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# Infrared spectroscopic and theoretical study of the reactions of cerium atoms with methanol in solid argon

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ABSTRACT

Reactions of cerium metal atoms with methanol are investigated using matrix isolation infrared absorption spectroscopy and density functional theoretical calculations. Upon reaction of the ground state cerium metal atoms with methanol, the insertion intermediate $CH_3OCeH$ is formed spontaneously on annealing in solid argon. Further sample annealing allows the reaction of $CH_3OCeH$ with another methanol molecule to form $H_2$ and $Ce(OCH_3)_2$. The divalent $Ce(OCH_3)_2$ molecule can further isomerize to the more stable tetravalent $CH_3OCe(O)CH_3$ isomer under UV–visible irradiation. The product species are identified via isotopic substitutions and vibrational frequency calculations.



## 1. Introduction

Methanol has promising application in direct methanol fuel cells (DMFC) and is widely viewed as a renewable alternative to petroleum-based hydrocarbons. Of particular importance is the direct reforming of methanol into hydrogen [1]. As metals are often used as catalysts for the chemical transformation of methanol, it is vital to understand the interactions of methanol with metal centers at the molecular level [2]. A number of investigations on methanol reactions with main group, transition metal, and actinide metal atoms as well as metal oxide molecules have been carried out using matrix-isolation infrared spectroscopy [3–16], a powerful method for depicting reaction mechanisms through the isolation and characterization of reactive intermediates [17–20]. Both the O—H and C—O bond insertion molecules have been diagnosed as major reaction products. We recently found that reactions of early transition metals (Sc, Ti, V, Nb) with methanol led to facile formation of $H_2$ molecules [11]. This approach provides a simple and convenient pathway for producing hydrogen from methanol, a process that is of particular interest in fuel industry. Recent matrix isolation infrared spectroscopic investigations revealed that actinide (U) metal atoms could also react with two methanol molecules in solid argon to produce the divalent $U(OCH_3)_2$ product with one $H_2$ molecule released [12].

The reactions involving lanthanide metals exhibit unique trends across the whole lanthanide series because of the presence of 4f electrons [21–26]. Reactions between lanthanide cations from $La^+$ to $Lu^+$ (except $Pm^+$) and methanol molecules and clusters were studied in the gas phase using mass spectrometric methods. The majority of the lanthanide cations react exothermically with the methanol molecules, forming the dehydrogenation products. The study of the reaction sequences and of the corresponding kinetics showed the existence of important difference in the relative reactivity of the lanthanide series cations [27,28]. Recently, the reactions of late lanthanide metal atoms with methanol were studied using matrix isolation infrared spectroscopy [10]. It was shown that the reactions of Dy through Yb and methanol initially produced the $Ln(CH_3OH)$ complexes spontaneously upon annealing, which isomerized to the $CH_3OLnH$ insertion products on visible light excitation. In addition, the Tb and Lu atoms could react with two methanol molecules to form the divalent $Ln(OCH_3)_2$ products spontaneously. In this paper, we report a combined matrix isolation infrared spectroscopic and theoretical investigation on the reaction of early lanthanide metal cerium atoms with methanol. Among the lanthanides, cerium is somewhat special because the easy conversion between trivalent and tetravalent Ce in chemistry. We will show that the reaction proceeds spontaneously on annealing to form the $CH_3OCeH$ insertion intermediates, which can react further with another methanol molecule to give

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the dimethoxyl cerium molecule $Ce(OCH_3)_2$. This molecule can further isomerize to the more stable tetravalent Ce(IV) complex of $CH_3OCe(O)CH_3$ under photo-excitation. Theoretical studies show that these divalent Ce species has a triplet ground state with bent structure, while the tetravalent Ce species has a singlet state with a tetrahedral local coordination. The difference of tetravalent Ce and other trivalent lanthanides in reactivity towards methanol underscores the importance of oxidation states in heavy-element chemistry [29,30].

## 2. Experimental and theoretical methods

The cerium atoms were prepared by pulsed laser evaporation of bulk cerium metal targets. The experimental setup for pulsed laser evaporation and matrix isolation infrared spectroscopic investigation has been described in detail previously [31]. Briefly, the 1064 nm Nd:YAG laser fundamental (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width) was focused onto a freshly cleaned metal target (Johnson Matthey) through a hole in a CsI window cooled normally to 6 K by means of a closed-cycle helium refrigerator. Laser-evaporated metal atoms were co-deposited with methanol in excess argon onto the CsI window. The methanol/argon mixtures were prepared in a stainless steel vacuum line using standard manometric technique. Isotopically labeled $^{13}CH_3OH$ (Isotec, 99%), $CH_3^{18}OH$ (Isotec, 99%), $CH_3OD$ (Isotec, 99%) and mixtures were used in different experiments. In general, matrix samples were deposited for 60 min at a rate of approximately 4 mmol/h. After sample deposition, infrared spectra of the resulting samples were recorded on a Bruker IFS 80 V spectrometer at a 0.5 $cm^{-1}$ resolution between 4000 and 450 $cm^{-1}$ using a liquid nitrogen cooled broad band HgCdTe (MCT) detector. Matrix samples were annealed to different temperatures and cooled back to 6 K for spectral acquisition. For selected samples, photoexcitations were performed through a quartz window mounted on the assembly. A 250 W high pressure mercury arc lamp ($250 < \lambda < 580$ nm) with different band pass filters (400 nm and 300 nm long-wavelength pass filters) was used.

Quantum chemical calculations were performed to determine the molecular structures and to help the assignments of vibrational frequencies of the observed reaction products. The calculations were performed at the level of density functional theory (DFT) with the hybrid B3LYP and BHandHLYP functionals [32–38]. The 6-311++G(d,p) basis sets were used for the H, C and O atoms, and the scalar-relativistic, energy-consistent effective-core potential (ECP) and corresponding SDD basis set was used for the Ce atom [39,40]. The 28 inert core electrons were included in the ECP, leaving the 4s, 4p, 4d, 5s, 5p, 5d, 6s and 4f electrons in the valence space for Ce. The SDD ECP and valence basis set were found to work well for similar reactions of Ln with $CH_2F_2$, $CH_3F$, $CHF_3$ and late lanthanide metal atoms with $CH_3OH$ [10,41–43]. The geometries were fully optimized via analytic energy gradient algorithm. The stationary point was characterized as a minimum with all real vibrational frequencies or a transition state with one imaginary frequency in vibrational frequency calculations using analytic second derivatives of energy. The unscaled harmonic vibrational frequencies were used to determine the zero-point vibrational energies (ZPVE). To verify the reliability of the DFT energies, the single-point energies were calculated at the *ab initio* CCSD(T) level using the structures optimized at the BHandHLYP level with the same basis sets [44]. This mixed approach is abbreviated as CCSD(T)//BHandHLYP hereafter. Moreover, minimum energy paths (MEPs) were calculated by performing intrinsic reaction coordinates (IRC) analysis at the B3LYP and BHandHLYP levels of theory in both the forward and backward directions to confirm the transition states connecting the desired reactants and products [45]. All these calculations were performed using the Gaussian 09 program [46].

## 3. Results and discussion

### 3.1. Infrared spectra

The infrared spectra in selected regions from co-deposition of laser-evaporated Ce atoms with methanol molecules in excess argon are illustrated in Figs. 1 and 2, respectively. The product absorptions are listed in Table 1. The stepwise annealing and irradiation behaviors of the product absorptions are also shown in the figures and will be discussed below. The reaction between a cerium atom and methanol did not occur during deposition because of the very low concentration of methanol used (only 0.2%) and low evaporation laser energy. So no product absorptions were observed after sample deposition at 6 K except for the absorption due to CeO (808.4 $cm^{-1}$) in the low-frequency region [47]. New product absorptions were produced at 1287.4, 1269.5, 1263.1, 1135.5, 1114.2, 1113.0, 1111.8 and 1106.2 $cm^{-1}$, and the CeO absorption increased when the sample was annealed to 25 K (Figs. 1 and 2). The bands at 1135.5 and 1106.2 $cm^{-1}$ increased, but other bands decreased slightly upon sample annealing to 35 K. When the sample was subjected to $250 < \lambda < 580$ nm broad band irradiation, the foregoing absorptions were completely destroyed, during which new absorptions at 1111.2 and 793.1 $cm^{-1}$ were produced. These two bands increased upon further sample annealing.

Carbon-13, oxygen-18 and deuterium substitution experiments were performed for product identification through isotopic shift and splitting, and the isotopic counterparts are also listed in Table 1. Representative spectra in selected regions with different isotopic samples are shown in Figs. 3 and 4, respectively. All products gave isotopic doublets containing the same absorptions as in the pure isotopic experiments using the mixed isotopic samples except for the 1135.5 and 1106.2 $cm^{-1}$ bands that produced triplets. The observation of triplet implies that these products require two methanol molecules as reactants.

### 3.2. Theoretical results

Geometry optimizations and frequency calculations were carried out on the stationary points in the reactions of Ce with methanol, including reactants, products, intermediates and transition states at the B3LYP and BHandHLYP levels of theory. The calculated vibrational frequencies of the species observed in our experiments are given in Table 2. The frequencies with isotopic substitutions are given in Table S1 of Supporting Information. The structural

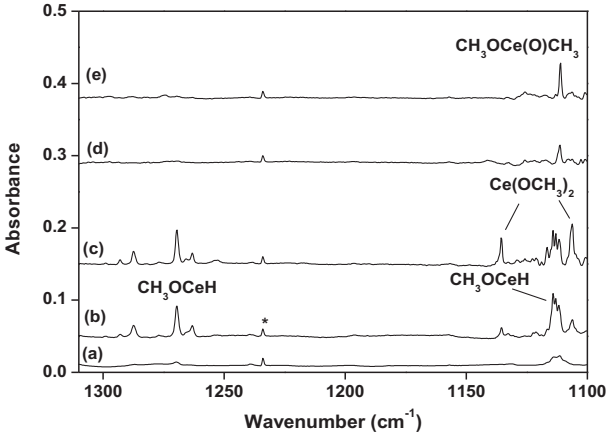


**Fig. 1.** Infrared spectra in the 1310–1100 $cm^{-1}$ region from co-deposition of laser-evaporated cerium atoms with 0.2% $CH_3OH$ in argon. (a) 1 h of sample deposition at 6 K, (b) after 25 K annealing, (c) after 35 K annealing, (d) after 15 min of $250 < \lambda < 580$ nm irradiation, and (e) after 30 K annealing (the asterisk denotes an unknown impurity absorption).