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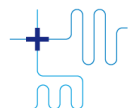
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ABSTRACT

Investigation of the interactions of methane with metal oxides is crucial for elucidating absorption configurations at active sites of catalysts, which has proven to be a challenging experimental target due to the difficulty in size selection of neutral systems. In this work, the interactions of methane with rare earth metal oxides are studied by using size-specific infrared-vacuum ultraviolet spectroscopy and quantum chemical calculations. Two distinct configurations of methane adsorption are found in the $\text{MO}(\text{CH}_4)_n$ ($M = \text{Ce}, \text{Y}$; $n = 1-3$) complexes. In the first configuration, the C and H atoms of methane are positioned between a Lewis acid-base pair ($\text{M}^{2+}-\text{O}^{2-}$); in the second configuration, one H atom of methane is oriented toward a Lewis basic oxygen anion (O^{2-}). Such adsorption features of methane on cerium and yttrium monoxides are dominantly governed by electrostatic interactions. These findings provide key microscopic information for methane adsorption on metal oxides that are helpful for understanding the crucial initial steps in the catalytic cycles.

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I. INTRODUCTION

Methane is the primary component of natural gas and a potent greenhouse gas. Its catalytic conversion into value-added products (i.e., methanol and acetic acid) constitutes a central goal in C1 chemistry.¹⁻³ Currently, metal oxides are widely used either as catalysts or catalytic supports in methane catalytic conversion.⁴⁻¹² The initial adsorption step of CH_4 onto catalyst surfaces is pivotal for affecting the activation barrier and overall reaction pathway.¹³⁻¹⁶ Consequently, deciphering the molecular-level details

of this adsorption enhances understanding of active sites and provides fundamental insights into activation mechanisms, enabling rational catalyst design.^{14,17} However, the precise characterization of methane absorption configurations at active sites remains challenging in the condensed-phase experiments due to spectroscopic interference from gaseous methane and the complex structures of metal oxide powders or supported nanoparticles.¹⁸⁻²⁰ By investigating the adsorption of intact methane onto isolated gas-phase clusters under high-vacuum conditions, it is possible to overcome these limitations and achieve atomically precise characterization.²¹

Methane-metal oxide complex ions have been pioneeringly studied due to their ease of detection and size selectivity. For instance, infrared photodissociation (IRPD) spectroscopy characterized the $V_5O_{12}(CH_4)^+$ and $V_5O_{13}(CH_4)^+$ complexes, revealing η^2 - CH_4 adsorption on a threefold coordinated V^{5+} site, indicative of a preference for Lewis acid sites with lower steric hindrance.²¹ In contrast with ionic complexes, structural characterization of neutral species involved in the reactions of methane with metal oxides is rather difficult experimentally due to the limitation in size selection. Matrix-isolation IR spectroscopic and theoretical studies have revealed photoinduced methane activation mediated by neutral metal oxides, as in the case of MO ($M = Fe, Mn, Nb, Ta, Ti$), NbO_2 , and TaO_2 .^{22–25} The $MO(CH_4)$ ($M = Fe, Mn$) complexes were predicted to adopt C_{2v} symmetry, with the metal center of MO engaging in η^2 - CH_4 coordination.²⁵ The $TiO(CH_4)$ complex was predicted to adopt C_{3v} symmetry, with the methane adopting an umbrella configuration on oxygen of TiO .²³ In addition to adsorption at Lewis acid sites, such as metal atoms, CH_4 also undergoes adsorption at oxygen-based Lewis base sites. Studies on the reaction intermediates mainly focused on the C–H bond cleavage, with much less attention to the characterization of methane adsorption structures.

As representatives of the light and heavy rare earth elements, cerium and yttrium are frequently introduced into catalysts for methane oxidation to methanol, methane C–C coupling to C_2 products, and dry reforming of methane (DRM).^{6,14,26,27} For example, yttrium can effectively enhance both the activity and stability of the catalyst for DRM.^{27–29} To investigate the methane adsorption configurations on the rare earth-oxygen pairs, the $MO(CH_4)_n$ ($M = Ce, Y; n = 1–3$) complexes were characterized by using size-specific infrared-vacuum ultraviolet (IR-VUV) spectroscopy and quantum-chemical calculations in this work. The results reveal that methane adsorbs in two distinct configurations: one with the C and H atoms being positioned between a Lewis acid-base pair ($M^{2+}-O^{2-}$) and another with a H atom being oriented toward Lewis basic oxygen anion (O^{2-}). The interaction mechanisms of such methane adsorption configurations have been elucidated by molecular orbital and bonding energy decomposition analyses.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Experimental methods

The measurements of IR spectra of the $MO(CH_4)_n$ ($M = Ce, Y; n = 1–3$) complexes were carried out by using an IR-VUV spectroscopy setup described previously.^{30,31} Briefly, neutral $MO(CH_4)_n$ ($n = 1–3$) complexes were produced via a laser-vaporization source under supersonic expansion conditions with a 0.2% CH_4 /helium mixture (Figs. S1 and S2). The cerium and yttrium targets (99.9% purity, subjected to periodic air exposure for native oxide layer formation) were ablated by using the Nd:YAG laser (Beamtech, Dawa-200, 532 nm, pulsed laser energy: 0.6 mJ). The reaction gas was introduced through a Parker valve (Series 009) with a pulse width of 212 μs . The molecular beam passed through a 4 mm diameter skimmer (Beam Dynamics, Model 50.8) into the ionization region where threshold ionization occurred. A DC voltage of +2950 V was applied to the extraction plate of the reflectron time-of-flight mass spectrometer (TOF-MS). Charged particles were deflected from the molecular beam by the DC electric field of the extraction plate. VUV

radiation at 193 nm was generated by an ArF excimer laser (Coherent, COMPex 50 F).

The pulsed valve, 532 nm laser, and VUV laser were synchronized at a repetition rate of 20 Hz. The tunable IR laser (10 Hz) was introduced ~ 50 ns prior to the VUV pulses, utilizing an optical parametric oscillator/amplifier (OPO/OPA, LaserVision) system pumped by a seeded Nd:YAG laser (Continuum Surelite EX). This system provided tunability from 700 to 7000 cm^{-1} with 1 cm^{-1} spectral resolution, calibrated by using a commercial wavelength meter (HighFinesse GmbH, WS6-200 VIS IR). The depletion of neutral cluster signals was monitored when IR excitation induced vibrational predissociation, and difference spectra were obtained by subtracting mass spectral intensities with and without IR irradiation (IR-ON minus IR-OFF). IR spectra were recorded by scanning the ion signal intensity as a function of IR wavelength in 2 cm^{-1} steps, with each data point averaged over 600 laser shots. The linear dependence of predissociation yield on photon flux was verified through power dependence measurements. The current IR photon flux from the tabletop LaserVision system proved insufficient for investigating CD_4 stretching vibrations (1800–2300 cm^{-1}) in the deuterated $MO(CD_4)_n$ clusters, suggesting the need for higher-intensity tunable IR sources such as free-electron lasers for such isotopic studies.

B. Computational methods

As the MO molecules have $M^{\delta+}-O^{\delta-}$ charge states with dipole moment, they can cause induced dipole moment of CH_4 molecules. Various adsorption configurations will therefore compete with each other through these weak interactions. Global-minimum structural search based on density functional theory (DFT) was performed for the $MO(CH_4)_n$ ($M = Ce, Y; n = 1–3$) complexes by using the Tsinghua Global Minimum (TGMin) code.^{32–34} Quantum chemical calculations were carried out to refine the energies of the low-lying isomers at the B3LYP/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Ce, Y) level with Grimme's dispersion correction method of the D3BJ version [abbreviated as B3LYP-D3(BJ)] using the Gaussian 16 package.^{35–38} Harmonic vibrational frequencies were calculated with analytical second derivatives of the total energy. A scaled factor of 0.964 was used for harmonic vibrational frequencies to account for the systematic errors in the calculations.³⁹ The resulting stick spectra were convoluted by a Gaussian line shape function with a 10 cm^{-1} full width at half maximum (FWHM). The relative energies of different isomers were calculated with corrections of zero-point vibrational energies (ZPVE). Gibbs free energies $G(T) = U(T) + PV - TS$ were calculated with statistical mechanics by using the Shermo package,⁴⁰ where U, S, P, V, and T stand for the internal energy, entropy, pressure, volume, and temperature, respectively.

The nature of bonding interactions in the global-minimum structures of the $MO(CH_4)_n$ ($n = 1–3$) complexes was analyzed with electrostatic potential (ESP) and interaction region indicator (IRI) analyses at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Ce, Y) level by using the Gaussian 16 package and Multiwfn, respectively.^{35,39,41–44} Isosurfaces were visualized by using VMD.⁴⁵ GnuPlot software was used to draw a scatter diagram. The chemical bonding analyses were elucidated via the energy decomposition analysis-natural orbitals for chemical valence (EDA-NOCV)⁴⁶ method at the B3LYP-D3(BJ)/TZ2P level by using the ADF (v2021.101) package.^{47–49} The EDA-NOCV scheme provides both qualitative density ($\Delta\rho_{orb}$) and quantitative energy (ΔE_{orb})

information about the strength and contribution of orbital interactions in chemical bonding, as demonstrated in the study of water clusters $(\text{H}_2\text{O})_n$ ($n = 2-10$).⁵⁰⁻⁵² The schematic Kohn-Sham molecular orbital correlation diagram, electron localization function (ELF),⁵³ and different schemes of spin densities of M atom in the MO and $\text{MO}(\text{CH}_4)_n$ ($n = 1-3$) complexes were calculated at the B3LYP-D3(BJ)/TZ2P level.

III. RESULTS AND DISCUSSION

A. Experimental infrared spectra

Mass spectrometry was primarily used to verify the possible molecular formulas of the $\text{MOC}_n\text{H}_{4n}$ ($\text{M} = \text{Ce}, \text{Y}; n = 1-3$) complexes. The reaction of Ce with trace water vapor led to a simple mass spectrum [Fig. S3(a)], whereas the mass spectrum for Y appeared relatively more complicated [Fig. S4(a)]. Due to the identical nominal mass of CH_4 and O (both 16 Da), it is difficult to determine

whether a mass difference of 16 Da in a cluster series arises from the addition of a CH_4 molecule or an O atom. Since deuterated methane (CD_4 , 20 Da) does not share this mass overlap with oxygen, CD_4 experiments were performed to confirm the mass spectral assignment of the cluster series. After switching CH_4 in the carrier gas to CD_4 , the molecular formulas could be rationalized from the mass spectra, as shown in Figs. S3 and S4 [(b) and (c)]. The comparison of experimental ionization potentials and calculated adiabatic ionization potentials (AIPs) of MO and MO_2 ($\text{M} = \text{Ce}$ and Y) is given in Table S1. The 193 nm VUV laser corresponds to photon energy of ~ 6.42 eV, so only species with IP less than this value can be ionized by a single photon. The experimental IPs of CeO_2 [9.7(5) eV] and YO_2 (8.23 eV) are much larger than 6.42 eV. Therefore, under the present single-photon ionization conditions, the appearance of CeO_2 and YO_2 species can be excluded on the basis of their IPs. The MO clusters exhibited mass spectral progressions, with peaks separated by integer multiples of either the CH_4 mass (16 Da) or the

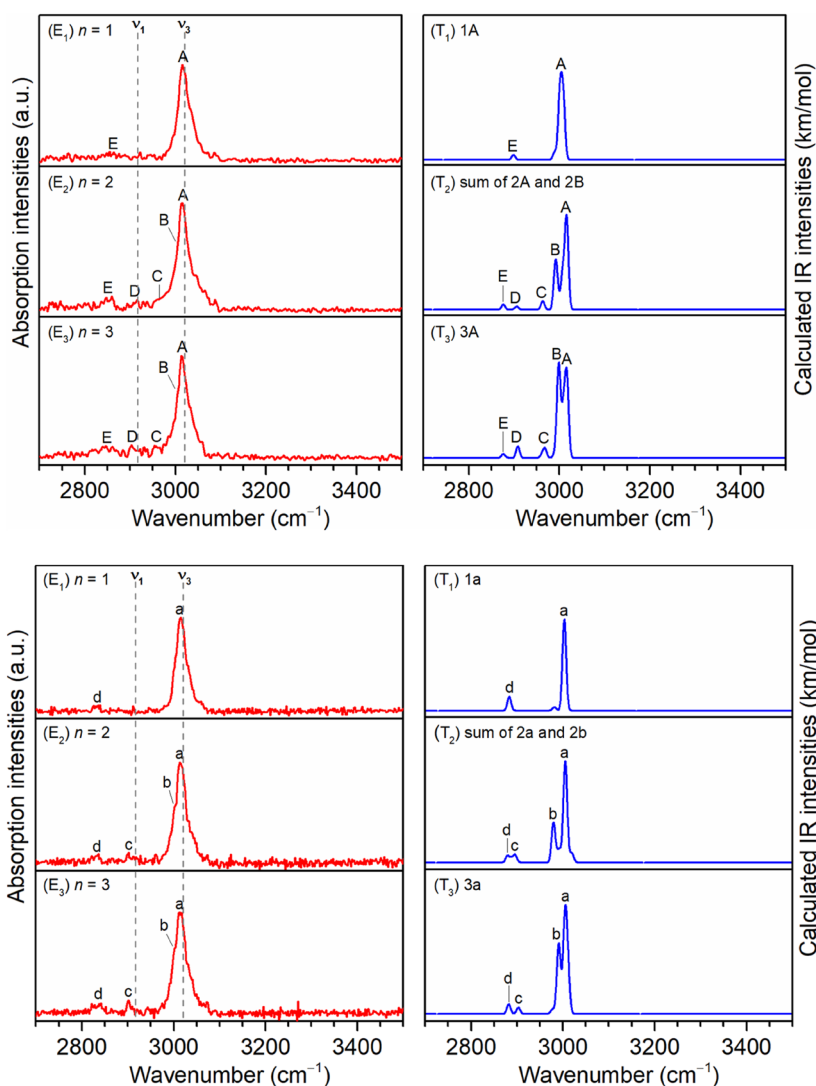


FIG. 1. (E_1) – (E_3) Experimental IR spectra of neutral $\text{CeO}(\text{CH}_4)_n$ ($n = 1-3$). (T_1) – (T_3) Theoretical IR spectra of isomers 1A, 2A, and 2B mixture (1:0.3), and 3A of $\text{CeO}(\text{CH}_4)_n$ ($n = 1-3$) calculated at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Ce) level of theory, with the harmonic vibrational frequencies scaled by 0.964. Frequencies for the ν_1 and ν_3 bands of the free CH_4 are indicated by the dashed lines.

FIG. 2. (E_1) – (E_3) Experimental IR spectra of neutral $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$). (T_1) – (T_3) Theoretical IR spectra of isomers 1a, 2a, and 2b mixture (1:0.3), and 3a of $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$) calculated at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Y) level of theory, with the harmonic vibrational frequencies scaled by 0.964. Frequencies for the ν_1 and ν_3 bands of the free CH_4 are indicated by the dashed lines.

CD₄ mass (20 Da), depending on the carrier gas used. Species with the molecular formulas of MOC_nH_{4n} (*n* = 1–3) were selected as the target compounds for IR spectroscopic measurements.

In the experimental IR spectra of MOC_nH_{4n} (*n* = 1–3) (Figs. 1 and 2), the observation of strong spectral features near the anti-symmetric (*v*₃) C–H stretching frequency of free CH₄ (3019 cm^{−1}), combined with the weak features at the red edge exhibiting small red shifts relative to the symmetric (*v*₁) C–H stretch of free CH₄ (2917 cm^{−1}), implies the adsorption of intact methane molecules. The similarity among the three spectra of either CeOC_nH_{4n} or YOC_nH_{4n} (*n* = 1–3) suggests that the adsorption characteristics of methane may be analogous. The 3100–3800 cm^{−1} region was scanned for possible O–H groups; the absence of any OH vibrational features rules out the presence of characteristic O–H bonds (e.g., hydroxyl groups) or water-based structures in MOC_nH_{4n}. Based on the above-mentioned analysis, species with the chemical formulas

of MOC_nH_{4n} (*n* = 1–3) can be assigned to MO(CH₄)_n (*n* = 1–3) formed through coordination of intact methane molecules to the MO core. For the MO(CH₄)_n (*n* = 1–3) complexes, the experimental spectra display no observable broad bands with fine vibrational-rotational structure at 2920 and 3075 cm^{−1} (characteristic of gaseous methane), indicating that the rotation of CH₄ is severely restricted upon adsorption on MO.

The experimental IR spectra of CeO(CH₄)_n (*n* = 1–3) is shown in Figs. 1(E₁)–1(E₃), and the band positions are listed in Table I. The experimental spectrum of CeO(CH₄) [Fig. 1(E₁)] exhibits two bands: an intense band is centered at 3015 cm^{−1} (labeled A) with full width at FWHM of 32 cm^{−1}, whereas a weak band is centered at 2864 cm^{−1} (labeled E). The experimental IR spectrum of CeO(CH₄)₂ [Fig. 1(E₂)] exhibits four resolvable bands: a band is centered at 3016 cm^{−1} (labeled A) with a shoulder peak at 2958 cm^{−1} (labeled C), and two weak bands are centered at 2907 cm^{−1} (labeled D) and

TABLE I. Comparison of the experimental band positions (cm^{−1}) of CeO(CH₄)_n (*n* = 1–3) with the calculated values of isomers *nA* obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Ce) level of theory (IR intensities are listed in parentheses in km/mol, and the harmonic vibrational frequencies are scaled by a factor of 0.964).

Clusters	Label	Exptl	Calcd	Mode
<i>n</i> = 1	A	3015	3006 (27)	Antisymmetric C–H stretching modes of CH ₄
	E	2864	2897 (3)	Symmetric C–H stretching modes of CH ₄
<i>n</i> = 2	A	3016	3016 (30) 3008 (28)	Antisymmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄ (isomer 2A)
	B		2992 (50)	Antisymmetric C–H stretching modes of C(1)H ₄ (isomer 2B)
	C	2958	2965 (3)	Antisymmetric C–H stretching modes of C(2)H ₄ (isomer 2B)
				Antisymmetric stretching modes of the proximal H–C–H [H(1)–C(1)–H(2) and H(1′)–C(2)–H(2′), isomer 2A]
	D	2907	2906 (3)	Symmetric C–H stretching modes of C(2)H ₄ (isomer 2B)
<i>n</i> = 3	E	2860	2876 (1)	Symmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄ (isomer 2A)
	A	3016	3017 (24)	Antisymmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄
	B		3000 (42)	Antisymmetric C–H stretching modes of C(3)H ₄
	C	2954	2967 (4)	Antisymmetric stretching modes of the proximal H–C–H [H(1)–C(1)–H(2) and H(1′)–C(2)–H(2′)]
	D	2904	2909 (5)	Symmetric C–H stretching modes of C(3)H ₄
	E	2860	2878 (1)	Symmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄

TABLE II. Comparison of the experimental band positions (cm^{−1}) of YO(CH₄)_n (*n* = 1–3) with the calculated values of isomers *na* and *2b* obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Y) level of theory (IR intensities are listed in parentheses in km/mol, and the harmonic vibrational frequencies are scaled by a factor of 0.964).

Clusters	Label	Exptl	Calcd	Mode
<i>n</i> = 1	a	3016	3004 (43)	Antisymmetric C–H stretching modes of CH ₄
	d	2833	2884 (7)	Symmetric C–H stretching modes of CH ₄
<i>n</i> = 2	a	3016	3005 (71) 3006 (38)	Antisymmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄ (isomer 2a)
	b	3002	2982 (44)	Antisymmetric C–H stretching modes of C(1)H ₄ (isomer 2b)
	c	2902	2897 (10)	Antisymmetric C–H stretching modes of C(2)H ₄ (isomer 2b)
	d	2836	2880 (4)	Symmetric C–H stretching modes of C(2)H ₄ (isomer 2b)
<i>n</i> = 3				Symmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄ (isomer 2a)
	a	3016	3006 (71)	Antisymmetric C–H stretching modes of C(1)H ₄ , C(2)H ₄ and C(3)H ₄
	b	3002	2990 (49)	Antisymmetric C–H stretching modes of C(3)H ₄
	c	2902	2904 (5)	Symmetric C–H stretching modes of C(3)H ₄
	d	2837	2881 (4)	Symmetric C–H stretching modes of C(1)H ₄ and C(2)H ₄

2860 cm^{-1} (labeled E). Similarly, the experimental IR spectrum of $\text{CeO}(\text{CH}_4)_3$ [Fig. 1(E₃)] exhibits four resolvable bands, which are centered at 3016 cm^{-1} (labeled A), 2954 cm^{-1} (labeled C), 2904 cm^{-1} (labeled D), and 2860 cm^{-1} (labeled E), respectively.

The experimental IR spectrum of $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$) is shown in Figs. 2(E₁)–2(E₃), and the band positions are listed in Table II. The experimental IR spectrum of $\text{YO}(\text{CH}_4)$ [Fig. 2(E₁)] exhibits two bands: band a (3016 cm^{-1}) and band d (2833 cm^{-1}). The experimental IR spectrum of $\text{YO}(\text{CH}_4)_2$ [Fig. 2(E₂)] exhibits four resolvable bands: a band is centered at 3016 cm^{-1} (labeled a) with FWHM of 29 cm^{-1} , which exhibits a shoulder peak at 3002 cm^{-1} (labeled b), whereas two weak bands are centered at 2902 cm^{-1} (labeled c) and 2836 cm^{-1} (labeled d), respectively. The experimental IR spectrum of $\text{YO}(\text{CH}_4)_3$ [Fig. 2(E₃)] exhibits four resolvable bands: band a (3016 cm^{-1}), band b (3002 cm^{-1}), band c (2902 cm^{-1}), and band d (2836 cm^{-1}), respectively.

B. Identification of geometric structures

To interpret the experimental spectra and analyze the geometries of the $\text{MO}(\text{CH}_4)_n$ ($\text{M} = \text{Ce}, \text{Y}; n = 1-3$) complexes, DFT calculations were performed at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(M) level. As shown in Table S1, the calculated AIPs of CeO and YO are 5.50 and 6.34 eV, respectively, which are consistent with the experimental values of 5.33 and 6.0(3) eV. The calculated bond dissociation energies of CeO and YO are 8.07 and 7.14 eV (Table S2), respectively, which are in accord with the experimental values of 8.33 and 7.31 eV.

The $\text{CeO}(\text{CH}_4)_n$ clusters exhibit a triplet ground state, whereas the $\text{YO}(\text{CH}_4)_n$ clusters possess a doublet ground state. The identified structures of $\text{MO}(\text{CH}_4)_n$ ($n = 1-3$) are labeled as 1A–3A (Ce)

and 2B (Ce), and 1a–3a (Y) and 2b (Y) in Fig. 3, respectively. The comparison of experimental IR spectra of neutral $\text{MO}(\text{CH}_4)_n$ ($n = 1-3$) and calculated IR spectra of low-lying isomers are shown in Figs. 1 and 2, respectively. The $\text{MO}(\text{CH}_4)_n$ complexes of two rare earth elements exhibit similarities in the experimental spectra as well as in the calculated configurations and energy rankings. The calculated band positions of identified structures for $\text{MO}(\text{CH}_4)_n$ ($n = 1-3$) are listed in Tables I and II, respectively. The Gibbs free energies of different isomers for $\text{MO}(\text{CH}_4)_2$ relative to the global minimum (GM) structures as a function of temperature are shown in Figs. S6 and S7, revealing the thermodynamic stability of the GM structure at low temperature and the possibility of coexistence of low-lying isomers at room temperature.

1. $\text{CeO}(\text{CH}_4)$

Isomer 1A has the structure with a methane adsorbed laterally entering between the O and Ce atoms, with one H atom pointing toward the O atom (Fig. 3). As shown in Fig. 1, the simulated IR spectrum of 1A [Fig. 1(T₁)] exhibits excellent agreement with the experimental spectrum [Fig. 1(E₁)]. In the simulated spectrum of 1A [Fig. 1(T₁)], the calculated band at 3006 cm^{-1} is attributed to the antisymmetric C–H stretching modes of CH_4 , which coincides with the experimental band A (3015 cm^{-1} ; Table I); the calculated band at 2897 cm^{-1} is due to the symmetric C–H stretching modes of CH_4 , which is consistent with the experimental band E (2864 cm^{-1}).

2. $\text{CeO}(\text{CH}_4)_2$

In isomer 2A, two methane molecules adsorb laterally, entering between the O and Ce atoms on opposite sides of Ce, with one H atom from each CH_4 pointing toward the O atom (Fig. 3). In isomer 2B, one more methane molecule adsorbs to the structure of 1A,

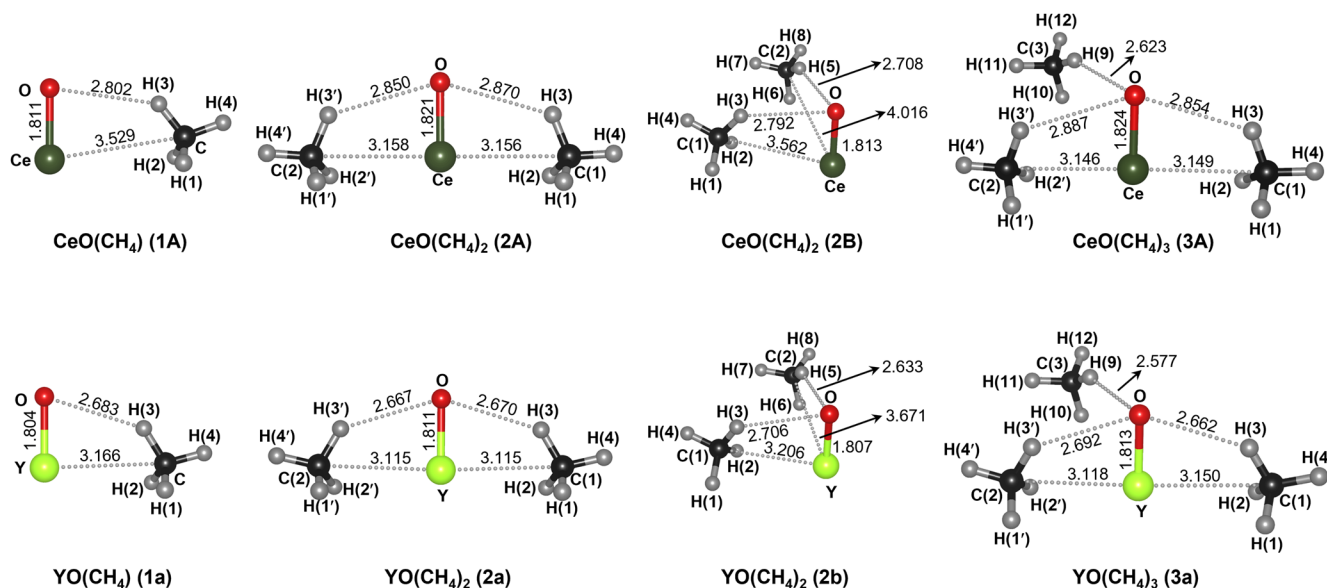


FIG. 3. Identified structures of neutral $\text{CeO}(\text{CH}_4)_n$ ($n = 1-3$) (isomers $n\text{A}$ and 2B) and $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$) (isomers $n\text{a}$ and 2b) clusters optimized at the B3LYP-D3(BJ)/aug-cc-pVTZ(C, H, O)/def2-TZVPP(Ce, Y) level of theory. The atoms are labeled for discussion, and the key Ce–O, Y–O, O···H, Ce···C, and Y···C distances (Å) are labeled for each cluster (O, red; C, gray; H, light gray; Ce, olive; and Y, light green).

with one H atom oriented toward the O atom, which lies above 2A by 0.50 kcal/mol. In the simulated IR spectrum of 2A [Fig. S5(c)], the calculated band at 3016 cm^{-1} is attributed to the antisymmetric C–H stretching modes of C(1)H₄ and C(2)H₄, which coincides with the experimental band A (3016 cm^{-1} ; Table I); the band at 2965 cm^{-1} is attributed to the antisymmetric stretching modes of the proximal H–C–H [H(1)–C(1)–H(2) and H(1')–C(2)–H(2')], Fig. 3], which aligns with the experimental band C (2958 cm^{-1}); the calculated band at 2876 cm^{-1} is assigned to the symmetric C–H stretching modes of C(1)H₄ and C(2)H₄, which is consistent with the experimental band E (2860 cm^{-1}). In the simulated IR spectrum of isomer 2B [Fig. S5(d)], the calculated band at 3008 cm^{-1} is attributed to the antisymmetric C–H stretching modes of C(1)H₄ (Fig. 3), which coincides with the experimental band A (3016 cm^{-1} ; Table I); the 2994 cm^{-1} band is attributed to the antisymmetric C–H stretching modes of C(2)H₄, which is likely obscured within the thermal broadening of band A; and the band at 2906 cm^{-1} is attributed to the symmetric C–H stretching modes of C(2)H₄, which coincides with the experimental band D (2907 cm^{-1}). The best experiment–calculation agreement is obtained when assuming a ratio of 1 (2A):0.3 (2B) mixture of isomers [Figs. 1(T₂) and S5(b)].

3. CeO(CH₄)₅

In isomer 3A, one more methane molecule adsorbs to the structure of 2A with one H atom oriented toward the O atom (Fig. 3). As shown in Fig. 1, the simulated IR spectrum of 3A [Fig. 1(T₃)] agrees well with the experimental spectrum [Fig. 1(E₃)]. In the simulated spectrum of 3A [Fig. 1(T₃)], the bands at 3017 and 3000 cm^{-1} are due to the antisymmetric C–H stretching modes of C(1)H₄, C(2)H₄, and C(3)H₄ (Fig. 3), respectively, merging into one band in the experimental spectrum (3016 cm^{-1} , labeled A; Table I); the calculated band at 2967 cm^{-1} is attributed to the antisymmetric stretching modes of the proximal H–C–H [H(1)–C(1)–H(2) and H(1')–C(2)–H(2')], which coincides with the experimental band C (2954 cm^{-1}); the calculated band at 2909 cm^{-1} is due to the symmetric C–H stretching modes of C(3)H₄, which is consistent with the experimental band D (2904 cm^{-1}); and the calculated band at 2878 cm^{-1} is due to the symmetric C–H stretching modes of C(1)H₄ and C(2)H₄, which is consistent with the experimental band E (2860 cm^{-1}).

4. YO(CH₄)_n (*n* = 1–3)

As shown in Fig. 3, the structures of YO(CH₄)_n (*n* = 1–3) are similar to those of CeO(CH₄)_n (*n* = 1–3). The simulated IR spectra of identified isomers also agree well with the experimental spectra (Figs. 2 and S5). The detailed spectral assignments are given in Table II.

C. Molecular orbital interaction analysis

To understand the electronic structure and bonding patterns of MO and MO(CH₄)_n (*n* = 1–3) (*M* = Ce, Y; isomers 1A–3A and 1a–3a), the spin densities of the *M* atom in these complexes are listed in Tables S3 and S4 and shown in Figs. S8 and S9, respectively. All different schemes of spin densities of the Ce atom (about 2.00) and the Y atom (about 1.00) indicate that the MO and MO(CH₄)_n (*M* = Ce, Y; *n* = 1–3) complexes can be described as formally as *M*²⁺–O^{2–} and *M*²⁺–O^{2–}(CH₄)_n, respectively, agreeing with the

divalent state of the metal atoms in these metal–oxygen complexes. The binding of MO and CH₄ is simply dipole-induced dipole interaction. Indeed, ELF analysis of these complexes (Figs. S10 and S11) shows that there is no significant electron density between CH₄ and MO, indicating that no covalent bond is formed between them.

The stepwise binding energy (*E*_{bind}) of CH₄ in CeO(CH₄)_n (*n* = 1–3) (isomers 1A–3A) is calculated to be –1.40, –1.89, and –1.37 kcal/mol, respectively (Table S5). The *E*_{bind} value of CH₄ in YO(CH₄)_n (*n* = 1–3) (isomers 1a–3a) is calculated as –2.30, –2.41, and –1.84 kcal/mol, respectively (Table S6). These small *E*_{bind} values indicate that methane essentially undergoes physisorption in the MO(CH₄)_n complexes.

The IRI analysis enables the visual discrimination between chemical bonding and weak intermolecular interactions via its characteristic isosurfaces.⁴⁴ As shown in Figs. S12 and S13, the results of IRI analysis exhibit the chemical bonding between *M* and O, weak van der Waals (vdW) interactions between the MO unit and the CH₄ molecules, and additional vdW interactions among the proximate CH₄ molecules. The methane–methane interaction is minimal, as demonstrated in the metal ion–methane solvation structures.⁵⁴ Thus, the present MO(CH₄)_n (*n* = 1–3) systems are mainly stabilized by the vdW interactions between the MO unit and CH₄ molecules.

Figure S14 displays the ESP mapped vdW surface of the individual MO and CH₄. The isosurface maps of the ESP for MO(CH₄)_n (*n* = 1–3) are shown in Figs. S15 and S16. For the optimized GM structures, methane preferentially adopts a configuration with its C atom near the *M* center and an H atom directed toward the O site (Figs. S15 and S16). Once the two favorable positions for this geometry are filled, the third CH₄ attaches near an already adsorbed CH₄, positioning one H atom toward the O atom and its C atom close to an H atom of the adjacent CH₄. This stacking motif follows the general rule of ESP complementarity, which drives systems toward configurations that maximize electrostatic stabilization. Thus, the CH₄ molecules occupying the two favorable positions could be classified as the core ligand [e.g., C(1)H₄ and C(2)H₄ in 3A, Fig. 3], and the CH₄ molecule at the alternative site as the outer ligand [e.g., C(3)H₄ in 3A, Fig. 3].

Due to the structural similarity between the CeO(CH₄)_n and YO(CH₄)_n systems, the CeO(CH₄)_n system is taken as an example to analyze the orbital interaction between CeO and CH₄. The bonding in cerium monoxide has been extensively explored,^{55–68} and a brief description is given here. As shown in Fig. S17, the highest occupied molecular orbitals are two singly occupied molecular orbitals (SOMOs, 15σ and 3δ), primarily derived from the Ce 5d and 4f atomic orbitals (AOs). In CeO, the HOMO-1 (14σ) mainly arises from the Ce 5d (13.28%) and the O 2p_z orbitals (66.17%). The HOMO-2 (7π_x) and HOMO-3 (7π_y) are degenerate π-type MOs contributed mainly from the Ce 5d_{xz} (or 5d_{yz}) (14.77%) and the O 2p_x (or 2p_y) orbitals (79.42%). HOMO-4 (13σ) is σ-type bonding MO via the combination of the Ce semi-core 5p_z (45.05%) and the O 2s (44.58%). These bonding analyses indicate that the stabilization contribution to CeO is mainly from the interaction between the 5d of Ce atom and the 2p of O atom.

Figure 4 illustrates the schematic Kohn–Sham molecular orbital correlation diagram for CeO(CH₄). The highest single occupied molecular orbital (SOMO, 29a') and SOMO-1 (28a') mainly arise from the (SOMOs, 15σ and 3δ) of CeO. The 27a', (10a'' and 26a'),

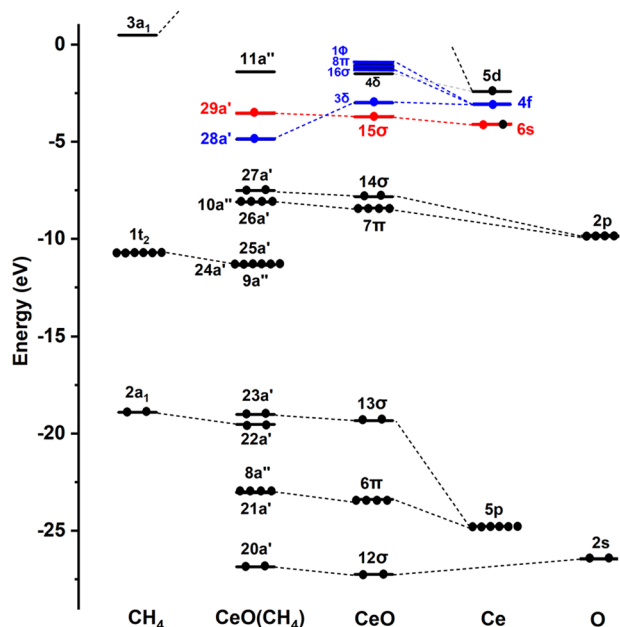


FIG. 4. Schematic Kohn–Sham molecular orbital correlation diagram for $\text{CeO}(\text{CH}_4)$ at the B3LYP-D3(BJ)/TZ2P level of theory.

$23a'$, ($8a''$ and $21a'$), and $20a'$ MOs of $\text{CeO}(\text{CH}_4)$ mainly arise from the 14σ , ($7\pi_x$ and $7\pi_y$), 13σ , ($6\pi_x$ and $6\pi_y$), and 12σ MOs of CeO , while the ($25a'$, $24a'$, and $9a''$) and $22a'$ MOs of $\text{CeO}(\text{CH}_4)$ mainly arise from the $1t_2$ and $2a_1$ MOs of CH_4 instead. The CeO moiety retains its f^1s^1 electronic ground state within the weak adsorption complex. The interaction between CeO and CH_4 is weak, as manifested by the negligible structural perturbation of methane ($<0.5\%$ bond elongation, $<1^\circ$ angle change) and the intact degeneracy of its $1t_2$ orbitals without significant energy-level splitting. These analyses reveal that there is relative weak bonding interaction between the CeO and CH_4 molecule and strong covalent bonding interaction between the Ce and O atoms.

D. Bonding energy decomposition analysis

To explore the interactions between the MO unit and $(\text{CH}_4)_n$ ($n = 1-3$) in isomers 1A–3A and 1a–3a, the EDA–NOCV analyses were performed, and the numerical results are given in Table III. The interaction energy (ΔE_{int}) between the MO and $(\text{CH}_4)_n$ fragment is decomposed into Pauli repulsive orbital interaction (ΔE_{Pauli}), dispersion interaction (ΔE_{disp}), electrostatic interaction (ΔE_{elstat}), and orbital interaction (ΔE_{orb}). As listed in Table III, the percentage contribution of ΔE_{elstat} to the total attractive interaction of isomers 1A–3A is calculated to be 65.93%, 59.02%, and 59.48%, respectively. The attractive interactions between the CeO and $(\text{CH}_4)_n$ ($n = 1-3$) fragments have a slightly higher electrostatic interaction (ΔE_{elstat}) (59%–66%) than the covalent character (ΔE_{orb}) (34–41%) (Fig. S18). Similar EDA–NOCV results of $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$) are also obtained (Table III and Fig. S19).

Figures S20 and S21 display the isosurfaces of deformation densities for the dominant NOCV pairs from the EDA–NOCV calculations, which elucidate the electron transfer between CH_4 and MO. The interaction is characterized by minor electron redistribution from both M and CH_4 , plus a slight transfer from the C s orbital to the M p/d orbitals. In particular, as CH_4 is absorbed laterally between the $\text{M}^{2+}-\text{O}^{2-}$ pair, a minor electron flow occurs from H to the nearby C s orbital, while a concurrent intra-M shift from the s to the p/d orbitals makes room for the incoming charge from the C atom. Because a small amount of electron density occupies the M p/d orbitals distal to CH_4 , further adsorption of CH_4 between the two existing core positions would induce significant Pauli repulsion between the C orbital electrons of CH_4 and the electrons in these orbitals, thereby limiting the number of core ligand to two. Compared to the outer ligands in isomers 3A and 3a, the core ligands position their C atoms closer to the Lewis acid site M^{2+} , resulting in more pronounced electron transfer and stronger orbital interactions with the MO moiety.

A pronounced correlation exists between ΔE_{disp} and ΔE_{int} , with their values being closely matched (Table III). This numerical proximity suggests that the dipole-induced dipole and dispersion interaction are the momentum for the interaction of the $(\text{CH}_4)_n$ ($n = 1-3$) moieties with MO. Meanwhile, we note that the sum of ΔE_{disp} and ΔE_{orb} is approximately counterbalanced by ΔE_{Pauli} . Compared to the dispersion interaction, the electrostatic interaction consistently exhibits a larger magnitude and the orbital interaction scales roughly proportionally with it. These results support that the interactions between the $(\text{CH}_4)_n$ ($n = 1-3$) moieties and MO are dominantly governed by electrostatic interactions.

E. Comparison of methane adsorption on MO (M = Ce and Y) unit and condensed-phase surfaces

Given that methane adsorption at distinct catalytic sites may drive divergent reaction pathways and product distributions,¹⁴ elucidating its precise adsorption sites and configurations becomes imperative. Fourier transform infrared (FTIR) spectroscopy in either diffuse reflectance or transmission mode has been extensively employed to study the interactions of methane with surface sites of metal oxides and metal-loaded zeolites.^{18,69} Some characteristic methane adsorption peaks have been assigned as follows: (1) the symmetric C–H stretching vibration (ν_1) at $2800\text{--}2860\text{ cm}^{-1}$ to interactions with metal sites, and (2) the ν_1 mode at $2875\text{--}2900\text{ cm}^{-1}$ to η^1 -coordination at oxygen sites in certain cases.^{18,20,21,70–75}

Our cluster spectroscopic approach provides insight into the molecular-level details of methane activation and adsorption site that are difficult to extract from the condensed-phase experiments. The ν_1 mode of CH_4 becomes observable and exhibits a red shift of ~ 50 and 80 cm^{-1} when activated by interaction with Lewis acid site in formally $\text{Ce}^{2+}-\text{O}^{2-}$ and $\text{Y}^{2+}-\text{O}^{2-}$ pairs, respectively. The red shift of the ν_1 mode to 2860 cm^{-1} upon Ce^{3+} site activation signifies inferior Lewis acidity relative to tri-coordinate V^{5+} in $\text{V}_5\text{O}_{12}\text{CH}_4^+$ (2767 cm^{-1}) and low-coordination Zn^{2+} in Zn-ZSM-5 (2805 cm^{-1}).^{20,21,75} The peak observed at $\sim 2902\text{ cm}^{-1}$ in the experimental spectra is attributed to the ν_1 mode of CH_4 that is involved in a single $\text{C-H}\cdots\text{O}^{2-}$ interaction with the $\text{M}^{2+}-\text{O}^{2-}$ moiety. Certain characteristic peaks in FTIR spectroscopy have also been assigned to CH_4 that interacts with surface oxygen species in CeO_2 (2875 cm^{-1})

TABLE III. EDA–NOCV results of $\text{CeO}(\text{CH}_4)_n$ ($n = 1-3$) (isomers 1A–3A) and $\text{YO}(\text{CH}_4)_n$ ($n = 1-3$) (isomers 1a–3a), with the MO ($M = \text{Ce}, \text{Y}$) and $(\text{CH}_4)_n$ ($n = 1-3$) moieties as two fragments at the B3LYP-D3(BJ)/TZ2P level of theory, respectively (energy values are given in kcal/mol; $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{disp}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$).

Clusters	$\text{CeO}(\text{CH}_4)$	$\text{CeO}(\text{CH}_4)_2$	$\text{CeO}(\text{CH}_4)_3$	$\text{YO}(\text{CH}_4)$	$\text{YO}(\text{CH}_4)_2$	$\text{YO}(\text{CH}_4)_3$
Fragments	$\text{CeO} + (\text{CH}_4)$	$\text{CeO} + (\text{CH}_4)_2$	$\text{CeO} + (\text{CH}_4)_3$	$\text{YO} + (\text{CH}_4)$	$\text{YO} + (\text{CH}_4)_2$	$\text{YO} + (\text{CH}_4)_3$
ΔE_{int}	−1.69	−3.98	−5.16	−2.17	−4.44	−6.31
ΔE_{Pauli}	9.36	43.48	47.78	15.95	36.12	38.82
ΔE_{disp}	−2.01	−4.23	−5.51	−2.30	−4.63	−6.31
$\Delta E_{\text{elstat}}^a$	−5.96 (65.93%)	−25.52 (59.02%)	−28.21 (59.48%)	−9.85 (62.22%)	−21.63 (60.20%)	−23.61 (60.82%)
ΔE_{orb}^a	−3.08 (34.07%)	−17.72 (40.98%)	−19.22 (40.52%)	−5.98 (37.78%)	−14.30 (39.80%)	−15.21 (39.18%)

^aThe values in parentheses provide the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$.

and MgO (2897 cm^{-1}) as well as with framework oxygen species in NaY-zeolites (2900 cm^{-1}).^{74,76,77} The difference in the red shift of the characteristic peak may arise from variations in the Lewis basicity of the coordinating O species or from environmental perturbations. Our experimental and theoretical studies demonstrate that methane adsorbs in two distinct configurations: one configuration entails lateral interaction between Lewis acid-base pairs, occurring chiefly at step-edge sites; the other configuration involves a methane molecule with one hydrogen atom directed toward a Lewis basic lattice oxygen atom, occurring prevalently at corner sites.

Charge- and dipole-induced dipole interactions and dispersion interactions are generally taken as the principal driving force, which initiate alkane adsorption on surfaces and induce charge flow from the alkane to the surface metal center.^{78,79} Intriguingly, previous studies suggest that the enhanced interaction of methane with open metal sites might originate from the unscreened electrostatic interactions.⁸⁰ In the $\text{MO}(\text{CH}_4)_n$ ($M = \text{Ce}, \text{Y}; n = 1-3$) system, electrostatic interactions are found to be the major factor responsible for structural stacking and stabilization, as evidenced by ESP and EDA–NOCV analyses. Thus, the present $\text{MO}(\text{CH}_4)_n$ ($M = \text{Ce}, \text{Y}; n = 1-3$) system affords a model of open sites in metal oxides, revealing that it is essential to account for electrostatic interactions when elucidating the exact adsorption sites and geometries of methane on the complicated metal oxide surfaces.

IV. CONCLUSION

The $\text{MO}(\text{CH}_4)_n$ ($M = \text{Ce}, \text{Y}; n = 1-3$) complexes are investigated by using the size-specific IR–VUV spectroscopy and quantum-chemical calculations. The C–H stretch vibrational spectral features reveal that methane adsorbs in two distinct configurations: one configuration consists of methane with the C and H atoms bonded with a Lewis acid-base pair ($\text{M}^{2+}-\text{O}^{2-}$), and another configuration consists of CH_4 with one H atom oriented toward a Lewis basic oxygen anion (O^{2-}). The ESP and EDA–NOCV analyses indicate that electrostatic interactions play the dominant role in stabilizing the methane adsorption system. The present findings provide key microscopic information for adsorption configuration of methane on metal oxides.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) encompasses mass spectra, comparison of the experimental and calculated IR spectra of neutral

$\text{MO}(\text{CH}_4)_2$ ($M = \text{Ce}, \text{Y}$), Gibbs free energies, spin densities, electron localization functions, interaction region indicator analysis results, ESP mapped vdW surfaces, isosurface maps of the ESP, schematic Kohn–Sham molecular orbital correlation diagram, percentage of ΔE_{elstat} and ΔE_{orb} , deformation density analysis results of NOCV pairs, binding energies, and Cartesian coordinates of the isomers.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jianxing Zhuang and Yang-Yang Zhang contributed equally to this work.

Jianxing Zhuang: Data curation (equal); Formal analysis (equal); Investigation (equal); Validation (equal); Visualization (equal); Writing – original draft (equal). **Yang-Yang Zhang:** Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Software (equal); Writing – original draft (equal). **Shuai Jiang:** Investigation (equal); Methodology (equal); Resources (equal). **Shangdong Li:** Formal analysis (equal); Investigation (equal); Visualization (equal). **Ailin Wang:** Investigation (equal); Methodology (equal); Resources (equal). **Yue Zhu:** Methodology (equal); Resources (equal). **Shiying Jiang:** Resources (equal); Validation (equal). **Hua Xie:** Funding acquisition (equal); Resources (equal); Validation (equal). **Gang Li:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jun Li:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Ling Jiang:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Project administration (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Xueming Yang:** Project administration (equal); Resources (equal); Supervision (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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