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Excited-State Chemistry: Photocatalytic Methanol Oxidation by Uranyl@Zeolite through Oxygen-Centered Radicals

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partial methanol oxidation, $H_3COH + O_2 \rightarrow H_2CO + H_2O_2$, at a visible-light-activated actinide photocatalyst. The reaction inertness of C—H bonds and O=O diradicals at ambient conditions is overcome through catalysis by photoexcited uranyl units (*UO₂²⁺) anchored on a mesoporous silicate. The electronic ground- and excited-state energy hypersurfaces are investigated with quasirelativistic density-functional and *ab initio* correlated wave function approaches. Our study suggests



that the molecular cluster can react on the excited energy surface due to the longevity of excited uranyl, typical for f-element compounds. The theoretically predicted energy profiles, chemical intermediates, related radicals, and product species are consistent with various experimental findings. The uranyl excitation opens various reaction pathways for the oxidation of volatile organic compounds (VOCs) by "hole-driven hydrogen transfer" (HDHT) through several exothermic steps over low activation barriers toward environmentally clean or chemically interesting products. Quantum-chemical modeling reveals the high efficiency of the uranyl photocatalysis and directs the way to further understanding and improvement of VOC degradation, chemical synthesis, and biologic photochemical interactions between uranyl and the environment.

■ INTRODUCTION

Uranium is a Janus-faced element. It has been in daily use since antiquity for ceramic glazes and fluorescing glassware. In 1789, it was recognized as an element and became famous for its unique rich chemistry and later for its nuclear physics. To the present public, uranium is known as the material for nuclear power and for radioactive pollution by the uranium technology being environmentally problematic, though CO_2-NO_x -lean in energy production. Uranium has an intermediate occurrence on earth, and so-called depleted ²³⁸U is comparatively cheap as a hardly used byproduct when recycling spent nuclear fuel. Due to its slow decay with a half-life of several 10⁹ years, it is only weakly radioactive (e.g., emitting less α radiation than natural uranium), but known in biology as one among the many chemically toxic heavy transition elements.^{1,2}

One of the most common forms of uranium, both in the natural environment and in man-made materials, is the uranyl cation $[U^{+6}O^{-2}_2]^{2+}$. (Throughout this work we write $\pm n$ for formal chemical oxidation states, and $\delta \pm$ for more realistic physical or effective charges.) As the functional unit in a multitude of compounds, uranyl is chemically notoriously unreactive, with a rigid linear covalent structure of the axial $[IO \equiv U \equiv OI]^{2+}$ group, formed by closed $O^{-2}(2p^6)$ dative shells and well overlapping with the empty $U^{+6}(5f/6d/7s)^0$ hybrid shells.^{3–7} The electron-pair acceptor activity of uranyl in the equatorial plane is well-known as being decisive for its coordination chemistry. Determining the interaction modes between uranyl ions and organic molecules or biochemical systems,^{9–19} it determines the uranium mobility in the natural

environment, thereby influencing the postprocessing of spent nuclear fuel. $^{\rm 8}$

Recently the activation and reactivity of the axial uranyl oxygen atoms (O_{ax}) have attracted increasing attention.^{1,3,10,20-25} Uranyl compounds, in particular in the long-living electronically excited state, can activate C–H and O–H bonds, which is of significance to C–C and C–O cleavages, too.²⁶ Excited uranyl species are also known to photocatalyze the bond breaking in the DNA double-helix.^{14,18}

Photoexcitation is the most important method of activating the axial oxygen atoms of uranyl.² (In this paper, electronic photoexcitation is designated by an asterisk *; a radicalic electron or hole by a dot • or circle °, respectively; and, if necessary, physical adsorption on a carrier surface by a chemical formula.) Resulting from the ligand-to-metal charge transfer (LMCT) in the dative $[IO \Longrightarrow > U (\Longrightarrow OI]^{2+}$ bonds upon photoexcitation, the $*[IO \Longrightarrow > U (\Longrightarrow OI]^{2+}$ species features a formally pentavalent $•U^{+5}$ center with an additional electron in the 5f shell, and a monovalent O_{ax}^{-1} radicalic ligand with an electron-hole.^{1,12,27-31} Compared with excited s-, p-, and dblock metal oxides, the excited state of $*[O^{\bullet}UO^{\circ}]^{2+}$ with

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separated electron and hole is relatively long-lived (at the scale of μ s to ms) and slowly luminescing, owing to the significantly weak interaction between the compact U(5f¹) electronic orbital and the hole in the oxygen shell. Excited *[UO₂]²⁺ is strongly oxidizing with a high redox potential ($E^{\circ} \sim +2.6$ V).^{1,13}

The electronic excitation can be quenched by various organic molecules through hydrogen-atom (•H) transfer to the $*[UO_2]^{2+}$ unit, saturating the $^{\circ}O_{ax}$ hole, thereby leaving $[IO \Longrightarrow)^{\bullet}U (=O-H]^{2+}$ and yielding some organic radicals. This process may be baptized "hole-driven hydrogen transfer" (HDHT), the new relative of common "proton-coupled electron transfer" (PCET).^{11-13,27,28,32-39} The HDHT is also called "light-driven oxyl formation causing H-abstraction and substrate oxidation".²⁴ In aqueous solution, two $^{\bullet}U^{+5}$ species can spontaneously disproportionate to a pair of $^{\bullet \bullet}U^{+4}$ and $U^{+6}.^{35,37,39}$ The reduced $[OU^{+5}O]^{1+}$ unit can also be directly oxidized to $[OU^{+6}O]^{2+}$ in the presence of oxygen, competing with the disproportionation.^{27,28,36,38} Concerning O₂-involving reactions, dioxygen peroxide (O_2^{-2}) and superoxide $(^{\bullet}O_2^{-1})$ anions and their conjugate acids have been suggested as intermediates in experimental works.^{27,28,36,38}

Uranyl cations strongly bind to defect-sites of oxidic support materials, which restrains disproportionation and mobility, thereby also suppressing the toxicity.³⁵ Uranyl-anchored silicate sieves have been proven as true *visible-light*-activated photocatalysts, ^{1,31,40–42} which could efficiently catalyze photooxidation reactions of various organic compounds under ambient conditions (Figure 1). In experimental photo-



Figure 1. Uranyl on microporous silicate (colors: gray, Si; red, O; blue, U) catalyzing the photo-oxidation of volatile organic compounds (VOCs).

oxidation experiments of "volatile organic compounds" (VOCs), uranyl doped silicates proved significantly more efficient than the more common TiO₂ catalysts, in particular in the visible region.^{40,43-47} Natural biological air pollutants dominantly comprise hydrocarbons (methane, isoprene, terpenes), while halogen derivatives and oxygen compounds (such as alcohols, aldehydes, ketones, esters) are among the dominating anthropogenic pollutants, all of which can be catalytically eliminated with the help of * $[UO_2]^{2+}$ from the environment, or transformed into chemically interesting intermediate products.

So far, there is little knowledge of excited-state reactions of actinide compounds, such as the photocatalytic oxidation by uranyl derivatives. Therefore, we have chosen the partial oxidation of methanol to active intermediate products formaldehyde and hydrogen peroxide by uranyl-photocatalysis, summarized as

$$H_{3}COH + O_{2} \xrightarrow[(at uranyl-silicate)]{+h\nu} H_{2}CO + H_{2}O_{2}$$
$$(\xrightarrow{+O_{2}}CO_{2} + 2H_{2}O) \qquad (1-4)$$

The individual reaction steps of eqs 1-4 are discussed in Scheme 1 below. Methanol is both a VOC, by which the biosphere pollutes the environment, as well as a basic industrial chemical. Formaldehyde and hydrogen peroxide may be either chemically useful or environmentally harmful but can be easily changed to the "neutral" products carbon-dioxide and water, if desirable.

Mesostructured large-surface silicates are ubiquitous in the environment and are common supports in heterogeneous catalysis. We have chosen a zeolitic model to anchor the uranyl unit. Zeolitic materials act as molecular sieves and can steer the reaction selectivity of organic mixtures. We note that aromatic compounds and nucleic acids, too, can be modified through uranyl-catalysis by C-C benzene ring-opening and by C-O ribose (DNA and RNA) photocleavage. Our proposed oxidation mechanism will give new insight and understanding of the photo-physico-chemical interaction phenomena between uranyl and its environment. In the present work, we have investigated and determined various mechanistic pathways of the methanol oxidation applying state-of-the-art quantumchemical approaches to uranyl-catalyzed model reactions at the levels of the "density-functional approximation" (DFA) and of the ab initio correlated "wave-function theory" (WFT).

THEORETICAL STRATEGY AND OVERVIEW OF THE REACTION MECHANISM

The density-functional approach has been widely used to explore the actinide chemistry, owing to low computational cost and acceptable accuracy in geometric and electronic structure determinations (concerning uranyl as a typical example, see Table S1).⁴⁸⁻⁵² Therefore, we here investigate the photocatalytic mechanisms of methanol oxidation by O_2 at a uranyl-anchored silicate model (Figure 2). We apply DFA and TDDFT (time-dependent density-functional theory) at the scalar-relativistic and spin-orbit coupled levels, in order to elucidate possible photocatalytic excited-state pathways (Scheme 1). The geometry of the silicate structure was optimized by a quantum+classical mechanical hybrid method (QM/MM). The energies of the main structures were then accurately redetermined by a correlated wave function approach (CCSD-(T)). Details of the applied theoretical strategy and computational methods including references are described in the Supporting Information (SI) in Section S1, "Computational Methodology".

The whole catalytic cycle, as emerging from our investigations below, consists of four steps (Scheme 1 and Figure 3): eq 1 represents the photoexcitation and formal *photoreduction of uranyl*(*VI*) by decoupling a dative $U^{+6} \leftarrow O_{ax}^{-2}$ electron pair, yielding formal ${}^{\bullet}U^{+5}$ and "oxygen-centered radical" ${}^{\circ}O_{ax}^{-1}$. The respective MO diagram is shown in Figure 4 (see also Figure S1). Equation 2 describes the *hydrogen activation and transfer* from the organic molecule HROH to the uranylic ${}^{\circ}O_{ax}^{-1}$ centered radical, and the formation of an organic oxyradical HRO[•], or alternatively an Scheme 1. Cyclic Uranyl-Catalytic Photo-Oxidation^a of H-R-OH with O₂

	$[O-U^{+6}-O]^{2+} + hv$	\rightarrow	*[O-'U ⁺⁵ -O'] ²⁺	(1)
:	$[O-U^{+5}-O]^{2+} + HROH$	\rightarrow	$[O-U^{+5}-OH]^{2+} + HRO' \text{ (or 'ROH)}$	(2)
	$\left[\mathrm{O-}^{\bullet}\mathrm{U}^{+5}\text{-}\mathrm{OH}\right]^{2+}+^{\bullet}\mathrm{OO}^{\bullet}$	\rightarrow	$[O-U^{+6}-O]^{2+}$ + HOO'	(3')
	HRO' + HOO'	\rightarrow	$RO + H_2O_2$	(4')
	HRO' + ' OO'	\rightarrow	RO + HOO'	(3")
	$\left[\mathrm{O}\text{-}^{\bullet}\mathrm{U}^{+5}\text{-}\mathrm{OH}\right]^{2+}+\mathrm{HOO}^{\bullet}$	\rightarrow	$[O-U^{+6}-O]^{2+} + H_2O_2$	(4")
Sum (1 to 4):	$hv + O_2 + H-R-OH$	\rightarrow	$H_2O_2 + R = O$	(1 to 4)

"Step 1: reductive photo-excitation of uranyl(VI). Step 2: by a hydrogen transfer, HROH yields an organic radical and hydro-uranyl(V). Bifurcation to steps 3' and 4': at first O₂ oxidizes the hydro-uranyl(V) with back-formation of uranyl(VI); then, H_2O_2 and RO are formed. Or to steps 3" and 4": at first, O₂ reacts with the organic radical forming RO; then, the hydro-uranyl(V) induces the formation of H_2O_2 and back-formation of uranyl(VI).



Figure 2. Geometric structure model, as optimized by a QM/MM hybrid procedure: Equatorially pentacoordinated $[UO_2]^{2+}$ on a hydroxylated SiO₂ layer, bonding also one H₃COH and two H₂O molecules. (a) Top view (note: overlaying OH groups look like HOH). (b) Side view—the ovals indicate the quantum mechanically (QM) treated section (enlarged in Figure 5).

alkyl radical $^{\circ}$ ROH. Either the hydro-uranyl or one of the organic radicals then reacts next. Equation 3' represents a complicated reaction mechanism, where the hydrogen is transferred from the hydro-uranyl to the diradicalic dioxygen molecule O₂, whereby uranyl(VI) is regenerated, and a

hydroperoxyl radical HO_2^{\bullet} is formed,⁶⁰ with spin-recoupling through the HRO[•] radical, in the vicinity of the heavy U atom. In the continuing eq 4 the two radicals form the final reaction products RO and H_2O_2 .

On the alternative path of eqs 3" and 4", at first an H atom is transferred from the HRO[•] radical to the O_2 , forming product RO and intermediate radical HO_2^{\bullet} with spin-coupling through the heavy U atom. Finally, the uranyl is regenerated, and hydrogen peroxide H_2O_2 is formed. In summary, the photoreaction induced by light absorption of uranyl effectively produces radicals which react with each other or with other species. Eventually, the organic and the hydroperoxyl radicals are eliminated by forming a carbonyl RO and a hydrogen peroxide H_2O_2 molecule.

Our nomenclature i through vi for the reacting and intermediate species is displayed in Figure 4 (see also Figure 3). "i" denotes the silicate-adsorbed uranyl; "ii" the equatorial uranyl coordination of a methanol molecule; "iii" a hydrogen atom (either the alcoholic H_0 , or the methylic H_{Me}) transferred from H_3COH to the radicalic ${}^{\bullet}O_{ax}$ of uranyl (see reaction step 2 in Scheme 1, and Figure 6); "iv" a dioxygen molecule being added; "v" a hydrogen atom transferred to the dioxygen; and "vi" a second H atom transferred to HO2• yielding HOOH. The respective transition states are denoted by "ii-iii", "iv-v", and so on. At each step, there are several different options, at ground and electronically excited levels, with singlet (S), triplet (T), or quintet/"pentet" (P) spincoupling, with different order of steps and different H atom transfers. For further specification we use subscripts G and G1 for the electronic ground states of two isomers, and E and E1 for their electronic excited states.

The elucidated reaction mechanism, whereby uranyl groups, being nonexcited or excited by one or two photons, convert one molecule of an alcohol and O_2 into a carbonyl and H_2O_2 , is described below in Figure 12 and the last two sections, the details being presented in the following extended section.

DETAILED RESULTS AND DISCUSSION

Uranyl Photoexcitation (Step 1 in Figure 3). We begin the discussion of the catalytic cycle with the electronic excitation of the coordinated uranyl from state ii_G to ii_E (see Figure 7), assuming that the uranyl is permanently ligated in its equatorial plane to the silica surface (in η^2 fashion) and to two water ligands. At this stage, the VOC species methanol is coordinated in addition. The uranyl unit [OUO]²⁺ remains



Figure 3. Schematic uranyl-catalytic cycle of alcohol (HROH) photo-oxidation by O_2 . (a, left) Step 1: uranyl photoexcitation, $|O \equiv U \equiv O|^{2+} \rightarrow |O \equiv^{\bullet}U =^{\bullet}O|^{2+}$. Step 2: formation of organic and hydro-uranyl radicals, $RO^{\bullet} + |O \equiv^{\bullet}U = O - H|^{2+}$. Steps 3 and the following ones: in a complicated net of reactions (see part b, right), products RO and H_2O_2 are formed through intermediate hydroperoxyl radical (HO_2^{\bullet}), and uranyl restitution (see Scheme 1)—The different species are numbered through as i, ii, etc. (nomenclature explained in Figure 4). Subscripts G and E mean ground and electronically excited states; S_0 , S_1 , T_0 , and T_1 mean lowest singlet (S_0), higher singlet (S_1), lowest triplet (T_0), and higher triplet (T_1) states. (b, right) Net of reactions from step 2 through step 3, similar for both cases of *ROH with C or O centered radicalic electron, *CH₂OH or CH₃O*.

nearly inversion-symmetric and is only weakly symmetrybroken by the fields of the five equatorial oxygen ligands (Figures 2 and 6). The highest occupied MOs (Figure 5, Figures S1 and S2) are of $O_{ax}(2p\sigma_{g,u})$ and $O_{ax}(2p\pi_{g,u})$ type, coordinatively stabilized by admixtures from the uranium valence shell $U(5f\sigma,\pi_u, 6d\sigma,\pi_g)$. The antibonding virtual orbital complements at higher energies are of dominant $U(5f\sigma\pi_u,$ $6d\sigma\pi_g)$ character with some oxygen admixture. In-between are the lowest virtual nonbonding MOs of $U(5f\rho,\delta_u)$ type, where the $5f\rho_u$ ones are a bit higher (Figure S1) due to interaction with the equatorial silicatic oxo-ligands (Figure S2). While free $[OUO]^{2+}$ has U–O distances of 1.72 Å,⁵⁴ equatorial ligation expands the U–O bonds by ca. 0.08 Å, namely, to 1.80(1) Å (Figure 7, ii_G).

The electronic absorption spectrum of the uranyl@zeolite system (Figure S3) with maxima in the wavelength region below 500 nm indicates activity under UV-vis sunlight irradiation. A comparison of our results with experimental⁴⁰ and theoretical literature data (Figure S3 and Table S1) verifies the reliability of the applied DF approximation and also documents the relevance of spin-orbit coupling. The lowestenergy photoexcitations correspond to electronic transitions from the highest bonding orbital of dominant $O_{ax}(2p)$ character to the lowest empty MOs of U(5f) character, $O_{ax}(2p\sigma\pi_u) \rightarrow U(5f\delta\varphi_u)$. They are of ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{3,1}\Delta \rightarrow \Pi_{g}$ "symmetry-forbidden" type, becoming "allowed" by U(5f) spin-orbit coupling and by coordinative and vibrational geometry-deformations. The lower excited levels become also populated from the higher UV-excited levels by intersystem coupling. They have some finite lifetime and cause the common uranyl luminescence.

The formal charge and oxidation state of U is photoreduced from $U^{+6}(5f^0)$ to ${}^{\bullet}U^{+5}(5f^1)$, while the originally closed-shell

O⁻² ions are partially photo-oxidized, $[^{-2}|O≡U^{+6}≡O|^{-2}]^{2+} + hv \rightarrow [^{-2}|O≡^{0}U^{+5}=^{\circ}O|^{-1}]^{2+} \leftrightarrow [^{-1}|O^{\bullet}=^{\bullet}U^{+5}≡O|^{-2}]^{2+}$. The U—O bonds are weakened and expand by another ca. 0.06 Å to 1.86 Å (Figure 7, ii_E). The excited *[OUO]^{2+} species has [•]uranium [•]oxygen diradicalic character, where the O-centered radical [•]O⁻¹ can efficiently activate bonded hydrogens in the neighborhood.¹

Excited Uranyl Breaks an O–H or C–H Bond (Step 2 in Figure 3). There is vast empirical evidence, and it is theoretically expected, that photoexcited diradicalic uranyl ions attract hydrogen atoms.^{11–13,24,27,28,32–39} Therefore, stage 2 of the reaction cycle is the H-transfer process from methanol to $*[O_{ax}-{}^{\bullet}U-{}^{\bullet}O_{ax}]^{2+}$. Owing to the well-documented equatorial oxophilicity of uranyl, the VOC-molecule methanol is bonded with its oxygen in the equatorial plane of uranyl, and either its hydroxylic (H_O) or its methylic hydrogen (H_{Me}) can be transferred, as shown in Figures 6 and 7.

The energies of the reaction paths for H_O transfer are shown in Figure 8. Since the inversion symmetry of the H-uranyl unit becomes strongly broken, we omit the g, u symmetry indices from now on. With increasing photoexcitation energy, the reaction barriers happen to become lower. Further, the vibrational energy in the lower electronically excited states, populated by intersystem crossing from the higher ones, provides additional energy to overcome the barriers of the ii_E to iii_E H-transfer reactions. The ground-state reaction from ii_G to iii_G with a higher barrier is known to occur only at elevated temperatures (i.e., above 400 K).⁴⁰

Different hydrogen transfers from methanol to uranyl are displayed in Scheme 2. Equation 6 represents the H_0 transfer to ground-state uranyl. Equations 2' and 5 represent H_{Me} and H_0 transfers to photoexcited uranyl. Equation 6 yields ground-

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Reaction	Spin	Basic	Transition	Spin
Species ^{a)}	Mult. ^{b)}	Struct. ^{c)}	State	Mult.
i	1	O _{ax} =U=O _{ax}		
iio	1	Oax=U=Oax	lla-lila	1
IIG		Н₃Со́Н	IIG-IIIG	
	3	Oax=U [•] -•Oax		2
IIE		Н₃СО́Н	115-1115	5
	1	O _{ax} =U_O _{ax} H	II. III. .	3
IIIG		H₃CÓ	IIE-IIIE1	
	3	O _{ax} =U [•] –O _{ax} H		
IIIE		H₃CO.		
	3	O _{ax} =Ų⁺–O _{ax} H	•	(1),3
IIIE1		H₂ · COH	IVG-VG	
ivg	3	O _{ax} =U–O _{ax} H		(1),3
		H₃CO Oʻ='O	IVG-VG1	
	1,3,5	O _{ax} =U⁺-O _{ax} H		1,(3)
İVE		H₃CO' O'='O	İVE-VG	
	1,3	O _{ax} =U⁺–O _{ax} H		
VG		н₂со ∙о-он	İVE-VG1	1,(3)
		O _{ax} =U=O _{ax}		
VG1	1,3	Н₃СОО-ОН	VG-VİG	1
	1	O _{ax} =U=O _{ax}		_
VIG		H₂CO HOOH	VG-VIE	3
	_	Oax= U'-'Oax		
VIE	3	H₂CO HOOH	VG1-VIG	1
		O _{ax} = U=O _{ax}		3
VİE1	3	H ₂ C''O HOOH	VG1 -Vİ E1	

Figure 4. Nomenclature of stable and metastable species and transition states. (a) Reaction species are numbered through from initial i to final vi. Subscripts: G = ground state, G1 = higher energy state of ground state structure; E and E1 = lowest and higher energy electronically excited states. (b) Spin multiplicity: 1, 3, and 5 for singlets (S), triplets (T), and quintets (=Pentets, P). (c) The "permanent" equatorial ligands of uranyl, namely, the two silica surface groups (>SiO⁻) and the two H₂O ligands, are shown neither here nor in several figures below, in order to avoid overloading.

state products, while eqs 2' and 5 at first reach some higherenergy minimum, from where internal energy conversion leads to product ground-state (iii_G), as shown in Figure 9.

After the transfer of the methoxy- H_O to the excited uranyl complex, the originally multiple $U-O_{ax}$ bond is expanded from 1.86 to 2.14 Å (Figure 7, ii_E to iii_E), corresponding to a strong U-O single bond. Pyykkö's⁵⁵⁻⁵⁷ covalent bond radii increments of U and O predict U-O triple/double/single bond distances around 1.7/1.9/2.3 Å. The spin-density plot (Figure 7, iii_E) shows unpaired electrons in U(5f δ) and O(2p π) type orbitals (the oxygen spin is distributed over the whole methoxy unit). If a methyl-H_{Me} is transferred, the unpaired electron density moves to a C(2sp³) hybrid orbital with only a little oxygen admixture (Figure 7, iii_E). The reaction paths for H_O



Figure 5. Qualitative orbital energy level scheme of uranyl (middle), on the left the U(5f6d) valence shells, and on the right the two $O_{ax}(2p)$ valence shells. Despite (weak) perturbation by the equatorial ligands, we use unperturbed D_{ooh} nomenclature (Sf $\sigma_{uv} \pi_{uv} \delta_{uv} \varphi_u$ and 6d $\sigma_{ev} \pi_{vv} \delta_{ev}$) for simplicity.⁵³



Figure 6. Central cluster model, corresponding to the oval sections in Figure 2, treated quantum mechanically. The uranyl unit $[O_{ax}UO_{ax}]^{2+}$ is equatorially pentacoordinated, permanently to two H₂O molecules and in η^2 -fashion to an $[(OH)_4Si_2O_3]^{2-}$ disilicate group (derived from the QM/MM optimization of the silicate slab), and to the reacting organic species (HOCH₃ = H_OO_{Me}CH₂H_{Me}). The two possible hydrogen transfer pathways are indicated by bent arrows.

transfer on the various excited potential energy surfaces all end up at very similar geometric structures of iii_E .

Concerning the potential energy surface crossings sketched in Figure 9, the S_0-S_1 states form a connected surface with the conical intersection in the many-dimensional configuration space. The T_1 surface becomes also connected to it through spin-orbit coupling. Accordingly, the excited system can change over to the ground state without radiation at $U-O_{Me}$ distances around 2.9 and 2.5 Å, respectively, whereby the $U(Sf\delta)$ and $O(2p\sigma,\pi)$ electrons become paired again. The energy surface crossings in the regions of the red circles induce radiationless $S_1 \leftrightarrow S_0$ and $T_1 \leftrightarrow S_0$ transitions that can provide thermal energy for the next reaction steps.

Experimental EPR investigations of $*UO_2^{2+}$ in liquid methanol detected both H_3CO^{\bullet} and $^{\bullet}CH_2OH$ radicals, 12,32,34 while no radicals were found upon irradiation of silicate-



Figure 7. Mechanistic model for the hydrogen transfer from H_3COH to O_{ax} of $[UO_2]^{2+}$: $H_{(O)}$ transfer in the bottom row for the ground state, and in the upper top row for the electronically photoexcited state of ${}^3(O_{ax}2p\sigma \rightarrow U-5f\delta)$ type, $H_{(Me)}$ transfer to excited uranyl in the lower top row. Some spin-density contour envelops are shown in blue in the top-left corners of some of the rectangles. ii, ii–iii, and iii indicate the initial, transition, and final states of the hydrogen transfer reactions (also see Figure 12 below), with G and E subscripts for the ground and excited states, respectively. Colors of the atomic cores: blue, U; red, O; dark-gray, Si; light-gray, C; white, H; the tube-and-knob models represent the two spectator-ligand water molecules. The numbers are the bond lengths in Å.

adsorbed uranyl alone.^{40,41,58} However, when the electron of ${}^{\bullet}O_{ax}{}^{-1}$ is coupled with a hydrogen atom ${}^{\bullet}H$ forming an $O_{ax}-H$ bond, a surviving electron on ${}^{\bullet}U^{5+}$ was detected.³⁵ Another experimental study could not detect radicals,⁴¹ however, which we here interpret as due to subsequent radiationless $S_1 \leftrightarrow T_1$ transitions.

Reactions of Radicals ${}^{\bullet}[UO_2H]^{2+}$ and ${}^{\bullet}(RHO)$ with Molecular Oxygen (Step 3 in Figure 3). Although the ${}^{\bullet}O_2{}^{\circ}$ dioxygen molecule is a diradical, it is not particularly reactive. This has been explained as due to strong static MO correlation, or VB resonance, of the $\pi_u{}^4\pi_g{}^{*2}$ triplet state.⁵⁹ However, ${}^{\bullet}O_2{}^{\circ}$ can be effectively attacked by the $[OU^{\bullet}OH]^{2+}$, ${}^{\bullet}ROH$, or HRO ${}^{\bullet}$ radicals (Schemes 1 and 3, Figures 3b and 10). With adsorbed dioxygen, iii_G(S₀)CH₃O– $[OUOH]^{2+}$ transforms to iv_G(T₀), and iii_E(T₁) CH₃O ${}^{\bullet}...*[OU^{\bullet}OH]^{2+}$ transforms to iv_E(S₁, T₁, Q₁), from where two reaction paths start. The other cases with ${}^{\bullet}CH_2OH$ instead of CH₃O ${}^{\bullet}$ are considered below.

Reactions 7 and 8 in Scheme 3 yield ground or excited state uranyl, the $^{\circ}OOH$ and $^{2}[O^{\circ}U^{+5}OH]^{2+}$ radicals as intermediates, and $H_{2}O_{2}$ and $H_{2}CO$ in their ground states as products. Reactions 9 and 10 yield ground-state uranyl, the two radicals $^{\circ}OOH$ and $^{\circ}OCH_{3}$ as intermediates, and again $H_{2}O_{2}$ and H_2CO as products (in its ground or excited triplet state ${}^{3}H_2CO^*$).

Reaction 7 is the ground-state transfer of H_{Me} from the *methyl* group to O_2 , i.e., from iv_G via $iv_G - v_G$ to v_G (Figure 10). The transition state $iv_G - v_G$ shows a single imaginary frequency of 1423 cm⁻¹ corresponding to the high activation barrier. The U-O_{Me} distance increases by 0.13 Å, and the C-O_{Me} distance decreases by 0.08 Å. The Mulliken atomic spin-populations (Table S2) of $iv_G - v_G$ are 0.72, 0.58, and 0.50 on O_a , O_b , and the methyl C atom, respectively, corresponding to 0.7 e charge transfer from methanol to O_2 , accompanying the H atom transfer. The reduced C-O_{Me} distance of 1.24 Å in the slightly cationic methoxy group of v_G indicates C=O double bond character, while the large equatorial U···O_{Me} distance of 2.53 Å implies a soft coordination bond.

The respective reaction from *excited state* iv_E also leads to ground state v_G . Structure iv_E with 3O_2 yields energetically near-degenerate singlet (S_1) , triplet (T_1) , and quintet (Q) states (Figure S6), with spin-populations of 1.02 and 0.98 on O_a and O_b of O_2 , and of 1.10 and 0.90 on U and O_{Mer} , respectively (see Table S2 and Figure 10, top right). While there may occur radiationless transitions iv_E $(S_1, T_1, Q) \rightarrow iv_G$ (T_0) , the reaction can start from excited state iv_E , if the lifetime



Figure 8. H_O-transfer from the hydroxyl group of H₃COH_O to one O_{ax} of $[O_{ax}UO_{ax}]^{2+}$: Energy profiles (in eV; form KS-DFA and TDDFT approximations) for different electronic states vs the H_O- O_{ax} distance (in Å, the initial state is on the left side). The geometries are optimized along the reaction paths, projected crossings corresponding to somewhat different substructures. The near-degeneracy of various excited states for small O_{ax} -H_O distances on the right is indicated by an ellipse.

of iv_E is long, and the reaction is fast enough. A theoretically approximated reaction path is shown in Figure S6. Under light irradiation, there is a dynamic equilibrium of iv_G (T_0) \leftrightarrow iv_E (S_1 , T_1 , Q). Since the energy of iv_E is above the ground state reaction barrier $iv_G - v_G$, the reaction should occur spontaneously.

The atomic spin-populations of the ground-state species v_G (S_0 , T_0) containing the $[OU^{\bullet}OH]^{2+}$ and ${}^{\bullet}O_bO_aH$ radicals are mainly centered on U (1.13) and on O_b (0.78); the triplet and singlet couplings of the two radicals have nearly the same energies and populations. The imaginary frequencies of the lower and higher barrier transition states $v_G - vi_G$ (S_0) and $v_G - vi_E$ (T) are 848i cm⁻¹ and 1753i cm⁻¹, respectively. The paths of the singlet and triplet reactions 8a,b are shown in Figure S7. They have nearly the same energies for $O_a - H_O$ distances from 2.8 Å down to 1.6 Å. The singlet (and triplet) path with lower (and higher) barrier ends at the ground (and excited) state of



Figure 9. Cuts through the potential energy surfaces (in eV) of the $[O_{ax}UO_{ax}H]^{2+} \leftarrow OCH_3$ complex along the $R(U-O_{Me})$ coordinate (in Å) for ground state S_0 ($\sigma^2 f^0$) and lowest excited states T_1 and S_1 ($\sigma^1 f^1$, scalar-relativistic KS-DFA, and TDDFT approximation). The energy surface crossings in the regions of the red circles induce radiationless $S_1 \leftrightarrow S_0$ and $T_1 \leftrightarrow S_0$ transitions that can provide activation energy for the next reaction steps.

uranyl. The reaction yields ${\rm UO_2}^{2+}$ and ${\rm H_2O_2}$, whereby the catalytic cycle is finished.

On the other alternative reaction path, O_2 first oxidizes the hydro-uranyl. When the H_O is transferred from the *uranyl* oxygen to O_2 in reaction 9 from iv_G via iv_G-v_{G1} to v_{G1} (Figure 10), the "upper" $U-O_{ax}$ length shrinks by 0.15 Å, while the equatorial $U-O_{Me}$ length expands by 0.3 Å. The transition state iv_G-v_{G1} on the triplet ground state potential surface is again characterized by a large imaginary frequency of 1405i cm⁻¹. The original ${}^{3}O_2$ unit in $iv_G(T_0)$ has spin-populations of 1.0 on both O_a and O_b atoms, while in the transition state $iv_G - v_{G1}$ the spin-populations are 0.51, 0.51, and 0.80, respectively, on O_a , O_b , and O_{Me} , and in product v_{G1} 0.83 and 0.31 on ${}^{\circ}O_bO_aH$, and 0.74 on ${}^{\circ}OCH_3$, respectively. Another possible reaction leads from excited state iv_E via transition state iv_E-v_{G1}

Scheme 2. Transfer of an H_0 (Eqs 2' and 6) or an H_{Me} (Eq 5) from Methanol to Uranyl in the Ground State (Eq 6) or Excited State (Eqs 2' and 5)

HCH ₂ OH + *[UO ₂] ²⁺ iie(T ₁)	$\rightarrow \stackrel{^{\bullet}\mathrm{CH}_{2}\mathrm{OH} + [\mathrm{OU}^{\bullet}\mathrm{OH}]^{2+}}{\mathrm{iii}_{E1}(T_{1})}$	(5)
(H transfer from C	H ₃ to excited Uranyl)	
HCH ₂ O H + *[UO ₂] ²⁺ iie(T 1)	$\rightarrow \begin{array}{r} CH_{3}O' + [OU'OH]^{2+} \\ iiie(T_{1}) \end{array}$	(2')
(H transfer from C	OH to excited Uranyl)	
HCH2O H + [UO2] ²⁺ iig (S 0)	$ \begin{array}{c} & & \\ & & \\ \hline & \\ \rightarrow & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$	(6)

(H transfer from OH to Uranyl ground-state)

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Scheme 3. Reaction Mechanism for the Oxidation of the Methoxy Anion on the Lower-Energy Potential Surface O₂ first oxidizes CH₃OH via Low Energy High Activation Path I

$${}^{1}(CH_{3}O)^{1-}{}^{1}[OU^{+6}OH]^{3+} + {}^{3}(O_{2})^{0} \rightarrow {}^{1}(OCH_{2})^{0} + {}^{2}[O \cdot U^{+5}OH]^{2+} + {}^{2}(\cdot OOH)^{0}]$$
(7)
iv_G(T₀) v_G(S,T₀)

$${}^{2}[O^{\bullet}U^{+5}OH]^{2+} + {}^{2}(\bullet OOH) \rightarrow {}^{1}[OU^{+5}O]^{2+} + {}^{1}(HOOH) \downarrow$$
(8a)

or
$${}^{2}[O^{\bullet}U^{+5}OH]^{2^{+}} + {}^{2}(^{\bullet}OOH) \rightarrow {}^{3}[O^{\bullet}U^{+5}O^{\bullet}]^{2^{+}} + {}^{1}(HOOH)$$
 (8b)

$$\Sigma: H_3COH + {}^{1}[OUO]^{2^+} + {}^{3}O_2 \longrightarrow {}^{1}(H_2CO) + {}^{1}[OUO]^{2^+} \text{or } {}^{3}[OUO]^{2^+} + HOOH \quad (2^+7+8)$$

O₂ first oxidizes ²[O[•]UOH]²⁺ via High Energy Level Path II

$${}^{2}[OU^{+5}OH]^{2+}\cdots^{2}(OCH_{3})^{0} + {}^{3}(O_{2})^{0} \rightarrow {}^{1}[OU^{+6}O]^{2+} + {}^{2}(\bullet OCH_{3})^{0} + {}^{2}(\bullet OOH)^{0}$$

$$iv_{E}(S,T_{1}) v_{G1}(S,T_{0})$$

$${}^{2}(\bullet OCH_{3}) + {}^{2}(\bullet OOH) \rightarrow {}^{1}(HOOH) + {}^{1}(O=CH_{2}) \qquad (10a)$$
or
$${}^{2}(\bullet OCH_{3}) + {}^{2}(\bullet OOH) \rightarrow {}^{1}(HOOH) + {}^{3}(O^{-}CH_{2}) \qquad (10b)$$

$$\sum : H_3 COH + {}^3[OUO]^{2+} + {}^3O_2 \longrightarrow {}^1(H_2 CO) \text{ or } {}^3(H_2 CO) + {}^1[OUO]^{2+} + HOOH (2'+9+10)$$

to v_{G1} (see Figure S6; reaction 9' in Scheme 3). The reaction from excited state iv_E to ground state v_{G1} is preferred to that from ground sate $iv_{G'}$ if it has reasonably long lifetimes of the excited state.

Furthermore, reactions may continue with reactions 10a or 10b from v_{G1} (S₀, T₀), the complex $H_3CO^{\bullet}[UO_2]^{2+}HO_aO_b^{\bullet}$, via $v_{G1}-vi_G$ (S, T) to vi_G (S), or via $v_{G1}-vi_{E1}$ (S, T) to vi_{E1} (T), as shown in Figure 10 and Figure S8. The spin-populations of v_{G1} are mainly centered on O_{Me} (0.91), and on O_b (0.70). On the reaction path from v_{G1} to vi_{E1} (T), the CH₂O is endothermally formed in the excited triplet state, with spindensity and a C–O single-bond distance of 1.36 Å. The imaginary frequency at transition state $v_{G1}-vi_{E1}$ is 1793i cm⁻¹, while for the lower path at $v_{G1}-vi_G$ it is only 960i cm⁻¹. The two reaction paths are again near-degenerate for O_b-H_{Me} distances from 2.7 down to 1.5 Å, where they begin to separate (Figure S8).

ENERGETIC ASPECTS OF THE REACTION CYCLE

We discuss the quantum-chemically determined reaction and activation free energies of the various reaction steps as displayed in the upper part of Figure 12. The respective chemical structures are shown in the lower part of Figure 12. Our Kohn-Sham density-functional and ab initio coupledcluster energies (with standard deviations of 0.3 eV) are listed in Figure 11. The lowest vertical and adiabatic excitation energies of uranyl complex ii are 2.37 (2.80) and 2.07 (2.54) eV, respectively [vertical and adiabatic B3LYP-DFA; in parentheses vertical EOM-CCSD(T) and adiabatic CCSD-(T)]. The experimental adiabatic value is 2.61 eV, showing a minor error of 0.1 eV for the ab initio approach, and 1/2 eV for the DFA. Concerning the reactants, transition states, intermediates, and products, the DFA estimates scatter by a few 0.1 eV around the closed-shell CCSD(T) and open-shell UCCSD(T) energies. Inasmuch as some species are of multiconfigurational type, the CC (as well as the DFA) calculations of single-reference type are less reliable, in some of these cases. Therefore, we have rounded all energies (in eV) in Figure 11 to one digit after the decimal point.

The barriers of the consecutive hydrogen-atom transfers from the organic hydroxy and methyl groups to the axial uranyl atoms and the O_2 molecule are rather large on the ground state energy surface, namely, 1.2 eV (1.5 eV) and 1.4 eV (1.3 eV). Methanol oxidation without irradiation has indeed been observed only upon thermal activation above 200 °C.⁴⁰ On the lowest excited energy surface, the barriers are much smaller, 0.88 eV (1.1 eV) and 0.1 eV (0.2 eV), respectively. In the first step, the lowest vertical photoexcitation to ${}^{3}\Delta_{g}$ - $[O \equiv U_{f\delta} = O_{2p\sigma}]^{2+}$ in the visible supplies some 0.3 eV (0.26) eV) relaxation energy, while the higher near-UV excited ${}^{1}\Delta_{g}$ and the ${}^{3,1}\Phi_{\rm g}({
m O}_{2
m p\sigma}
ightarrow{
m U}_{
m f arphi})$ states provide more energy to overcome the barrier directly. The photoexcited states were determined by applying the TDDFT approach, using B3LYP or SAOP functionals and the spin-orbit coupled relativistic ZORA approach as implemented in the ADF quantumchemical package.⁶⁵ In Figure 8, we had also considered the next higher ${}^{3}\Pi_{g}(O_{2p\pi} \rightarrow U_{f\delta})$ state with an even lower barrier.

The calculations show significant *spin*-density at the U atom upon visible and near-UV absorption (Table S2), corresponding to formal ${}^{\bullet}U^{+5}$ and ${}^{\circ}O^{-1}$ atoms. However, the *charge* density distribution and the effective atomic partial charges change only a little upon photoexcitation. Apparently, one of the pair-bonds is broken, $U\equiv OI \rightarrow U^{\bullet}={}^{\circ}OI$, basically changing the spin-coupling and the two-electron distribution. The unpaired electron density on the U atom is spatially rather contracted due to the nature of 5f orbitals and does not play a big role in the subsequent reactions of the organic ligand that is weakly bound in the equatorial plane of the uranyl due to U-6d overlap. However, the open-shell character of the formal monovalent ${}^{\circ}O^{-1}$ atom makes excited uranyl very electronattractive, as is well-known experimentally,⁶⁰ and eases the transfer of a H atom that was bound before in methanol.

The states of the intermediate complex iv, $H_3CO-[OUOH]-O_2$ on silicate, form the starting point of a complex reaction network (Figure 12), also including radiationless transitions and absorptive re-excitations, and conversions between °CH₂OH and CH₃O° (a previous study showed an activation barrier around 0.65 eV).⁶¹ However, some experimental studies revealed no EPR signals in such



Figure 10. Regeneration of $[UO_2]^{2+}$ and oxidation of the CH₃O group. Spin-density contours are shown in the upper left corners of some of the boxes.

heterogeneous systems, while both $^{\circ}CH_2OH$ and CH_3O° signals were detected in homogeneous solution.^{40,41} Obviously, the pinning at the silicate surface conserves the complex and eases the energetic stabilization of the [OU[•]OH] CH₃O[°]/ $^{\circ}CH_2OH$ radical pairs in singlet-coupled form. One also can expect that the abundant O₂ molecules in heterogeneous systems easily oxidize the [OU[•]OH], CH₃O[°], and $^{\circ}CH_2OH$

radicals to [OUOH], H₂O, and CO₂, along the reaction path $ii_G \rightarrow ii_E \rightarrow iii_E \rightarrow iv_{G/E} \rightarrow v_G \rightarrow vi_G$ (Figure 12). Based on our theoretical model, we predict that easy coupling of unpaired electrons and the resulting short lifetime of the radicals make them difficult to be observed in the heterogeneous system. Such a prediction is consistent with experimental observations. In ref 40, it was mentioned that the catalytic oxidation reaction

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Species 1)		İİE	TS ii _e -iii _e	E a ²⁾	iii _E ~iv _E	TS iv _g -v _{g1}	Ea	V _{G1}	TS v _{G1} -vi _G	Ea	
$\Delta F / eV$	DFA CC	- 0 - - 0 -	0.75 1.15	0.8 1.1	-0.2 -0.45	-0.1 -0.3	<0.1 0.2	-0.4 -0.7	-0.1 -0.3	0.3 0.35	
Species 1)		İİG	TS ii _g -iii _g	Ea	iii _G ∼iv _G	TS iv _G -v _G	Ea	VG	TS v _G -vi _G	Ea	vi _G
$\Delta F / eV$	DFA CC	-2.1 -2.6	-0.9 -1.1	1.2 1.5	-1.6 -1.65	-0.2 -0.35	1.4 1.3	-1.7 -2.0	-1.1 -1.25	0.6 0.75	-2.3 -3.2

Figure 11. Relative free energies (ΔF , in eV; 1 eV \approx 96.5 kJ/mol) and Activation Barriers with respect to the previous minimum (E_a), from scalar relativistic B3LYP-D3 density-functional approximations (DFAs) and ab initio EOM-CCSD(T) theory (CC), both with thermal corrections from DFA. ¹⁾ For nomenclature of the species, see Figure 4. ²⁾ For activation by the lowest visible-light excited state.



Figure 12. Relative free energies (in eV; from scalar-relativistic density-functional approximations) of reactant, intermediate, and product species of (photo)catalytic methanol oxidation at UO_2^{2+} @silicate. (The nondisplayed physical SCF adsorption energy of O_2 is -0.2 eV. The hydrogen bonding energy between the H_2O_2 and the $H_2CO-[UO_2^{2+}]$ is -0.62 eV and has been subtracted from v_{iG} .)

of CH₃OH occurs above 400 K without photoabsorption. This is consistent with a reaction path $ii_G \rightarrow iii_G \rightarrow iv_G \rightarrow v_G \rightarrow vi_G$ on the ground-state potential energy surface.

The ubiquitous dioxygen is bonded through a hydrogen bond of 2.0 Å length with an adsorption energy of ca. -0.2 eV. As discussed in previous sections, there are two broad options

for the order of hydrogen transfers and uranyl(VI) regeneration, from the two species $iv_{G,E}$ to the end point of species v_{i_G} (Figure 12). The pathways in blue start (i) from the triplet iv_G (T_0) $\rightarrow iv_G - v_{G1} \rightarrow v_{G1}$ (T_0 , S_0) with a large barrier of ~1.48 eV (~1.37 eV) and a significant endothermicity of ~+1.21 eV (+0.95 eV), which might be overcome only if previous energy gain is available in direct connection; or (ii) from the iv_E state during its lifetime or after an additional red-light absorption of the iv_G state, with negligible barrier. The first result is the regeneration of $[UO_2]^{2+}$, followed by final oxidation of H_3CO^{\bullet} to H_2CO . The barriers of this last step at the v_{G1} - v_{i_G} singlet and v_{G1} - v_{i_E1} triplet states are, respectively, 0.3 eV (0.35 eV) and 1.25 eV, indicating the reaction possibility for the singlet state.

The other pathways (in red in Figure 12) begin with the oxidation of CH_3O^{\bullet} via $iv_G(T_0) \rightarrow iv_G - v_G \rightarrow v_G (T_0, S_0)$ with a barrier of 1.4 eV (1.3 eV) and slight exothermicity of -0.1 eV (-0.35 eV). The same argument for reaction possibility via the photoexcited state applies as above. The final steps lead to the regeneration of $[UO_2]^{2+}$, via the v_G -vi_G singlet transition state with a barrier of 0.6 eV (0.75 eV), while the v_G -vi_E triplet transition state has a too high barrier of 1.65 eV. For both red and blue pathways, an early transition to singlet states is preferred.

CONCLUSIONS AND PROSPECTS

The reaction mechanism of oxidation of methanol by O_2 at ambient conditions, triggered photocatalytically by excited uranyl, has here been elucidated in detail. The catalytic cycle can be split up into three comparatively simple steps i–iii and a final complex network (iv).

(i) Composing the reacting complex: A methanol molecule coordinates at a silicate-attached diaquo-uranyl unit in its equatorial plane forming a common pentacoordinated structure. Also, a dioxygen molecule may be adsorbed in the neighborhood. Now, the complex requires uranyl photoexcitation to react.

(ii) Uranyl photoexcitation (left side of Figure 13): The functional uranyl complex harvests a visible or near-UV light photon (<500 nm, Figure S3) and jumps to one of its low-lying excited states of ${}^{1,3}\Phi_g$, Δ_g (O-2p $\sigma_u \rightarrow U$ -5f φ_u , δ_u) or ${}^{1,3}\Pi_g$ (O-2p $\pi_u \rightarrow U$ -5f δ_u) type. Stronger absorption occurs at the higher energies, whereby vibrational energy can be gained for enhanced reactivity. The essence is photo-oxidation of the



Figure 13. Sketch of ground and excited state reaction paths for the uranyl-catalyzed methanol oxidation.

uranyl oxygen O(II) to radicalic oxygen $^{\circ}O(I)$ with simultaneous formal reduction of U(VI) to $^{\bullet}U(V)$. This process has sometimes been labeled as photoinduced ligandto-metal charge transfer (LMCT). However, the main point is electron-spin decoupling of a Lewis electron pair, while there is little charge-density reorganization on the uranyl. The rather long-lived excited *uranyl possesses two electrons in two orbitals, one being of compact $^{\bullet}U^{+5}(Sf)^{\bullet}$ type, and the other of $^{\circ}O_{ax}^{-1}$ type with strong oxidative power of the hole in the O-2p shell. We note the trend from very short-lived excited p-

block (main group) compounds, to medium short-lived excited d-block (transition metal) complexes, to long-lived excited fblock compounds (lanthanides and actinides). The f-element compounds may play an important role in designing photocatalysts possessing significant lifetime of electron—hole separation.

(iii) Hole-driven hydrogen transfer (HDHT) (right side of Figure 13): The key point is that the monovalent $^{\circ}O_{ax}^{-1}$ atom of *uranyl attracts a single electron, that is, an atom supplying it. To get the reaction rolling, a H gets abstracted from the methanol molecule, either from the hydroxyl group or from the methyl group (see Figure 11). H₃CO° or $^{\circ}$ CH₂OH then remains as intermediate species.

(iv) The final steps in the reaction network of organic molecule didehydrogenation and dioxygen dihydrogenation lead to $[UO_2]^{2+}$ recovery, in various orders: The hydrogen of $*[O^{\bullet}UOH]^{2+}$ can be transferred to ${}^{\bullet}OO^{\bullet}$, which is usually rather inactive at ambient conditions, forming reactive ${}^{\bullet}OOH$. Eventually, $[UO_2]^{2+}$, H_2O_2 , and H_2CO are obtained.

In summary, under the action of light at ambient conditions, $CH_3OH + O_2$ at uranyl-silicate surfaces form H_2CO and H_2O_2 with intermediate radicalic species HOO[•] and H₃CO[°] or $^{\circ}$ CH₂OH. With final products CO₂ and H₂O, uranyl@zeolite has the potential as a powerful green photocatalyst for cleaning the air. The porous sizes of the support materials acting as a molecular sieve can be exploited to control the selectivity for different applications. The present elucidation of the various pathways provides insight when searching for possible applications that can make profitable use of nuclear waste. Concerning the biological aspect, our studies also provide insight into the photochemical interaction of uranyl with biological molecules, such as uranyl triggered photocleavage of DNA. The wide availability of the depleted uranium and the special photocatalytic properties of uranyl compounds make it possible to carry out visible-light photocatalysis. The present work might provide insights for developing f-block-element photocatalysts with far longer-lived excited states than the dblock-element compounds (such as TiO₂) ever achieved. Because of the well-defined active center and surrounding atomic structures, this kind of actinide photocatalysts can serve as highly efficient visible-light single-atom catalysts with longlived excited states of actinide atoms at the core of the active sites.^{62–64}

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00388.

Computational methodology and software references, molecular orbital energy scheme and orbital envelop plots of the uranyl complex, predicted and observed UV-vis absorption spectra of the uranyl complex, energy profiles of various reaction steps, uranyl cation: U-O bond lengths and lowest vertical electronic excitation energies, and atomic charges and spin-populations at various stationary states (PDF)

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Notes

The authors declare no competing financial interest.

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