in which the MO and MO$^+$ species are difficult to treat theoretically, not least because the metals have electronic configurations with unfilled f shells and give rise to a number of low-lying states in MO and MO$^+$. Correlation, relativistic and spin–orbit effects must therefore be included.

This situation is in marked contrast with the chemiionization reactions O+CH($X\,^2\Pi$), O+CH($a\,^4\Sigma^-$), O+CH$_3$C($\tilde{X}\,^2A''$), and O+CH$_3$C($\tilde{a}\,^4A_2$), which have been identified in hydrocarbon flames.[1,4] For each reaction, potential energy surfaces for the neutral and ion states involved have been computed (e.g., HCO and HCO$^+$ in the case of O+CH) and the maximum electron kinetic energy for the chemiionization reaction calculated.[8–12] These potential curves have allowed the mechanisms for the observed chemiionization processes to be established and the chemielectron bands to be assigned.

One of the simplest M+O chemiionization reactions for which a chemielectron spectrum has been recorded and the chemiions (MO$^+$) detected is the samarium plus oxygen atom reaction. Metal oxidation chemiionization reactions play important roles in the upper atmosphere, where collisions involving ground and excited metal atoms with oxidants, such as atomic oxygen, are a major source of ions.[13] M+O chemiionization reactions, such as the Sm+O associative ionization reaction, have also been considered as a way of monitoring atomic oxygen in the upper atmosphere.[5–7]

Although lanthanide monoxides (LnO) have been the subject of extensive theoretical and experimental studies, there are no *ab initio* studies on the electronic structures of SmO and SmO$^+$. This is because of the complexity of the electronic structures of these species, in particular the high angular momentum and spin multiplicity of the low-lying states involved. These in turn derive from the low-lying electronic states of the samarium atom, which have partially filled $4f$ and $5d$ shells. Therefore a large number of molecular electronic states that are close in energy result, and these are further split and mixed by spin–orbit interaction. Hence, accurate calculations on SmO and SmO$^+$ require incorporation of both relativistic and correlation effects to obtain reliable results.

This work calculates potential energy curves of SmO

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and SmO^+, with the treatment of correlation, relativistic effects and spin–orbit coupling, to allow a comparison with available spectroscopic and thermodynamic values for these species and to allow a mechanism for the observed $Sm+O$ chemiionization to be proposed. This work represents the first theoretical attempt to study the energetics and mechanism of a metal-plus-oxidant chemiionization reaction.

II. COMPUTATIONAL DETAILS

The study was performed using the complete active space (CAS) SCF method[14] with dynamic electron correlation added using multiconfigurational second order perturbation theory (CASPT2).[15–17] Scalar relativistic effects were included via Douglas–Kroll (DK) Hamiltonian.[18,19] The effects of spin–orbit (SO) coupling were calculated by using a newly developed method based on the CASSCF state interaction method (CASSI).[20,21] Here, the CASSCF wave functions generated for a range of electronic states are allowed to mix under the influence of a spin–orbit Hamiltonian. The method has recently been described;[22] see that article for details. It has been shown to be successful in the study of actinide compounds.[23,24] All calculations were performed with a prerelease of the software MOLCAS 6.0.[25]

A newly developed basis set of the ANO type was used for the Sm atom.[26] The exponents were optimized, including scalar relativistic effects, through the use of the Douglas–Kroll Hamiltonian.[18,19] A primitive set of $25s22p15d11f4g$ functions[27] was contracted to $9s8p6d4f2g$. For the O atom the ANO-L basis set[28] of the MOLCAS library was used. A primitive set of $14s9p4d3f$ basis functions was contracted to $7s7p4d3f$.

In the CASSCF treatment, the [Kr] $4d$, $5s$, $5p$ orbitals of Sm and $1s$, $2s$ of O were kept doubly occupied. In total, 12 electrons were distributed over 13 active orbitals, i.e., $4f$ of Sm and $2p$, $3p$ of O. In the subsequent MS-CASPT2 method, [Kr] $4d$, $5s$, $5p$ orbitals of Sm and $1s$, $2s$ of O were frozen.

The potential energy curves for several electronic states of SmO and SmO^+ were calculated at the CASPT2 level. Spectroscopic constants for the ground state of SmO and SmO^+ were determined by using the program VIBROT, available in the MOLCAS 6.0 package. VIBROT fits the potential to an analytical form using cubic splines and computes the vibration and rotation constants for a diatomic molecule.

III. RESULTS

The ground states of SmO and SmO^+ are $^7\Delta$ and $^6\Gamma$, respectively. The computed equilibrium spectroscopic constants (R_e, D_e, ω_e) for the ground states for SmO and SmO^+ are reported in Table I, together with the calculated first ionization energies (IEs) for SmO and Sm. The calculated values of D_e for SmO and SmO^+ are within the quoted errors of the experimental values. Similar satisfactory agreement is obtained for the first IEs of Sm and SmO (see Table I). As mentioned in the Introduction, it is important to obtain reliable values for these D_e's and IE's as a prerequisite to obtaining a reliable quantitative calculation of chemielectron energies. The computed R_e value for SmO ($^7\Delta$) is too low

TABLE I. Spectroscopic constants for the ground state of SmO and SmO^+. Bond length, R_e, in Å and dissociation energy, D_e, in eV. Harmonic constant, ω_e, in cm^{-1}. First ionization energy, IE, (eV) for SmO, and Sm atom. Experimental values are in parentheses.

	R_e	D_e	D_0	ω_e	IE^d
$^7\Delta$ SmO	1.774	5.97	5.92	852	5.58
Expt.	(1.807^a)	(5.95 ± 0.09^b)	(5.90 ± 0.09)	(819^c)	(5.50 ± 0.10^e)
$^6\Gamma$ SmO$^+$	1.7414	5.80	5.74	781	
Expt.			(6.04 ± 0.19)		

[a]Reference 29.
[b]Reference 32.
[c]Reference 33.
[d]IE for Sm in its ground state, ^7F, = 5.69 eV (Expt.= 5.64 eV Ref. 35).
[e]Reference 34.

(by ca. 0.03 Å) and the computed value of ω_e is too high (by ca. 50 cm^{-1}). There are no experimental values available for $SmO^+(^6\Gamma)$.

The ground state electronic configurations of Sm and O atoms are [Xe] $4f^66s^2$, $^7F_0$ and [He] $2s^22p^4$, $^3P_2$, respectively. The electronic states of SmO are of the Σ, Δ, Γ, Π, and Φ types. In C_2 symmetry, the Σ, Δ, and Γ states transform as irreducible representation 1 (irrep 1), while the Π and Φ states transform as irreducible representation 2 (irrep 2). From the above atomic electronic configurations of Sm and O, the following electronic states of SmO will arise in C_2: 11 septets, 11 quintets, and 11 nonets in irrep 1, and 10 septets, 10 quintets, and 10 nonets in irrep 2 (441 components in all). The potential energy curves for all these states have been calculated at the CASPT2 level of theory. In Fig. 1, the most significant spin-free curves of SmO are shown (i.e., the lower potential energy curves that are most relevant to the $Sm+O$ chemiionization process), together with the spin-free potential energy curve for the ground state of SmO^+.

At the equilibrium bond length, the ground state of SmO is $^7\Delta$. The spin-free energy levels of SmO arising from the ground states of the Sm and O atoms lying within an energy range of 4.91 eV above the ground state at the equilibrium Sm–O bond length were allowed to mix under the spin–orbit
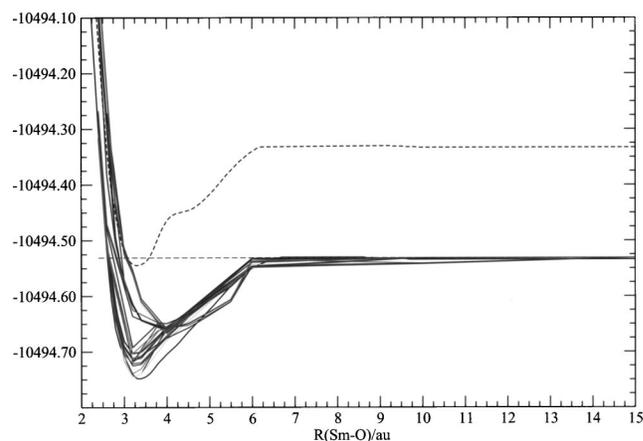
FIG. 1. The spin-free potential energy curves for several states of SmO arising from the ground state of SmO^+ (dotted line). The dotted horizontal line is the energy of Sm and O atoms at dissociation.
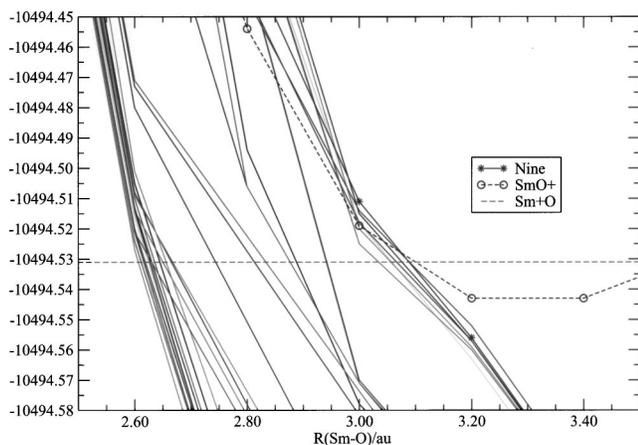
FIG. 2. Enlarged region of the spin-free potential energy curves for several states of SmO and the ground state of SmO^+, in the Sm–O bond length region where the chemiionization occurs (see text). The horizontal potential (dashed) corresponds to Sm+O dissociation limit. The dotted line ($\bigcirc$) is the SmO^+ ground state curve. The potential curve (*) is the SmO $^9\Pi$ state involved in the chemiionization (see text). The curves on the left (crossing the Sm+O dissociation limit in the Sm–O bond length range 2.60 and 2.70 a.u.) are SmO quintet states and the curves on the right (crossing the Sm–O dissociation limit in the Sm–O bond length range 3.05–3.10 a.u.) are SmO nonets.

Hamiltonian, and they give rise to more than 320 spin–orbit states. The first 12 spin–orbit states lie within an energy range of 1500 cm^{-1}. A definite assignment of the Ω value for such states is not possible, because of the small energy differences between the various states, which are far below the accuracy of the present quantum chemical method in determining electronic excitation energies, and the large mixing of the spin-free states. We will thus only compare the computed relative energies of the lowest spin states at the equilibrium bond length with the experimental values.[29–31]

The spin–orbit ground state is doubly degenerate according to our calculation, and thus it cannot be a state with $\Omega = 0$. This is not in agreement with the assignment of Linton *et al.*,[29] who identified the ground state as an $\Omega = 0$ state. Our calculated first excited state lies 202 cm^{-1} above the ground state and it is assigned to the $\Omega = 1$ level at 150 cm^{-1} reported by Linton.[29] We then compute a state at 217 cm^{-1}, which is not seen experimentally. Further states are calculated at 550, 558, and 1013 cm^{-1}, and these are assigned to the 565, 580, and 880 cm^{-1} experimental excitation energies, respectively.

The chemielectron spectrum recorded for an effusive beam of samarium reacted with atomic oxygen shows a band with a maximum at (0.02 ± 0.07) eV electron kinetic energy that decreases in intensity to meet the baseline at (0.28 ± 0.07) eV, the high kinetic energy offset (HKEO).[5,7] SmO^+ ions were observed under the same conditions with a mass spectrometer. In the original paper,[5] the HKEO value, the enthalpy of the reaction, was calculated from available thermodynamic values as (0.4 ± 0.02) eV. The shape of the SmO^+ curve in the bond length range of 4–5 a.u. is presumably due to a change in nature of the electron distribution and an avoided crossing with another state.

Inspection of an expanded section of Fig. 1, shown in Fig. 2, notably the region where the horizontal line from the

Sm+O reactants crosses the SmO^+ potential curve, indicates that this horizontal line first encounters an SmO nonet state at an Sm–O distance of 3.08 a.u. At this bond length, the vibrational wave function at this left-hand turning point overlaps with a SmO^+ potential curve (the SmO^+ $^6\Gamma$ ground state). Autoionization will therefore occur from this SmO left-hand turning point down to vibrational levels of the lowest SmO^+ state, a $^6\Gamma$ state. As the SmO nonet autoionizing state and the SmO^+ $^6\Gamma$ state have essentially the same energy at 3.08 a.u. bond length, the Franck–Condon envelope for the chemielectron band is expected to show a maximum in intensity at zero electron kinetic energy and decrease exponentially to a limit of 0.38 eV, the energy difference between the Sm+O reactants, and the lowest vibrational level of SmO^+ $^6\Gamma$. This is consistent with the experimentally observed chemielectron band, although no intensity is observed at higher electron energies than 0.28 eV because of the poor Franck–Condon factors between the neutral state vibrational wave function at the left-hand turning point and the lower vibrational levels of the lowest SmO^+ state.

The energy levels of SmO have been analyzed at a bond distance of 3.08 a.u., where the chemiionization occurs. At this bond distance, the electronic state of SmO that intersects the asymptotic curve of Sm and O atoms is a $^9\Pi$ state. This state is lowered in energy by 0.027 eV (226 cm^{-1}) by the inclusion of spin–orbit coupling and the total splitting of its spin–orbit manifold is 600 cm^{-1}. Inspection of Fig. 2 shows that the Sm+O reaction coordinate (the horizontal dotted line from the Sm+O reagents) crosses a group of SmO nonet states in the bond length region 3.05–3.10 a.u. The first neutral excited state encountered is a $^9\Pi$ state as described above. At shorter bond lengths, the Sm+O horizontal dotted line crosses SmO quintet states in the bond length region 2.8–3.0 a.u. and excited septet states in the bond length region 2.6–2.8 a.u. It is interesting that the $SmO^*(^9\Pi) \rightarrow SmO^+(^6\Gamma) + e^-$ associative ionization process is spin-forbidden, if MO is a light diatomic where spin–orbit coupling is small, as ΔS must be zero between the initial neutral and final (ion plus free electron) state. However, for the states of SmO and SmO^+ in the left-hand turning point region between 3.05 and 3.10 a.u. bond lengths, spin–orbit coupling is significant and therefore the less restrictive autoionization selection rule $\Delta \Omega = 0$ must be applied between the initial and final (ion plus free electron) states. Spin–orbit coupling in the excited SmO* states therefore allows the above $SmO^*(^9\Pi) \rightarrow SmO^+(^6\Gamma) + e^-$ autoionization to take place, as the $\Delta \Omega = 0$ selection rule is now satisfied.

If the mechanism for the autoionization is considered in a little more detail, for the initial $SmO^*(^9\Pi)$ state, S is equal to 4, and possible values of S in the final state $SmO^+(^6\Gamma) + e^-$ are 3 or 2. Therefore the $\Delta S = 0$ selection rule cannot be satisfied. However, if the Ω values in the initial and final state are considered, the Ω values for the $^9\Pi$ state are 5, 4, 3, 2, 1, 0 and the Ω values for the $^6\Gamma$ (13/2, 11/2, 9/2, 7/2, 5/2, 3/2) plus e^- ($\Omega = 1/2$) final state are (7, 6, 5, 4, 3, 2, 1). Hence it can be seen that the $\Delta \Omega = 0$ selection rule can be satisfied between the Ω values 5, 4, 3, 2, 1 in the $^9\Pi$ state and the final state. It should also be noted that for both the $SmO^*(^9\Pi)$ and $SmO^+(^6\Gamma)$ states, each Ω component is

mixed with other components of the same Ω value arising from other neutral and ionic states.

IV. CONCLUSIONS

In conclusion, this study is the first theoretical investigation of a metal-plus-oxidant chemiionization reaction. A variety of these reactions involving lanthanides and actinides have been studied experimentally in the gas phase,[5–7] but this is the first time that one of these reactions has been investigated with quantum chemical methods. The mechanism of the Sm+O chemiionization reaction has been established from the computed potential curves of SmO and SmO$^+$ and the states involved have been identified. The position and shape of the experimental chemielectron band has also been explained on the basis of these potential curves, and the important role of spin–orbit coupling in the nonet excited state of SmO, in allowing the chemiionization to take place, has been revealed. It is proposed to extend these studies to other metal-plus-oxidant chemiionization reactions.

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