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Formation and Characterization of ZrO₃ and HfO₃ Molecules in Solid Argon[†]

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ZrO₃ and HfO₃ molecules were prepared via reactions of metal monoxides with dioxygen in solid argon and were characterized using matrix isolation infrared absorption spectroscopy as well as theoretical calculations. Unlike the titanium monoxide molecule, which reacted spontaneously with dioxygen to form TiO₃, the ZrO and HfO molecules reacted with dioxygen to give the ZrO₃ and HfO₃ molecules only under visible light irradiation. Density functional calculations predicted that both the ZrO₃ and HfO₃ molecules possess a closed-shell singlet ground state with a non-planar C_s geometry, in which the side-on coordinated O₂ falls into the peroxide category.

Key words: Matrix isolation, Transition metal oxide, Dioxygen complex, Infrared spectrum**I. INTRODUCTION**

Transition metal oxides and dioxygen complexes are of great interest due to their important roles in various catalytic processes. As the microscopic counterparts of such macroscopic species, simple transition metal oxide and dioxygen complexes may serve as simple models for both experimental and theoretical investigations at the molecular level. For the first element in group IV, we have recently prepared and characterized some oxygen-rich mononuclear metal oxide/dioxygen complexes in solid argon. Two oxo-superoxo titanium ozonide complexes with TiO₆ stoichiometry in solid argon were prepared via the reaction of titanium dioxide with dioxygen [1]. These two isomers are interconvertible, that is, visible light induces the conversion of the side-on bonded O₃ ligand to the end-on fashion, and vice versa upon annealing. Titanium oxide/dioxygen complexes, TiO₃ and TiO₅ with odd number of oxygen atoms were also formed via the reactions of titanium monoxide with O₂ [2]. As for zirconium and hafnium, most experimental and theoretical efforts were made on the simple diatomic and triatomic molecules, from which detailed information on their structure and bonding was provided [3-24]. Examples on the neutral oxygen rich species were only limited to the recently characterized HfO₆ and HfO₈ complexes in this lab [25]. The HfO₂ molecule reacts with dioxygen in forming a side-on bonded oxo-superoxo hafnium ozonide complex, which either pho-

tochemically rearranges to a more stable Hf(η²-O₂)₃ isomer, a side-on bonded di-superoxo hafnium peroxide complex, or reacts with dioxygen to form an unprecedented homoleptic tetra-superoxo hafnium complex: Hf(η²-O₂)₄.

In this paper, we provide a combined matrix isolation infrared absorption spectroscopic and density functional theoretical study on the formation and characterization of the ZrO₃ and HfO₃ species in solid argon.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experimental setup for pulsed laser-evaporation and matrix isolation infrared spectroscopic investigation has been described in detail previously [26]. Briefly, the 1064 nm fundamental of a Nd:YAG laser (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width) was focused onto a rotating bulk zirconium or hafnium dioxide target through a hole in a CsI window cooled normally to 6 K by means of a closed-cycle helium refrigerator (ARS, 202N). The laser-evaporated species were co-deposited with O₂/Ar mixtures onto the CsI window. In general, matrix samples were deposited for 1 h at a rate of approximately 4 mmol/h. The O₂/Ar mixtures were prepared in a stainless steel vacuum line using standard manometric technique. Isotopic ¹⁸O₂ (ISOTECH, 99%) was used without further purification. The infrared absorption spectra of the resulting samples were recorded on a Bruker IFS 66V spectrometer at 0.5 cm⁻¹ resolution between 4000 and 450 cm⁻¹ using a liquid nitrogen cooled HgCdTe (MCT) detector. Samples were annealed to different temperatures and cooled back to 6 K for spectral acquisition. Selected

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TABLE I Infrared absorptions (cm^{-1}) from co-deposition of laser-evaporated ZrO and HfO with O_2 in solid argon.

$^{16}\text{O}_2$	$^{18}\text{O}_2$	$^{16}\text{O}_2+^{18}\text{O}_2$	$^{16}\text{O}_2+^{16}\text{O}^{18}\text{O}+^{18}\text{O}_2$	Assignment
885.7	885.4, 843.5	885.6, 843.5	885.4, 843.7	ZrO ₃ Zr=O str.
808.8	787.9, 765.8	808.8, 787.9, 765.8	807.9, 788.0, 765.8	ZrO ₃ O–O str.
590.8	580.5, 560.0	590.8, ... ^a , 560.0	591.1, ... ^a , 560.0	ZrO ₃ Zr–O ₂ asym. str
580.2	562.1, 554.7	580.2, 562.1, 554.7	580.2, 562.1, 554.7	ZrO ₃ Zr–O ₂ sym. str
879.4	878.7, 834.1	879.3, 834.1	878.9, 834.3	HfO ₃ Hf=O str.
782.8	762.4, 740.8	782.8, 762.4, 740.8	782.8, 781.2, 762.5, 740.8	HfO ₃ O–O str.
614.9	598.6, 581.3	614.9, 598.6, ... ^b	614.9, 598.6, ... ^b	HfO ₃ Hf–O ₂ asym. str
557.3	542.2, 529.8	557.3, 542.2, 529.8	557.2, 542.1, 529.8	HfO ₃ Hf–O ₂ sym. str

^a Absorptions not resolved due to band overlap.

^b Absorptions too weak to be observed.

samples were subjected to broad band irradiation using a tungsten lamp or a high-pressure mercury arc lamp with glass filters.

Quantum chemical calculations were performed using the Gaussian 03 program [27]. The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr (B3LYP) was utilized [28]. The 6-311+G(d) basis set was used for the O atom, and the scalar-relativistic SDD pseudopotential and basis set were used for the Zr and Hf atoms [29,30]. The geometries were fully optimized; the harmonic vibrational frequencies were calculated, and zero-point vibrational energies (ZPVE) were derived. The single point energies of the newly observed products optimized at B3LYP level of theory were calculated using the CCSD(T) method with the same basis sets.

III. RESULTS AND DISCUSSION

A. Infrared spectra

The ZrO₃ and HfO₃ molecules were prepared via the reactions of metal monoxides with dioxygen in solid argon, and their infrared absorptions were listed in Table I. The zirconium and hafnium monoxide reactants were prepared via pulsed laser evaporation of bulk metal dioxide target. In the blank experiment, the zirconium oxide species produced by pulsed laser evaporation using about 5 mJ/pulse laser energy were co-deposited with pure argon at 6 K. The as-deposited spectrum is dominated by the strong ZrO and ZrO₂ absorptions [20]. Sample annealing allowed the zirconium dioxide molecules to diffuse and react with each other to give the recently characterized Zr₂O₄ cluster whose terminal Zr=O stretching vibration was observed at 870.6 cm^{-1} [31]. The infrared spectra in selected regions from co-deposition of laser evaporated zirconium oxides with 0.1%O₂ doped in argon are shown in Fig.1. The as-deposited spectrum (Fig.1(a)) is about the same as that of the blank experiment without O₂ doping. When the

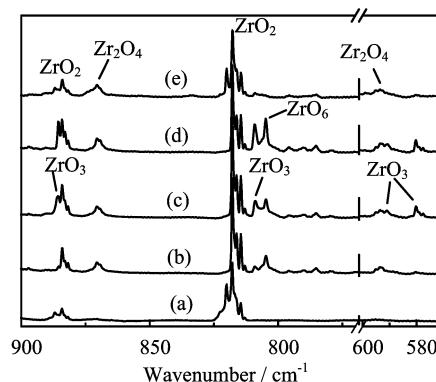


FIG. 1 Infrared spectra of laser-evaporated zirconium oxides with 0.1% O₂ in argon. (a) 1 h of sample deposition at 6 K, (b) after 25 K annealing, (c) after 15 min of $\lambda > 600$ nm irradiation, (d) after 30 K annealing, and (e) after 15 min of $250 \text{ nm} < \lambda < 580 \text{ nm}$ irradiation.

sample was annealed to 25 K (Fig.1(b)), absorptions due to $\text{OZr}(\eta^2\text{-O}_2)(\eta^2\text{-O}_3)$ (labeled as ZrO₆ in Fig.1) were produced. This complex is a major product in the reaction of zirconium atoms and O₂, which was characterized to have infrared absorptions at 1117.8, 1015.2, 912.9, 796.4, 668.3, and 472.2 cm^{-1} . When the sample was subjected to visible light irradiation using a tungsten lamp with a $\lambda > 600$ nm long wavelength pass filter (Fig.1(c)), a set of new absorptions at 885.7, 808.8, 590.8, and 580.2 cm^{-1} were produced, which were sharpened upon subsequent sample annealing to 30 K (Fig.1(d)). All of the four new absorptions were completely destroyed when the sample was exposed to broad band irradiation with the output of a high-pressure mercury arc lamp ($250 \text{ nm} < \lambda < 580 \text{ nm}$, Fig.1(e)).

The spectra in selected regions from a similar experiment using a hafnium dioxide target are shown in Fig.2. Besides the previously reported HfO, HfO₂ and Hf₂O₄ absorptions, a group of new absorptions at 879.4, 782.8, 614.9, and 557.3 cm^{-1} were produced upon visible light irradiation ($\lambda > 600 \text{ nm}$).

To help the product identification, experiments were

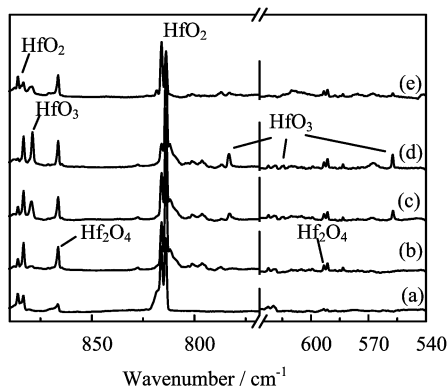


FIG. 2 Infrared spectra of laser-evaporated hafnium oxides with 0.5% O₂ in argon. (a) 1 h of sample deposition at 6 K, (b) after 25 K annealing, (c) after 15 min of $\lambda > 600$ nm irradiation, (d) after 30 K annealing, and (e) after 15 min of $250 \text{ nm} < \lambda < 580$ nm irradiation.

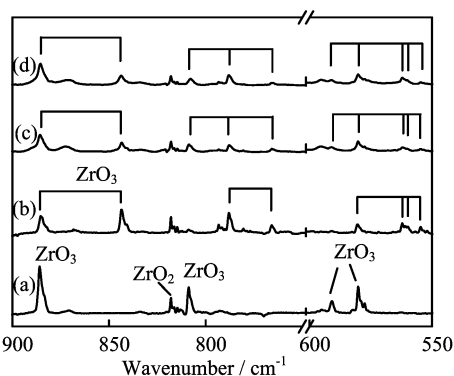


FIG. 3 Difference infrared spectra of laser-evaporated zirconium oxides with isotopic-labeled oxygen in excess argon. (Spectrum taken after 15 min of $\lambda > 600$ nm irradiation minus spectrum taken right after sample deposition or after sample annealing) (a) 0.5% ¹⁶O₂, (b) 0.5% ¹⁸O₂, (c) 0.25% ¹⁶O₂+0.25% ¹⁸O₂, and (d) 0.15% ¹⁶O₂+0.3% ¹⁶O¹⁸O+0.15% ¹⁸O₂.

repeated with isotopic substituted ¹⁸O₂, ¹⁶O₂+¹⁸O₂, and ¹⁶O₂+¹⁶O¹⁸O+¹⁸O₂ mixtures. The infrared spectra using different isotopic samples are shown in Figs. 3 and 4, respectively, and the product absorptions are listed in Table I.

B. ZrO₃

The absorptions at 885.7, 808.8, 590.8, and 580.2 cm⁻¹ exhibited identical behavior throughout the experiments, indicating that these four absorptions are due to different vibrational modes of the same molecule. Note that these absorptions were not produced in the experiments on the reaction of laser-evaporated zirconium atoms with dioxygen, during which the zirconium monoxide absorption is very weak. The observation of these absorptions only in the experiment

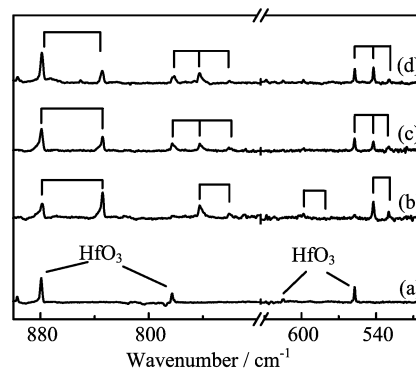


FIG. 4 Difference infrared spectra of laser-evaporated hafnium oxides with isotopic-labeled oxygen in excess argon. Spectrum taken after 15 min of $\lambda > 600$ nm irradiation minus spectrum taken right after sample deposition or after sample annealing. (a) 0.5% ¹⁶O₂, (b) 0.5% ¹⁸O₂, (c) 0.25% ¹⁶O₂+0.25% ¹⁸O₂, and (d) 0.15% ¹⁶O₂+0.3% ¹⁶O¹⁸O+0.15% ¹⁸O₂.

with co-condensation of laser-evaporated zirconium oxide species with dioxygen suggests that the absorber is produced via the reaction between zirconium monoxide and dioxygen. The 885.7 cm⁻¹ absorption lies close to the symmetric stretching mode of ZrO₂. It shifted to 843.5 cm⁻¹ upon O-18 substitution with an isotopic ¹⁶O/¹⁸O ratio of 1.0500. No intermediate absorptions were observed in the experiments with mixed ¹⁶O₂+¹⁸O₂ and ¹⁶O₂+¹⁶O¹⁸O+¹⁸O₂ samples. The band position and isotopic frequency ratio suggest that this absorption is due to a terminal Zr=O stretching vibration. The absorption at 808.8 cm⁻¹ exhibited an isotopic ¹⁶O/¹⁸O frequency ratio of 1.0562, which is a typical value for O-O stretching vibration. When the mixed ¹⁶O₂+¹⁶O¹⁸O+¹⁸O₂ sample was used, this mode splits into a triplet at 807.9, 788.0, and 765.8 cm⁻¹, indicating that one O₂ fragment with two equivalent oxygen atoms is involved in this mode. The absorptions at 590.8 and 580.2 cm⁻¹ are too low for terminal Zr=O stretching vibrations, and are assigned to the corresponding antisymmetric and symmetric Zr-O₂ vibrations based on their isotopic frequency ratios and band positions. Accordingly, we assign the four absorptions at 885.7, 808.8, 590.8, and 580.2 cm⁻¹ to a ZrO₃ species with a terminal Zr=O bond and a side-on bonded O₂ fragment.

The experimental assignment is confirmed by theoretical calculations. It was found that the ZrO₃ molecule possesses a closed-shell singlet ground state with a non-planar C_s symmetry (Fig.5), similar to the recently characterized TiO₃ molecule [2]. The Zr=O bond length was calculated to be 1.779 Å, which is very close to the values of previously identified ZrO containing species [32,33]. The O-O bond distance was calculated to be 1.493 Å, which approaches the values of the recently characterized peroxide complexes [34,35]. Hence, the ZrO₃ molecule can be regarded as (O₂)²⁻(ZrO)²⁺,

TABLE II Comparison between the observed and calculated vibrational frequencies (cm^{-1}) and isotopic frequency ratios of the product molecules.

Molecule	Mode	Frequency (intensity)		$^{16}\text{O}/^{18}\text{O}$	
		Calcd.	Obsd.	Calcd.	Obsd.
ZrO_3 ($^1\text{A}'$, C_s)	Zr=O str (a')	908.9 (206)	885.7	1.0508 ^a	1.0500
	O–O str (a')	843.5 (105)	808.8	1.0575 ^b	1.0562
	Zr–O ₂ asym str (a'')	570.4 (55)	590.8	1.0563 ^b	1.0550
	Zr–O ₂ sym str (a')	576.9 (23)	580.2	1.0461 ^b	1.0460
	(a')	216.6 (27)			
	(a'')	177.4 (18)			
HfO_3 ($^1\text{A}'$, C_s)	Hf=O str (a')	875.4 (140)	879.4	1.0547 ^a	1.0543
	O–O str (a')	801.2 (89)	782.8	1.0578 ^b	1.0567
	Hf–O ₂ asym str (a'')	591.2 (15)	614.9	1.0585 ^b	1.0578
	Hf–O ₂ sym str (a')	548.4 (53)	557.3	1.0522 ^b	1.0519
	(a')	211.0 (22)			
	(a'')	173.3 (17)			

^a ^{18}O refers to $(\eta^{2-16}\text{O}^{18}\text{O})\text{M}^{18}\text{O}$ (M=Zr and Hf).

^b ^{18}O refers to $(\eta^{2-18}\text{O}_2)\text{M}^{16}\text{O}$ (M=Zr and Hf).

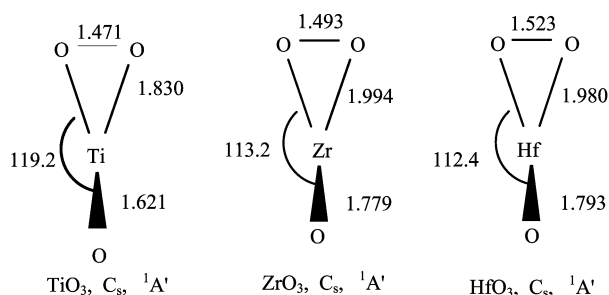


FIG. 5 Optimized structures (bond lengths in Å and bond angles in $^\circ$) of the observed products. The structure of TiO_3 [2] was included for comparison.

a peroxo-zirconium monoxide complex. Frequency calculations showed that the strongest absorption of ZrO_3 is the terminal Zr=O stretching vibration, which was predicted at 908.9 cm^{-1} , ca. 23.2 cm^{-1} higher than the observed value. As listed in Table II, the O–O and Zr–O₂ stretching vibrations were predicted at 843.5, 576.9, and 570.4 cm^{-1} with isotopic frequency ratios (1.0575, 1.0461, and 1.0563) in good agreement with the observed values. Geometry optimization on the triplet state of ZrO_3 converged to $a^3\text{A}''$ state lying 108.26 kJ/mol higher in energy than the singlet ground state at the DFT/B3LYP level of theory. The $^3\text{A}''$ state has a predicted O–O bond length of 1.322 \AA with the two unpaired electrons mainly located on the zirconium center and the O₂ ligand. Therefore, the triplet state ZrO_3 is a superoxo-zirconium monoxide complex with a predicted O–O stretching vibration at 1194.8 cm^{-1} .

C. HfO_3

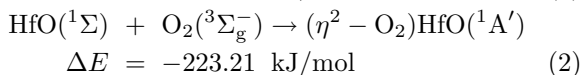
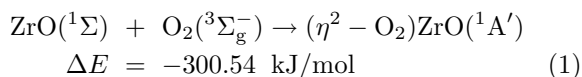
Following the example of ZrO_3 , the absorptions at 879.4, 782.8, 614.9, and 557.3 cm^{-1} observed in the reaction of hafnium monoxide with dioxygen are assigned to the HfO_3 molecule. Density functional calculations predicted that HfO_3 has a singlet ground state with its geometric structure very similar to that of ZrO_3 . As listed in Table II, the experimental frequencies and isotopic frequency ratios match the calculated values very well, which add strong support to the assignment.

With the ZrO_3 and HfO_3 molecules reported here, all three MO_3 species of group IV metals were characterized. These species were predicted to have a singlet ground state with a non-planar C_s symmetry and all of them can be regarded as peroxo-metal monoxide complexes. The predicted O–O bond length increases from titanium (1.471 \AA) [2] to zirconium (1.493 \AA) and to hafnium (1.523 \AA) (Fig.5). Consistent with this notion, the Mulliken charge on the O₂ fragment increases from $-0.50e$ for Ti to $-0.59e$ for Zr and to $-0.65e$ for Hf, which implies that the metal center tends to donate more electrons to the oxygen ligand going down the series. As a result, the HfO_3 molecule has the longest O–O bond length and lowest O–O stretching vibrational frequency (782.8 cm^{-1}). Similar periodic trend has been observed in group IV metal monocarbonyls [36].

D. Reaction mechanism

Based upon the experimental observations, the ZrO_3 and HfO_3 molecules were formed via the reactions of zirconium and hafnium monoxides with dioxygen in

solid argon. The spectra shown in Fig.1 and Fig.2 indicate that the ZrO₃ and HfO₃ molecules were produced upon visible light irradiation instead of on sample annealing, which suggests that the ground state ZrO and HfO molecules are unreactive toward molecular oxygen in solid argon. As has been pointed out, the ground state titanium monoxide molecule is able to react with dioxygen to form TiO₃ spontaneously upon sample annealing [2]. The discrepancy in reactivity between TiO and ZrO/HfO toward dioxygen can be rationalized in terms of their different electronic ground states. The TiO molecule possesses $a^3\Delta$ ground state [20], in which the two unpaired electrons occupy two MOs which are Ti 4s and $3d_{x^2-y^2}$ in character (taking the Ti=O bond as the z axis). The $d_{x^2-y^2}$ orbital of Ti is able to interact with the π^* orbital of O₂ effectively in the side-on fashion. However, both the zirconium and hafnium monoxide molecules have a singlet ($^1\Sigma$) ground state [20]. The interaction between ZrO (or HfO) and O₂ in their ground states is repulsive due to the lack of symmetry-adapted orbitals. Therefore, photoexcitation is required to initiate the association reaction during which some excited state of ZrO and HfO may be involved. Previous experiments have shown that several low-lying electronic states in the visible region are available for the diatomic ZrO and HfO molecules [37,38]. According to the CCSD(T)//B3LYP calculations, the formation of ZrO₃ and HfO₃ species is highly exothermic by 300.54 and 223.21 kJ/mol, respectively, with respect to the ground state precursors.



It can be found in Figs. 3 and 4 that the oxygen atoms of the peroxy ligand can be interconverted with the oxygen atom of the monoxide subunit during the association reaction process as observed in the TiO₃ case [2]. The large exothermicity of reactions (1) and (2) is sufficient to overcome the barrier for oxygen atom exchange reaction. The formation mechanism of ZrO₃ and HfO₃ is similar to that of silicon trioxide, which also requires photoexcitation and involves atomic exchange [39]. The silicon monoxide molecule has a singlet ground state, the same as ZrO and HfO. In the reaction of SiO and O₂, the SiO₃ molecule could only be produced via 240 nm UV irradiation. The excitation of SiO to its more reactive excited states is responsible for the formation of silicon trioxide.

IV. CONCLUSION

The reactions of zirconium and hafnium monoxide molecules with dioxygen have been studied using matrix isolation infrared absorption spectroscopy and density

functional calculations. The ZrO and HfO molecules were produced by pulsed laser evaporation of bulk metal oxide targets. It was found that the ground state ZrO and HfO molecules are unreactive toward O₂. The ZrO and HfO molecules reacted with dioxygen to form the ZrO₃ and HfO₃ molecules only under visible light irradiation ($\lambda > 600$ nm) during which some excited states may be involved. Theoretical calculations predicted that the ZrO₃ and HfO₃ molecules have a singlet ground state with a non-planar C_s symmetry, which can be regarded as peroxy-metal monoxide complexes.

V. ACKNOWLEDGMENTS

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