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Citation: The Journal of Chemical Physics **147**, 234311 (2017); View online: https://doi.org/10.1063/1.5008423 View Table of Contents: http://aip.scitation.org/toc/jcp/147/23 Published by the American Institute of Physics

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Electronic structure of SmO and SmO⁻ via slow photoelectron velocity-map imaging spectroscopy and spin-orbit CASPT2 calculations

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(Received 5 October 2017; accepted 29 November 2017; published online 21 December 2017)

The chemi-ionization reaction of atomic samarium, $\text{Sm} + \text{O} \rightarrow \text{SmO}^+ + e^-$, has been investigated by the Air Force Research Laboratory as a means to modify local electron density in the ionosphere for reduction of scintillation of high-frequency radio waves. Neutral SmO is a likely unwanted byproduct. The spectroscopy of SmO is of great interest to aid in interpretation of optical emission spectra recorded following atmospheric releases of Sm as part of the Metal Oxide Space Cloud (MOSC) observations. Here, we report a joint experimental and theoretical study of SmO using slow photoelectron velocity-map imaging spectroscopy of cryogenically cooled SmO⁻ anions (cryo-SEVI) and high-level spin-orbit complete active space calculations with corrections from second order perturbation theory (CASPT2). With cryo-SEVI, we measure the electron affinity of SmO to be 1.0581(11) eV and report electronic and vibrational structure of low-lying electronic states of SmO in good agreement with theory and prior experimental work. We also obtain spectra of higher-lying excited states of SmO for direct comparison to the MOSC results. *Published by AIP Publishing*. https://doi.org/10.1063/1.5008423

I. INTRODUCTION

The ionization energies of many of the lanthanide oxides (LnO) are smaller than their bond strengths. This results in the unusual situation of dissociative recombination of the cations with electrons,

$$LnO^{+} + e^{-} \rightarrow Ln + O \tag{1}$$

being endothermic.¹ Therefore, lanthanide oxide cations of this type should be long-lived in a weakly ionized plasma, a property generally only pertinent for atomic cations for which recombination must be slowly stabilized by radiative decay as opposed to the rapid dissociative stabilization² available to most polyatomics.

Recently, the Air Force Research Laboratory has sought to exploit this energetic quirk to create regions of elevated electron density in the E-region of the ionosphere by releasing small amounts of lanthanide metals from sounding rockets. These experiments were originally carried out with samarium (Sm) due to its high vapor pressure and ease of atomization. The atomic metal can associatively ionize (chemi-ionize) with ambient atomic O to yield the metal oxide cation and an electron, i.e., the reverse of Eq. (1). Regions of artificial ionosphere above the ambient density reduce inhomogeneities in the opacity of the ionosphere to radio waves (i.e., scintillation effects) resulting in more predictable radio wave propagation.³ One of these releases, the Metal Oxide Space Cloud (MOSC) experiment, is the subject of a recent special issue of the journal *Radio Science.*^{4–8}

Unlike some prior efforts, the two samarium releases comprising MOSC were characterized spectroscopically, with temporally resolved emission spectra recorded over a range of 400-800 nm. At dusk on the ground, the high-altitude cloud was illuminated by remaining sunlight. Thus, the clouds provided a brilliant display across the visible against the night sky. Both red and blue features were apparent, slowly separating from each other. This drifting was attributed to disparate effects of the wind and the magnetic field on neutral and charged species, although deconvoluting those factors was unexpectedly difficult. The time evolution of different spectral features should indicate the competition between the desired sustained SmO⁺ density and electron scavenging processes resulting in SmO or other neutral species. The information in the spectral data can then support or refute an updated analysis of the Sm system based on laboratory data correcting some of the literature energetics, offering a possible explanation for lower than expected electron densities observed in MOSC.^{9,10} Unfortunately, the existing spectral analysis⁴ was hampered by a lack of information on the emission spectra of the diatomic species SmO and SmO⁺, relying instead on

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inferences drawn from the well-detailed atomic spectra of Sm and Sm⁺.

In principle, if the excited state energies of the diatomic species as well as the transition probabilities between those states are known, the emission spectra can be predicted from the known distribution of sunlight at the altitude of the release, but this is a daunting task. Some information on the spectral structure of SmO is known from prior experimental and theoretical work. Linton and co-workers reported detailed energetics and state assignments for twelve low-lying states of SmO derived via high-resolution fluorescence measurements from excited states at term energies near 2 eV.11-13 Willson and Andrews¹⁴ reported infrared spectra of SmO^{0/-} in an argon matrix. Kafader et al.¹⁵ measured the anion photoelectron spectrum of SmO-, reporting an electron affinity (EA) of 1.067(6) eV and a dense manifold of overlapping low-lying electronic states of SmO, as well as a continuum of higher-lying excited states spanning term energies of 1-2 eV. On the theoretical front, early work used ligand field theory to predict the complex electronic structure of lanthanum monoxides.^{16–18} More recently, Paulovič et al. calculated the potential energy curves of SmO at the CASPT2 level, identifying several hundred spin-orbit (SO) states arising from the ground septet states alone.¹⁹

Here we seek to improve on previous work via a joint experimental and theoretical investigation of the spectroscopy and electronic structure of SmO, using slow photoelectron velocity-map imaging (VMI) spectroscopy of cryogenically cooled SmO⁻ anions (cryo-SEVI), a high-resolution variant of anion photoelectron spectroscopy, alongside high-level spinorbit (SO) complete active space calculations with corrections from second order perturbation theory (CASPT2). The inherent high resolution of the SEVI technique in combination with the spectral clarity afforded by cold ions reveals detailed spectral information. We obtain an accurate electron affinity for SmO along with term energies and vibrational fundamental frequencies of several low-lying electronic states. We also observe higher-lying excited states which can be compared directly to emission spectra from the MOSC experiments. The experimental results are interpreted with the aid of the SO-CASPT2 calculations, and, complementarily, the experimental work is used to validate our choice of theoretical methods.

II. EXPERIMENTAL METHODS

The cryo-SEVI method and instrument have been described in detail elsewhere.^{20–22} In this study, SmO⁻ anions are prepared in a laser ablation source operating at 20 Hz, wherein a 2-10 mJ pulse of 532 nm light from a frequency doubled Nd:YAG laser is focused onto a pure samarium ablation target. A burst of He carrier gas from an Even-Lavie valve²³ quenches and entrains the resulting plasma. Trace oxygen in the buffer gas and on the surface of the ablation target allows the desired SmO⁻ anions to form.

The ions then pass through a radiofrequency (RF) hexapole and quadrupole mass filter (QMF) *en route* to a cryogenic linear octopole ion trap held at 5 K. The QMF is tuned to ensure that only the desired 154 Sm 16 O⁻ ions enter the trap; the 154 Sm isotope is chosen because it is both reasonably intense

in the mass spectrum and well separated from its neighboring isotopes. The ions are held within the cryogenic trap for 40 ms, with the aim of cooling them to their ground vibrational and electronic states by collisions with a cold 80:20 He:H₂ buffer gas mixture. Molecular ion temperatures of as low as 10 K have been measured at the time of photodetachment, after extraction from the trap.²²

The ions are extracted from the trap into an orthogonal Wiley-McLaren time-of-flight mass spectrometer. They are steered and focused into the laser interaction region inside the velocity-map imaging (VMI) spectrometer and photode-tached either with the fundamental of a Nd:YAG laser or with the output of an Nd:YAG-pumped tunable dye laser. The nascent photoelectrons are focused with the VMI electrostatic lens^{24,25} onto a position-sensitive detector consisting of two chevron-stacked microchannel plates and a phosphor screen.²⁶ Photoelectron events on the screen are captured with a CCD camera, and their centroids are computed and binned in real time during data acquisition.²⁷ A single VMI image is obtained at a fixed photodetachment wavelength by accumulating electron centroids over several thousand experimental cycles.

The radial and angular photoelectron distributions are reconstructed from an accumulated image using the maximum-entropy velocity Legendre reconstruction method.²⁸ The electron kinetic energy (eKE) scale is calibrated as a function of radial displacement from the center of the image using SEVI images of well-known photodetachment transitions of atomic O⁻ and F⁻.^{29,30} As the eKE changes with the photodetachment laser energy hv, we report SEVI spectra in electron binding energy (eBE), using the relation eBE = hv - eKE.

Because VMI spectrometers have a relatively constant Δ eKE/eKE resolving power, they yield the best absolute Δ eKE energy resolution at low eKE. As discussed previously,^{21,25} we therefore make measurements at discrete photodetachment energies across the eBE range over which signal is observed, yielding a set of energy windows within which each feature is obtained at low eKE and hence high resolution. These high-resolution windows are then stitched together to create a composite SEVI spectrum. The intensity of each section of the composite spectrum is scaled to match its intensity in an overview spectrum acquired at a photon energy well above the band of interest, in order to minimize any threshold effects that may distort relative peak intensities at low eKE.

III. COMPUTATIONAL METHODS

Complete active space self-consistent field calculations with corrections from second order perturbation theory (CASSCF/CASPT2) were performed for neutral and anionic SmO^{0/-}.^{31–33} All calculations were performed using the Molcas 8.0 software package (service pack 1).³⁴ The linear keyword was used to limit some degrees of freedom in the orbital rotations. Real abelian subgroups of $C_{\infty\nu}$ were used in the calculations. $C_{2\nu}$ symmetry was imposed for the dissociation curves and C_2 symmetry was imposed for calculations at a fixed bond distance. Scalar relativistic effects were treated through the use of the Douglas-Kroll-Hess (DKH) Hamiltonian.^{35,36}



FIG. 1. The natural state-averaged orbitals for the (12e/13e, 14o) active space used in this work. In the ground state of neutral SmO, the 6s orbital is singly occupied while in the anion, it is doubly occupied.

The active space molecular orbitals used in this work are shown in Fig. 1. The active space included the nonbonding 6s and 4f orbitals on the Sm atom and the six σ and π orbitals that are linear combinations of the Sm 5d and O 2p orbitals, resulting in a (12e,14o) active space for the neutral and a (13e,14o) active space for the anion. Note that the remaining two 5d orbitals not included in the active space are sufficiently high in energy. The orbitals were state-averaged within each irreducible representation.

Dissociation curves were computed ranging from 1.3 to 2.4 Å using an ANO-RCC basis set of triple- ζ quality with the following contractions: (8*s*,7*p*,5*d*,3*f*,2*g*,1*h*) for samarium and (4*s*,3*p*,2*d*,1*f*) for oxygen.^{37,38} Five states were computed with *A*₁, *B*₁, and *B*₂ symmetry while three states were computed for *A*₂. The same number of states was included for the calculations of the quintet, septet, and nonet spin-free states of neutral SmO as well as for the sextet spin-free state of anionic SmO⁻.

Additional calculations were performed for SmO with a bond distance of 1.80 Å and for the anion with a bond distance of 1.85 Å. ANO-RCC basis sets of quadruple- ζ quality were employed with the following contractions: (9*s*,8*p*,6*d*,4*f*,3*g*,2*h*) for samarium and (5*s*,4*p*,3*d*,2*f*,1*g*) for oxygen. Eight states of symmetry *A* were computed and ten states of symmetry *B* for the spin-free states (in total, 18 quartets, 18 septets, and 18 nonets for neutral SmO and 18 quartets, 18 sextets, and 18 octets for the anion).

Spin-orbit coupling effects were computed for the neutral complex *a posteriori* using the state interaction approach (RASSI).³⁹ The diagonal elements of this effective Hamiltonian were replaced with the CASPT2 energies in the so-called SO-CASPT2 approach.

IV. RESULTS

A. Electronic structure of SmO and SmO⁻

For SmO, septet states lie lowest in energy, with quintet states slightly higher in energy and nonet states considerably higher-lying. The lowest-energy spin-free CASPT2 SmO septet states have doubly occupied σ and π bonding orbitals (occupation numbers of 1.96) and a singly occupied 6*s* orbital. The remaining unpaired electrons are distributed among the 4*f* orbitals (see Fig. 1). The literature is in agreement regarding the preferred septet spin state and 4*f*⁵6*s*¹ configuration of SmO.^{11–13,15,17–19,40} Higher-lying states involve excitations

TABLE I. Theoretical SO-CASPT2 and experimental cryo-SEVI energies of low-lying states of neutral SmO from this work, compared to state assignments and experimental fluorescence measurements from the work of Linton and co-workers.¹³ Relative energies are given in cm⁻¹ with respect to the ground state of neutral SmO (peak A1). Septet, quintet, and nonet spin-free states were included when computing the SO-CASPT2 states. The SO-CASPT2 results are generally paired with experimental states based on energies and the selection rules of Jarrold and co-workers.¹⁵ SO-CASPT2 states that are singly degenerate appear in bold and are paired with states labeled $\Omega = 0$ in the work of Bujin and Linton.¹³

SO-CASPT2	State label ¹³	Cryo-SEVI		Fluorescence ¹³
0	X(0 ⁻)	A1	0	0
128	(1)1	B1	148	147
502	(1)2			567
702	(2)0+	C1	573	582
876	(2)1	D1	879	879
1156		E1	1150	
1405	(1)3			1280
1540	(3)0-			1546
1718	(2)2			1604
1794	(3)1	F1	1656	1661
1950	(4)1	G1	2014	2014
2108	(3)2			2240
2268	(1)4			2287

out of the σ bonding orbitals and eventually the π bonding orbitals. For SmO⁻, sextet states lie considerably lower in energy than the quartet and octet states. The electronic structure of the SmO⁻ sextet states is similar to that of the neutral septets, albeit with a doubly occupied 6*s* orbital. Anionic configurations differing from the neutral in the occupation of the 6*s* orbital have also been predicted in the literature.^{15,40}

Because of the near degeneracy of the 4*f* orbitals, spinorbit coupling is known to be important in SmO^{0/-}. Therefore, the spin-free states were allowed to mix using the RASSI approach. The energies of the spin-free CASPT2 states are given in Table S1 of the supplementary material for SmO and Table S2 of the supplementary material for SmO⁻. Dissociation curves for relevant SmO^{0/-} states are plotted in Fig. S1 of the supplementary material. The resulting SO-CASPT2 states are given in the leftmost column of Table I for SmO and in Table II for SmO⁻. The nine lowest-lying spin-orbit states of neutral SmO can be thought of as linear combinations of several spin-free septet states. Only by the

TABLE II. Theoretical SO-CASPT2 energies (cm^{-1}) of low-lying states of the SmO⁻ anion from this work. Sextet, quartet, and octet spin-free states were included when computing the SO-CASPT2 states.

SO-CASP	Γ2
0	
298	
992	
1055	
1548	
2081	
2274	
2277	
2607	

tenth state do quintet contributions appear in any appreciable percentage. The energetics of all calculated SO-CASPT2 SmO states are plotted in Fig. S2 of the supplementary material according to the dominating spin state contribution.

In much of the spectroscopic literature on SmO, ^{11–13,18} the electronic states are labeled with an (*N*) Ω convention, which represents the *N*th state with a value of Ω for the projection of the total electronic angular momentum onto the internuclear axis. As has been discussed by Paulovič *et al.*,¹⁹ a definitive assignment of the Ω value cannot be made for the lowest-energy CASPT2 states due to the very small energy separations between the states with respect to the resolution of the method. Fortuitously, the X(0⁻) ground state of SmO identified by Linton and co-workers^{11–13} is an $\Omega = 0$ state; the lowest-energy SO-CASPT2 state reported here (Table I) is singly degenerate and therefore consistent with this assignment. Furthermore, the splitting between the lowest SO-CASPT2 states is in good agreement with experimental results, as will be discussed in detail below.

B. Experimental cryo-SEVI results

Experimental cryo-SEVI spectra of SmO⁻, taken at an ion trap temperature of 5 K, are presented in Figs. 2(a) and 3(a). We observe two main regions of structure: a low-eBE region between roughly 8000 and 12 000 cm⁻¹ [Fig. 2(a)] and a higheBE region between 19 000 and 27 000 cm⁻¹ [Fig. 3(a)]. The low-eBE cryo-SEVI spectra are marked by irregularly spaced but clearly resolved features; several sets of features are spaced by ~820 cm⁻¹, suggestive of excitation of the SmO vibrational fundamental. The higher-eBE spectra are considerably more congested. Peak positions and assignments of labeled features in Fig. 2(a) are reported in Table III and are compared to SO-CASPT2 results and experimental fluorescence results¹³ in Table I. The positions of features labeled in Fig. 3(a) are reported in Table IV alongside available literature values.



FIG. 2. (a) Lower-eBE region of the cryo-SEVI spectrum of SmO⁻. The blue trace is an overview spectrum taken at 12 914 cm⁻¹ while the black segments are high-resolution windows taken at lower photon energies. Peaks labeled in red exhibit temperature-dependent intensities (see Fig. 4) and are therefore considered hot bands. (b) SO-CASPT2 energy levels of SmO from Table I, shifted by the experimental position of peak A1 (8534 cm⁻¹). Levels assigned as $\Omega = 0$, 1 states, corresponding to nominally allowed photodetachment transitions from an $\Omega = \frac{1}{2}$ SmO⁻ anion, are shown in solid lines. All other levels are shown with dashed lines.



FIG. 3. (a) High-eBE region of the cryo-SEVI spectrum of SmO⁻. The blue trace is an overview spectrum taken at 27 978 cm⁻¹ while the black segments are high-resolution windows taken at lower photon energies. (b) Optical emission spectrum from the MOSC observations collected 9 and 68 s after Sm release (see Ref. 6) and shifted by the eBE of peak A1 (8534 cm⁻¹) for comparison to the cryo-SEVI spectrum. Gray dashed lines indicate the alignment of several features in panels (a) and (b). (c) SO-CASPT2 energy levels of SmO, shifted by the experimental position of peak A1 (8534 cm⁻¹). States are shown in black, red, and blue, when the largest contribution is from a septet, quintet, or nonet, respectively.

TABLE III. Peak positions (cm^{-1}) , offsets from peak A1 (cm^{-1}) , assignments, and vibrational fundamental frequencies for the low-eBE cryo-SEVI spectra of SmO⁻ given in Fig. 2. Peak positions represent the center of Gaussian fit to the experimentally observed peak. Peaks labeled in lowercase have increasing intensity with increasing temperature (Fig. 4) and are therefore considered hot bands.

Peak	eBE	Shift from A1	Assignment	Vib. fundamental
a	7712	-822		
b	8 0 5 4	-480		
c	8 3 5 1	-183		
A1	8 5 3 4	0	$X(0^{-}) 0_{0}^{0}$	
B1	8 6 8 2	148	$(1)1 0_0^0$	
d	8 774	240	-	
e	9 0 2 4	490		
C1	9 107	573	$(2)0^+ 0_0^0$	
A2	9355	821	$X(0^{-}) 1_{0}^{1}$	821
D1	9413	879	$(2)1 0_0^0$	
B2	9 506	972	$(1)1 1_0^{1}$	824
e	9 595	1060		
E1	9 684	1150		
f	9726	1192		
C2	9934	1400	$(2)0^+ 1^1_0$	821
F1	10 190	1656	$(3)1 0_0^0$	
D2	10 227	1693	$(2)1 1^{1}_{0}$	814
G1	10 548	2014	$(4)1 0_0^0$	
C3	10750	2216	$(2)0^+ 1^2_0$	
F2	11012	2478	$(2)2 1^{1}_{0}$	822
F3	11 830	3295	$(2)2 \ 1_0^2$	

TABLE IV. Peak positions (cm⁻¹) for the high-eBE cryo-SEVI spectra of SmO⁻ given in Fig. 3. Comparison is also made to relevant states observed in the fluorescence measurements of Linton and co-workers.^{11,13}

Peak	eBE	Shift from A1	Fluorescence
A	18 860	10 325	
В	19026	10 491	
С	19614	11 079	
D	20138	11 604	
E	20 240	11 705	
F	21 176	12 642	
G	21 248	12714	
Н	22366	13 831	
Ι	23 569	15 035	
J	23 886	15 352	
Κ	24114	15 580	15 570 ^a
L	24 556	16 022	
М	24 650	16116	
Ν	25 1 1 5	16 581	16 585 ^b
0	25 4 56	16922	16 923 ^b
Р	25 540	17 006	16 998 ^b
Q	25 709	17 175	
R	25 796	17 262	
<u>S</u>	25 893	17 359	

^aLinton *et al*.¹¹

^bBujin and Linton.¹³

The weak features labeled in lowercase in Fig. 2(a) demonstrate intensities that increase with temperature, as observed by acquiring spectra under different trapping conditions (Fig. 4(a)). These peaks are therefore assigned to vibrational or electronic hot bands, while those temperature-independent features labeled in uppercase originate from the SmO⁻ ground state.

Given the limited wavelengths accessible with our laser system, the eBE range of the SmO features in Fig. 2(a) is



FIG. 4. (a) Cryo-SEVI spectra of SmO⁻ taken with a photon energy of 10 689 cm⁻¹ and the ion trap held at 5 K. The buffer gas pressure in the trapping chamber is varied from lowest (orange) to highest (blue). Lower pressures lead to less efficient cooling in the trap and a corresponding enhancement of hot bands. The features labeled a-g correspond to the same peaks labeled in Fig. 2. (b) SmO state levels from the work of Linton and co-workers¹³ plotted to demonstrate possible assignments of hot bands. Red lines and blue lines correspond to $\Omega = 1, 2$ levels of SmO, shifted in eBE to simulate photodetachment from two excited $\Omega = 3/2$ states of SmO⁻ at term energies of 331 cm⁻¹ and 628 cm⁻¹, respectively.

not conducive to measurement with the optimal resolution of SEVI. The dye laser is only tunable down to 935 nm $(10\ 700\ \text{cm}^{-1})$; features lower in eBE are also accessible with the 1064 nm (9400 cm⁻¹) Nd:YAG fundamental. Typical peak widths for the low-eBE band therefore range from 6 cm⁻¹ fullwidth at half maximum (fwhm) for peak A2, which lies close to threshold with 1064 nm light, to 35 cm⁻¹ for peak D1, which lies considerably farther from threshold with dye laser light.

SEVI images also contain information about the anisotropy of photodetachment transitions. For one-photon photodetachment with linearly polarized light, the photoelectron angular distribution (PAD) is given by⁴¹

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} [1 + \beta P_2(\cos\theta)],$$

where θ is the angle relative to the polarization axis of the laser, P₂ is the second order Legendre polynomial, and β is the anisotropy parameter. β ranges from -1 to +2 for PADs aligned perpendicular and parallel to the laser polarization, respectively.

All features in the low-eBE range in Fig. 2(a) have PADs aligned strongly parallel to the laser polarization. In Fig. 3(a), peaks A-H have PADs aligned weakly parallel to the laser polarization, while the higher-energy peaks I-S appear anisotropic. These observations are in close agreement with the conventional PES anisotropy measurements of Kafader *et al.*¹⁵

V. DISCUSSION

A. Low-eBE structure of SmO

The features observed in the low-eBE cryo-SEVI spectra of SmO [Fig. 2(a)] are analyzed through comparison with our theoretical results as well as the experimental fluorescence measurements of Linton and co-workers.^{11–13} Cryo-SEVI, SO-CASPT2, and literature fluorescence state energies are summarized and compared in Table I. The SO-CASPT2 state energies, shifted by the eBE of peak A1, are also plotted in Fig. 2(b) alongside the cryo-SEVI spectra.

The features labeled A1-G1 in Fig. 2(a) are assigned to the vibrational origins of electronic transitions from the sextet ground state of SmO⁻ to low-lying septet states of SmO. The energies of many of these features relative to the eBE of peak A1 are a close match to term energies of SmO states identified by Linton and co-workers; good agreement is also seen with our calculated SO-CASPT2 states for many features (Table I). The pairing of experimental and theoretical features is partially guided by pairing singly degenerate SO-CASPT2 states with $\Omega = 0$ states, which Linton and co-workers were able to identify by studying intensity distributions of rotational lines.¹³

Peaks A1-D1, F1, and G1 correspond closely to transitions to neutral states that Linton and co-workers labeled with $\Omega = 0$, 1. Work by Jarrold and co-workers on photoelectron spectroscopy of lanthanide monoxides^{15,42,43} has determined that photodetachment from the metal-centered 6*s* orbital, as we have here, imposes a $\Delta\Omega = \pm \frac{1}{2}$ selection rule. Our results therefore strongly suggest detachment from an SmO⁻ ground electronic state with $\Omega = \frac{1}{2}$, giving spectroscopic access to neutral states with $\Omega = 0$, 1. Additionally, the Jarrold group's work suggests that allowed transitions should conserve the angular momentum of the metal-centered $4f^5$ electrons, J_f , which has a value of 2.5 in the SmO⁻ anion.¹⁵ Considering the neutral states calculated by Carette and Hocquet,¹⁸ our peaks A1-D1, F1, and G1 line up most closely with $\Omega = 0$, 1 states at term energies of 0, 115, 640, 873, 1472, and 1962 cm⁻¹. The authors calculate the lowest five of these states to have significant $J_f = 2.5$ character. Transitions from the SmO⁻ anion ground state to our assigned neutral states should therefore be fully allowed, with $\Delta \Omega = \pm \frac{1}{2}$ and $\Delta J_f = 0$.

Peak A1 is the lowest-eBE feature with a temperatureindependent intensity. The excellent agreement between the positions of cryo-SEVI peaks A1-D1, the term energies from the fluorescence measurements, and the spacing of low-lying SO-CASPT2 states confirms that peak A1 represents photodetachment to the ground electronic state of neutral SmO. We therefore report an electron affinity of SmO of 1.0581(11) eV determined by the eBE of peak A1. For comparison, spin-free CASPT2 predicts an EA of 0.8214 eV between the lowestlying sextet anion and septet neutral states. Kafader *et al.*¹⁵ report an EA of 1.067(6) eV, though the authors arrive at this value indirectly due to a different assignment of the SmO⁻ anion ground state.

There remain some small discrepancies between the states seen with cryo-SEVI, fluorescence, and SO-CASPT2. The (3)0⁻ state identified in the fluorescence experiments at 1546 cm⁻¹ is not seen with cryo-SEVI despite being accessible with $\Delta\Omega = -\frac{1}{2}$ from the proposed $\Omega = \frac{1}{2}$ anion state. Additionally, the weak peak E1 seen with cryo-SEVI at 1150 cm⁻¹ lines up with a SO-CASPT2 state but is not observed in the fluorescence data. It is therefore unclear what electronic state this line corresponds to.

Several additional features in the cryo-SEVI spectra involve vibrational structure of the SmO electronic states discussed above. Peaks A2, B2, C2-C3, D2, and F2-F3 are part of vibrational progressions beginning with the corresponding vibrational origin (peaks A1-D1 and F1); peak assignments and vibrational fundamentals are listed in Table III. We measure vibrational fundamentals of ~820 cm⁻¹ for most low-lying SmO electronic states, in agreement with the measurements of Linton and co-workers, who found a fundamental of 822 cm⁻¹ for the neutral X(0⁻) ground state.

Finally, the anisotropy information available in the loweBE cryo-SEVI spectra of SmO⁻ can also illuminate the electronic structure. The low-lying states of neutral SmO are predicted to differ in electron occupation from those of SmO⁻ primarily in occupation of the 6*s* orbital (Fig. 1). The low-eBE photodetachment transitions therefore correspond largely to detachment of a photoelectron of this orbital, which is highly localized on the Sm atom. Detachment from an atomic *s* orbital is expected to yield a photoelectron angular strongly enhanced parallel to the laser polarization,⁴¹ in good agreement with what we observe experimentally for the low-eBE cryo-SEVI spectrum.

B. Hot bands and structure of SmO⁻

Further complicating the SmO⁻ cryo-SEVI spectrum are several weak features (peaks a-g) labeled in red in Fig. 2(a). The temperature-dependence of these peaks, reinforcing their assignment as hot bands, is demonstrated in Fig. 4(a). It proves difficult to conclusively assign these features due to spectral congestion and lack of prior spectroscopic investigation of the SmO⁻ anion. However, we present one possible assignment of the observed hot bands drawing on our predicted SO-CASPT2 SmO⁻ state energies as well as the positions of neutral SmO states identified in the fluorescence work.

In Fig. 4(b), we show SmO state levels from the measurements of Linton and co-workers¹³ (Table I) simulating detachment from two excited $\Omega = 3/2$ electronic states of SmO⁻ with term energies of 331 cm⁻¹ (red lines) and 628 cm⁻¹ (blue lines). Detachment from these proposed states could access neutral states with $\Omega = 1$, 2, leading to two interspersed manifolds of electronic hot bands and clearly accounting for peaks b, c, and d. Higher-lying hot bands in the vicinity of peaks e-g are also largely reproduced with this scheme. Our SO-CASPT2 calculations support the existence of such lowlying anion electronic states. Our calculated states at 298 and 992 cm⁻¹ (Table II) are in reasonable agreement with the proposed levels of 331 and 628 cm⁻¹ from inspection of the cryo-SEVI data.

Peak a, the lowest-eBE feature we observe, also warrants mention. This feature lies 822 cm⁻¹ below A1, and its intensity is insensitive to temperature compared to the nearby hot bands. Due to the similarity of this spacing with the vibrational fundamental of SmO, one might tentatively assign this feature to a vibrational hot band, i.e., the 1^0_1 transition between anion and neutral ground electronic states. However, Willson and Andrews¹⁴ report a vibrational fundamental of only 770 cm⁻¹ for the SmO⁻ anion in an argon matrix, contradicting this assignment. We therefore do not venture a conclusive assignment for peak a.

C. Higher-energy structure of SmO

The higher-eBE structure seen in the cryo-SEVI spectra of SmO in Fig. 3(a) is considerably harder to analyze than the lower-eBE structure. This energy window corresponds to term energies of $\sim 10\ 000-17\ 000\ cm^{-1}$ above peak A1, where there appears to be a much higher density of states. The irregularity of peak spacings in this region (Table IV) prevents clear assignment of vibrational progressions.

Prior experimental work is consistent with our measurements. In their fluorescence measurements, Linton and coworkers^{11,13} report a few states at term energies in the range of peaks K-Q, though they do not attempt state assignments. Their values are reported in the rightmost column of Table IV where available. Kafader *et al.*¹⁵ observe broad, unresolved bands of states at eBEs of 2-2.5 eV and above 3 eV in their photoelectron spectra, corresponding roughly to our clusters of peaks A-H and I-S, respectively.

While the cryo-SEVI results in this energy regime agree with the prior experimental work, they are more difficult to match with theoretical results. The SO-CASPT2 state energies we calculate in this region are plotted in Fig. 3(c), shifted by the eBE of peak A1. Overlapping states with dominant contributions from septet and quintet configurations shown in black and red, respectively, are prevalent up to an eBE of ~23 000 cm⁻¹. Transitions to this manifold of states can easily explain the presence of peaks A-H. Interestingly, however, there is a complete gap in SO-CASPT2 states from $\sim 23\ 000$ to 28 500 cm⁻¹, precisely the region where peaks I-S appear in the cryo-SEVI spectra.

Peaks I-S may potentially arise from states with electronic configurations not captured by the active space used here. Indeed, the fact that the groups of peaks A-H and I-S have distinct photoelectron angular distributions suggests that they correspond to neutral states with significantly different orbital occupations. Kafader et al.¹⁵ invoke the possibility of "shake-up transitions" that violate the typical one-electron photodetachment rule. For instance, one of the two 6s electrons could be detached from the anion while the other is simultaneously promoted to a 5d neutral orbital, leaving the neutral in a $4f^5$ 5d configuration. Such $4f^5$ 5d neutral states did not appear in our exploratory CASSCF calculations, as the non-bonding 5d orbitals consistently rotated out of the active space. This suggests that the $4f^5$ 5d states are very high in energy at the CASSCF level of theory, but it is possible that with a better treatment of dynamical correlation they may fall in the range of the unassigned experimental features I-S. On the other hand, the fact that states in the range of peaks I-S appear in the fluorescence spectra of Linton and co-workers (Table IV) and in the MOSC emission spectra (vide infra) calls into question their assignment to shake-up transitions, as 5d-6s fluorescence to the ground state is nominally forbidden.

Regardless of state assignments, the positions of cryo-SEVI features in this region can be compared directly to the MOSC emission spectra to determine whether spectral signatures of SmO appear following atmospheric Sm release. The emission spectra in the 550-750 nm region reported by Bernhardt *et al.*⁶ taken 9 and 68 s after the Sm release are reproduced in Fig. 3(b). The spectra have been converted to eBE by shifting the energy scale by the EA of SmO. The relative intensities of features will differ between the cryo-SEVI and MOSC emission spectra due to differences in selection rules for the two spectroscopies, but peak positions are directly comparable.

Several spectral features align between the cryo-SEVI spectra in Fig. 3(a) and the MOSC emission spectra in Fig. 3(b); dashed gray lines are drawn to guide the eye. In particular, peaks I, J, K, and L correspond quite closely to MOSC emission peaks at 667, 652, 643, and 625 nm, respectively, which grow over time between the 9 and 68 s traces. This observation supports the conclusion reached by Holmes *et al.*⁴ that the spectral features in the 650 nm range observed in the MOSC release are attributable to neutral SmO.

While the present work is an important start, further work is needed to truly assess the roles of the numerous chemistries taking place during these release experiments, including oxidation of Sm by molecular O_2 , dissociative recombination of SmO⁺ with electrons, and photoionization processes. Specifically, determination of the relative intensities of emission lines resulting from solar excitation would allow quantification of SmO formed in these releases, in turn allowing for improved evaluation of other experimental uncertainties, such as the efficiency of vaporization or the rate of dissociative recombination. Greater experimental knowledge of the rich electronic structure of SmO and the development of increased computational precision for these systems is vital to aid in these efforts. Moving forward, a more complete understanding of the chemistry taking place in the MOSC releases will allow for better constraints to be placed on the role of other atmospheric influences, such as the magnetic field or neutral winds, leading to development of a predictive model for future release efforts.

VI. CONCLUSIONS

Chemical release experiments have motivated the need for improved understanding of the spectroscopy of SmO. Low-lying excited states of SmO up to 3000 cm⁻¹ above the ground state and higher-lying states at term energies between 9000 and 19 000 cm⁻¹ have been identified using the cryo-SEVI technique. Observed states are in general agreement with the literature data where comparisons can be made. Additionally, we report an electron affinity for SmO of 1.0581(11) eV. CASSCF and CASPT2 calculations accounting for spin-orbit effects of the SmO neutral and anion were performed. Calculated energetics are in good agreement with experimental observations, allowing for definitive assignment of several low-lying excited electronic states of SmO, and some proposed assignments for low-lying states of the SmO⁻ anion.

Transitions to the observed higher-lying excited electronic states are consistent with observed spectra from chemical release experiments, supporting a prior attribution of spectral features in this region to neutral SmO. The present results lay the groundwork for further efforts to understand emission spectra observed in the release experiments, required for full analysis of the existing data and development of predictive modeling capabilities. For example, we aim to extend our theoretical treatment to determine transition probabilities and subsequently estimate the optical emission spectrum of SmO. In addition, recent considerations suggest that Nd is an attractive target for ionospheric release, so analogous experiments on NdO could be of considerable interest.

SUPPLEMENTARY MATERIAL

See supplementary material for additional theoretical results including spin-free CASPT2 dissociation curves, a complete energy diagram of all SO-CASPT2 states of SmO, and relative energies of spin-free CASPT2 states for SmO and SmO⁻.

ACKNOWLEDGMENTS

This research is funded by the Air Force Office of Scientific Research under Grant No. FA9550-16-1-0097 (M.L.W., J.A.D., and D.M.N.), the Air Force Office of Scientific Research Young Investigator Program under Grant No. FA9550-15-1-0031 (B.V. and T.S.), and the Air Force Office of Scientific Research in-house program (No. AFOSR-16RVCOR276, A.A.V., S.G.A., and N.S.S.). M.L.W. thanks the National Science Foundation for a graduate research fellowship. S.G.A. is supported through the Institute for Scientific Research of Boston College under Contract No. FA9453-10-C-0206. Helpful discussions with Caroline Chick Jarrold, Todd Pedersen, and Jeffrey Holmes are appreciated.

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