

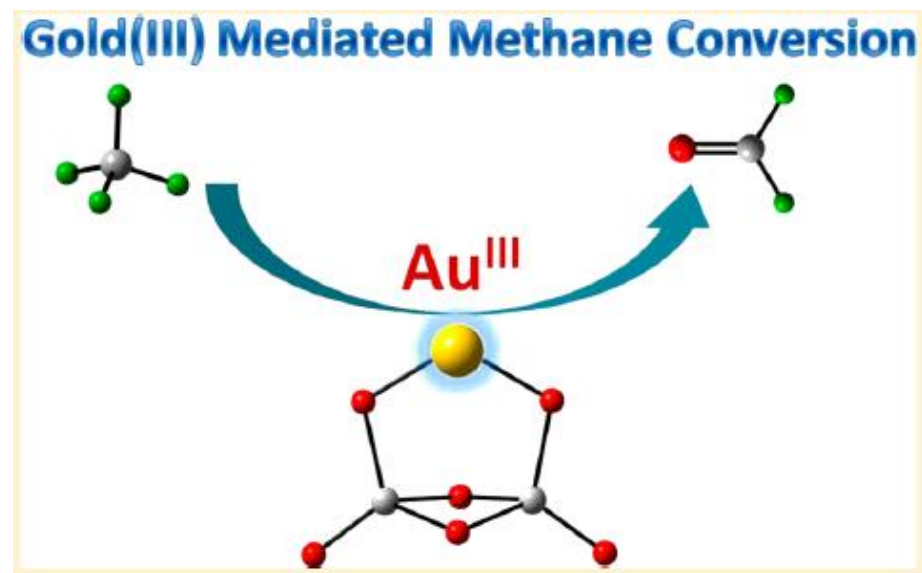
Gold(III) Mediated Activation and Transformation of Methane on Au₁-Doped Vanadium Oxide Cluster Cations AuV₂O₆⁺

Zi-Yu Li,[†] Hai-Fang Li,^{†,‡} Yan-Xia Zhao,^{*,†} and Sheng-Gui He^{*,†}

[†]Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

J. Am. Chem. Soc. 2016, 138, 9437–9443



Madhuri Jash
 15/07/2017

Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century

Jack H. Lunsford*

Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

J.H. Lunsford / Catalysis Today 63 (2000) 165–174

energy&fuels

Article

pubs.acs.org/EF

Catalytic Upgrading of Methane to Higher Hydrocarbon in a Nonoxidative Chemical Conversion

Energy Fuels 2016, 30, 2584–2593

Shaima Nahreen,[†] Supareak Praserttham,[‡] Saul Perez Beltran,[‡] Perla B. Balbuena,^{*,‡} Sushil Adhikari,^{*,§} and Ram B. Gupta^{*,||}

Communications

Homogeneous Catalysis

VIP

Selective Oxidation of Methane to Methanol Catalyzed, with C–H Activation, by Homogeneous, Cationic Gold**

CJ Jones, Doug Taube, Vadim R. Ziatdinov, Roy A. Periana, Robert J. Nielsen, Jonas Oxgaard, and William A. Goddard III*

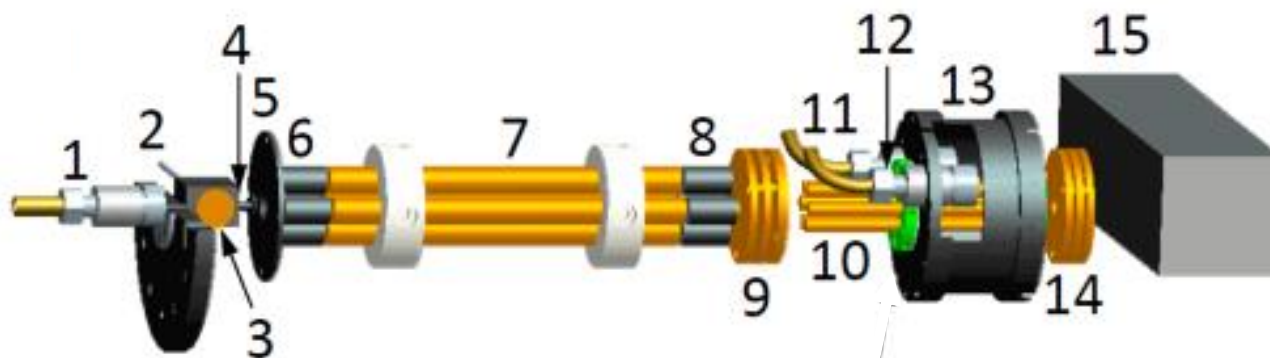
Angew. Chem. Int. Ed. 2004, 43, 4626–4629

INTRODUCTION:

- There are so many applications for gold catalysts like – CO oxidation, Hydrogenation, C-H activation.
- The cationic gold in +III oxidation state has a high standard reduction potential and strong Lewis acid property which provide new opportunities in challenging reactions.
- Though the understanding and development of the Au(III) are limited due to the difficulties in characterizations.
- The investigations of the Au₁-doped metal oxide clusters have demonstrated that the conversion of Au-O into Au-M (M=Ti, Fe, Nb, Ce and Al) species could drive the main catalysis step.

In this paper...

- In this paper, by doping Au atoms into gas-phase vanadium oxide clusters, it has been demonstrated that the Au(III) cation in the AuV₂O₆⁺ cluster is active for activation and transformation of methane, the most stable alkane molecule, into formaldehyde under mild conditions.
- In contrast, the AuV₂O₆⁺ cluster isomers with the Au(I) cation can only absorb CH₄.

Experimental Method:

Schematic diagram of a linear ion trap reactor. 1, 11 and 12 (pulsed valves), 2 (ablation laser), 3 (sample disk), 4 (cluster formation channel), 5 (electric shielding plate), 6 and 8 (prefilters), 7 (quadrupole mass filter), 9 and 14 (ion focusing assembly), 10 (hexapole rods), 13 (cell for confining reactant gas), 15 (reflectron time-of-flight mass spectrometer).

- Laser ablation of a mixed metal disk with Au and V powders (molar ratio: 1/1) in the presence of 0.5 % O₂ seeded in He carrier gas.
- Mass selected by a quadrupole mass filter and ¹⁸O₂ was used instead of ¹⁶O₂ to well resolve AuV₂O₆⁺ from Au₂⁺.
- Then mass selected cluster ions entered into a linear ion trap where they were confined and cooled with a pulse of He gas for 0.9 ms.
- Interacted with a pulse of CH₄, CD₄ and CH₂D₂ for around 1.2 ms.
- The cluster ions ejected from the LIT were detected by a reflectron time-of-flight mass spectrometer (TOF-MS).
- CID and PID experiments were done for structural investigations.

RESULTS AND DISCUSSION:

Cluster Reactivity:

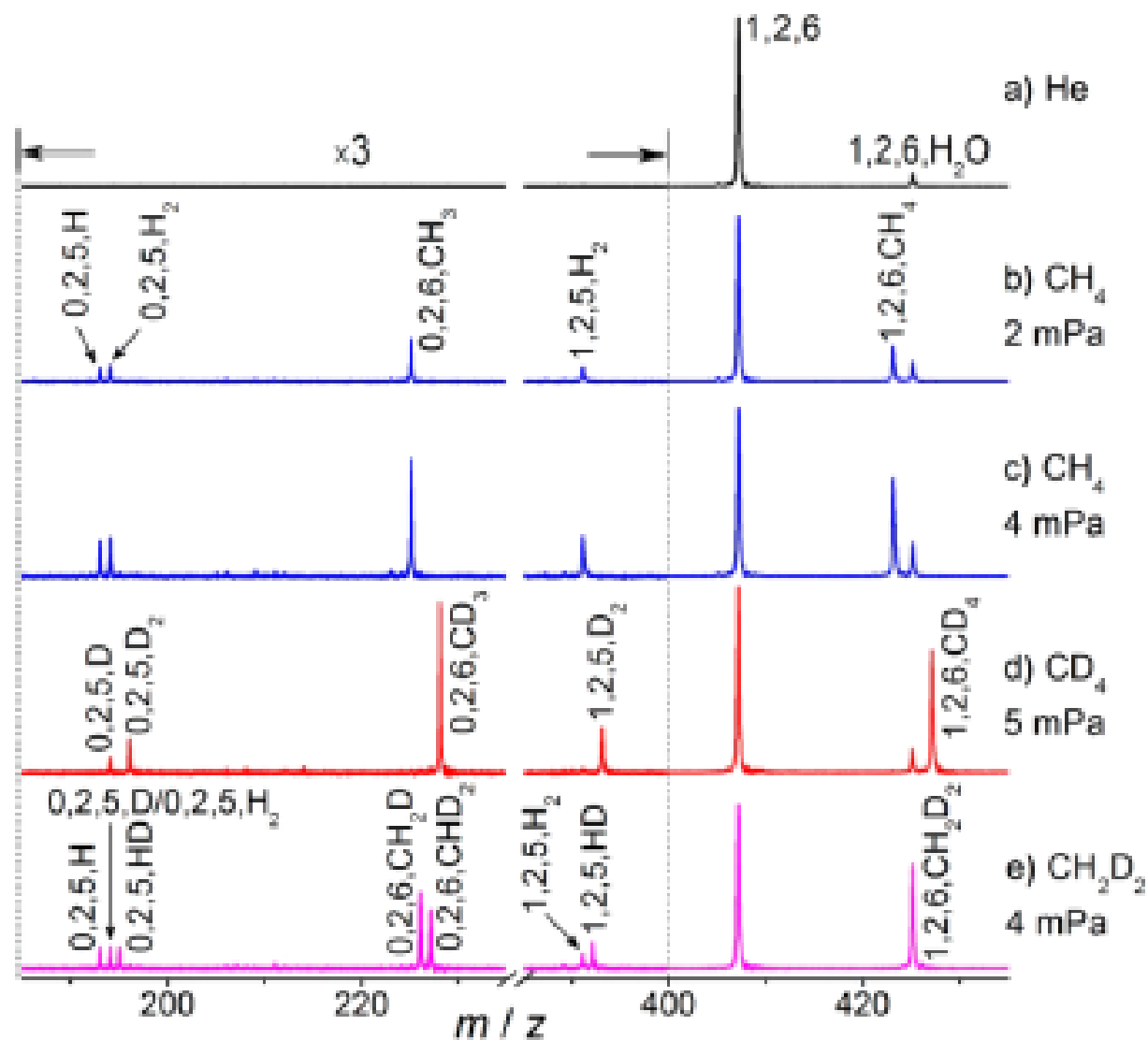
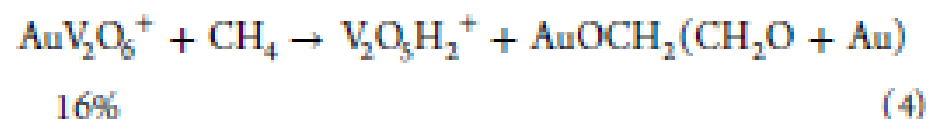
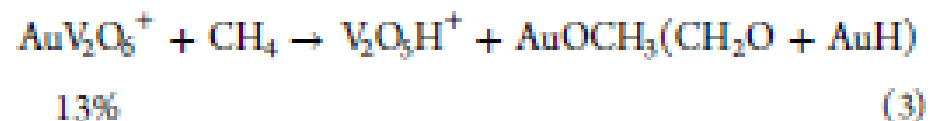


Figure 1. TOF mass spectra for the reactions of $\text{AuV}_2^{18}\text{O}_6^+$ (a) with 2 mPa CH_4 (b) 4 mPa CH_4 (c), 5 mPa CD_4 (d) 4 mPa CH_2D_2 (e) for 1.2 ms. The $\text{Au}_x\text{V}_y\text{O}_z^+$ and $\text{Au}_x\text{V}_y\text{O}_z\text{X}^+$ are labeled as x,y,z and x,y,z,X respectively. The weak $\text{AuV}_2\text{O}_6\text{H}_2\text{O}^+$ in (a) is due to the reaction of AuV_2O_6^+ with residual water from the gas handling system.

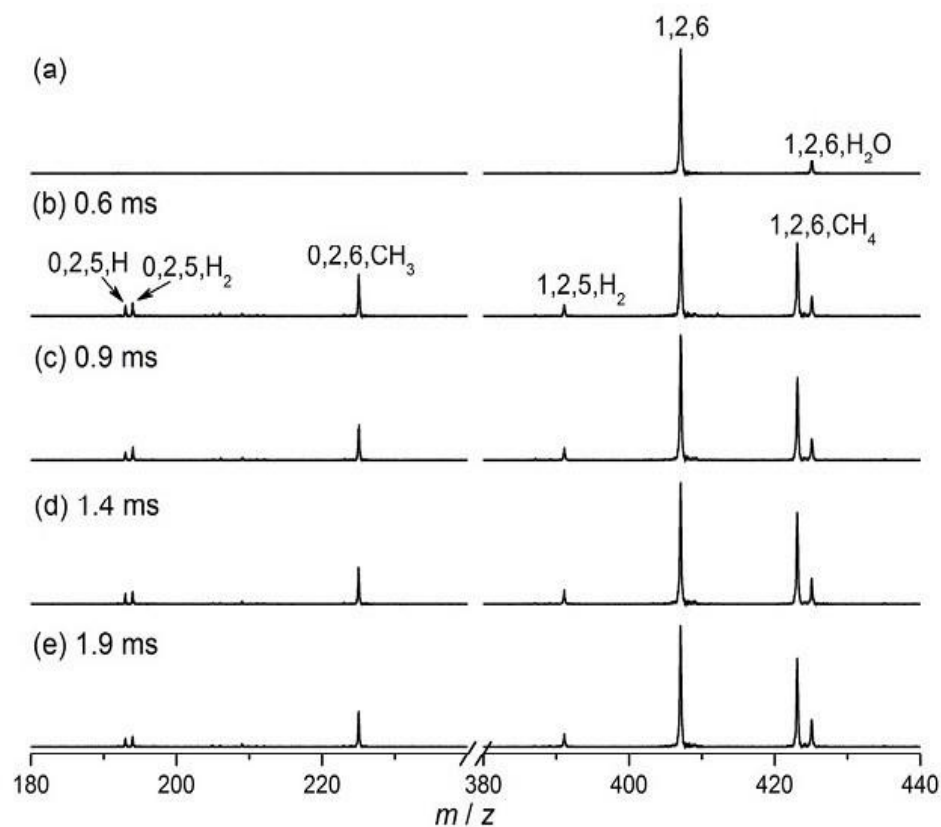


Figure 2. TOF mass spectra for the reactions of mass-selected $\text{AuV}_2^{18}\text{O}_6^+$ (a) with 5 mPa CH_4 for about 1.2 ms (b-e). Before reacting with methane, the $\text{AuV}_2^{18}\text{O}_6^+$ cluster ions are cooled for 0.6 ms (b), 0.9 ms (c), 1.4 ms (d), and 1.9 ms (e), respectively. The $\text{Au}_x\text{V}_y\text{O}_z^+$ and $\text{Au}_x\text{V}_y\text{O}_z\text{X}^+$ species are labeled as x,y,z and x,y,z,X , respectively.

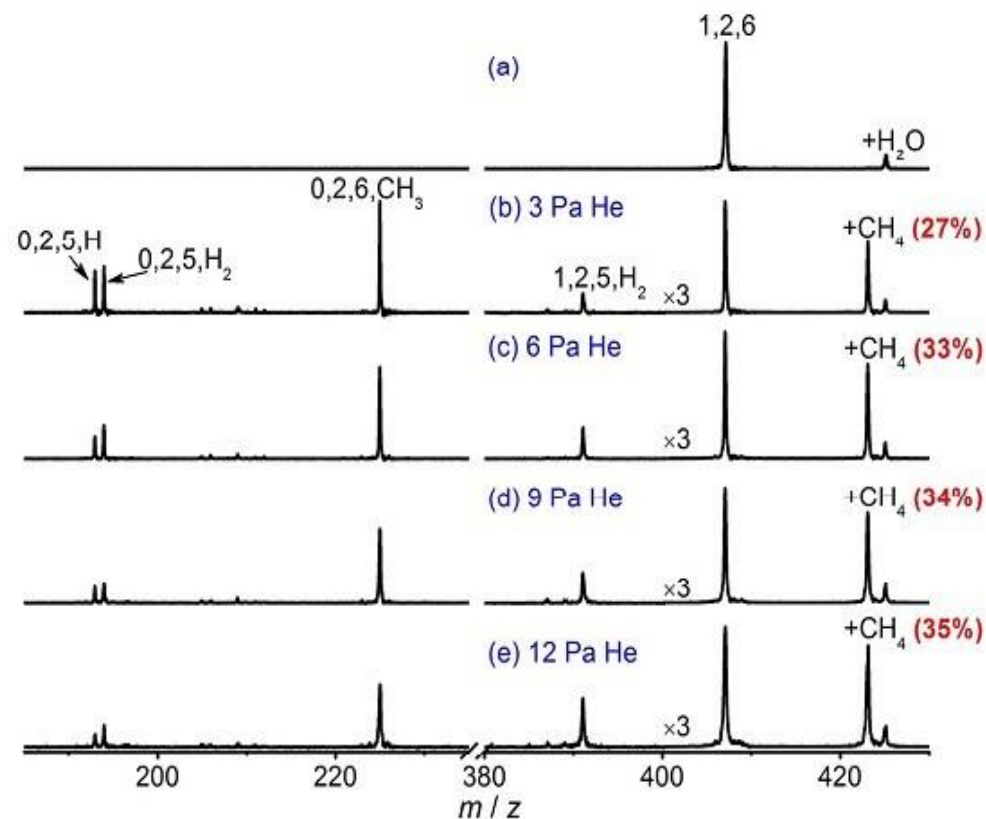


Figure 3. Time-of-flight mass spectra for the reactions of mass-selected $\text{AuV}_2^{18}\text{O}_6^+$ (a) with 5 mPa CH_4 for about 1.2 ms (b-e). Before reacting with methane, the AuV_2O_6^+ cluster ions had been cooled for 0.9 ms under the cooling gas pressures of 3 Pa (b), 6 Pa (c), 9 Pa (d), and 12 Pa (e). The relative intensity of the adsorption products ($I_{\text{ads}}/I_{\text{T}}$, in which I_{ads} is the intensity of $\text{AuV}_2\text{O}_6\text{CH}_4^+$, I_{T} is the total ion intensity) is given.

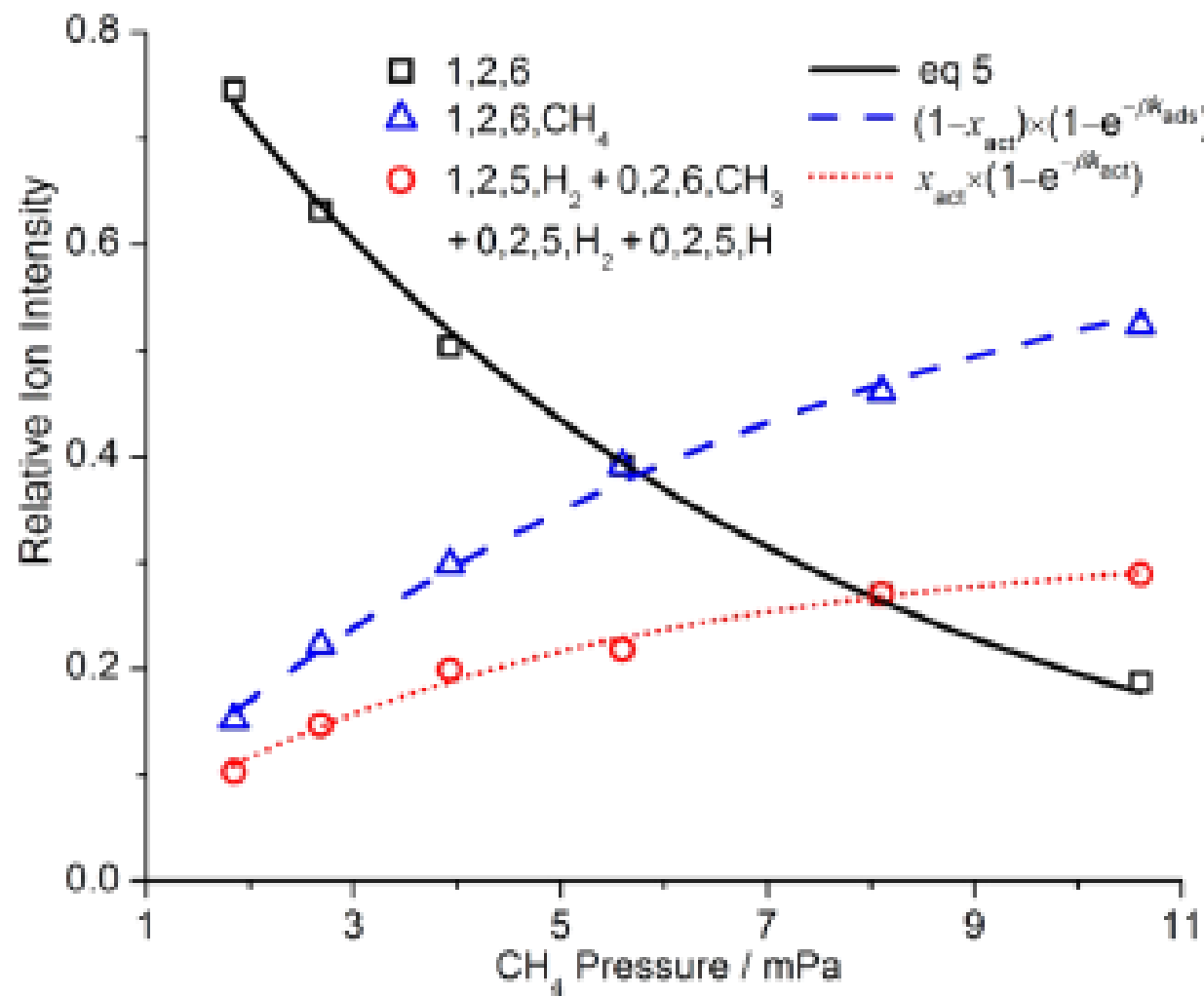


Figure 4. Variations of relative ion intensities with respect to the CH_4 pressure in the reaction of AuV_2O_6^+ with CH_4 .

$$I_{\text{R}} = x_{\text{act}} \times \exp(-\beta k_{\text{act}}) + (1 - x_{\text{act}}) \times \exp(-\beta k_{\text{ads}})$$

$$I_{\text{ads}} = (1 - x_{\text{act}}) \times [1 - \exp(-\beta k_{\text{ads}})]$$

$$I_{\text{act}} = x_{\text{act}} \times [1 - \exp(-\beta k_{\text{act}})]$$

$$I_{\text{act}} = I_1 + I_2 + I_3 + I_4$$

$$\frac{I_1}{I_2} = C_1, \quad \frac{I_3}{I_4} = C_2, \quad \frac{I_1 + I_2}{I_3 + I_4} = C_3$$

Table 1. Relative Abundance of the Reactive Cluster Isomer and the Rate Constants (k_{act} and k_{ads} in $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for Methane Transformation and Adsorption in the Reactions of AuV_2O_6^+ with CH_4 , CD_4 , and CH_2D_2

molecules	$x_{\text{act}} \times 100\%$	k_{act}	k_{ads}
CH_4	(32 ± 1)	7.8 ± 0.7	5.0 ± 0.2
CD_4	(35 ± 2)	5.4 ± 0.6	5.1 ± 0.3
CH_2D_2	(36 ± 1)	6.4 ± 0.4	5.1 ± 0.2

Structural Characterization:

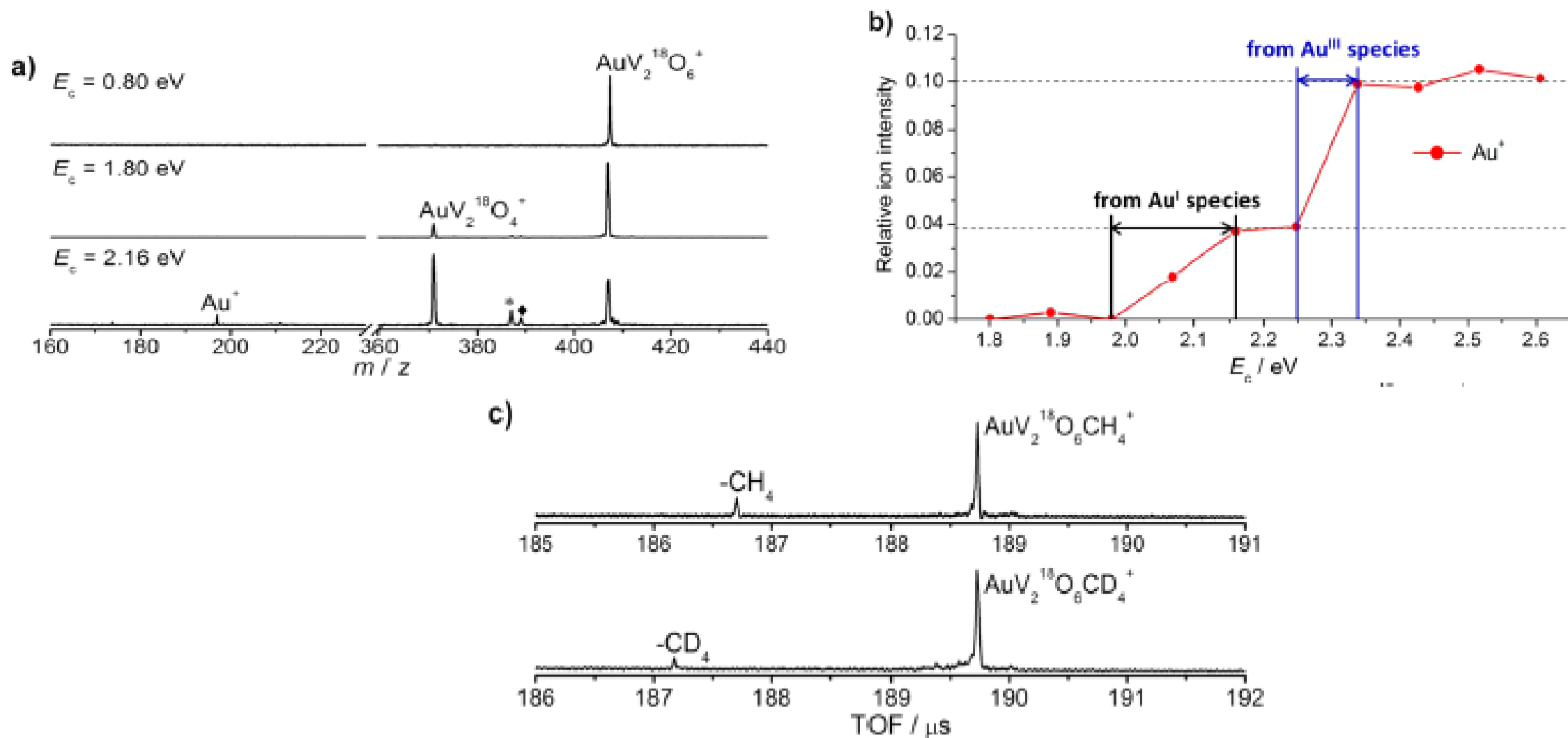


Figure 5. (a) CID spectra of $\text{AuV}_2^{18}\text{O}_6^+$ with 30 mPa Ar. Peaks marked as “*” and “◆” are due to water impurities. (b) The relative ion intensity of Au^+ with respect to E_c . (c) PID of $\text{AuV}_2^{18}\text{O}_6\text{CH}_4^+$ and $\text{AuV}_2^{18}\text{O}_6\text{CD}_4^+$ at 425 nm.

Structures and Reaction Mechanisms:

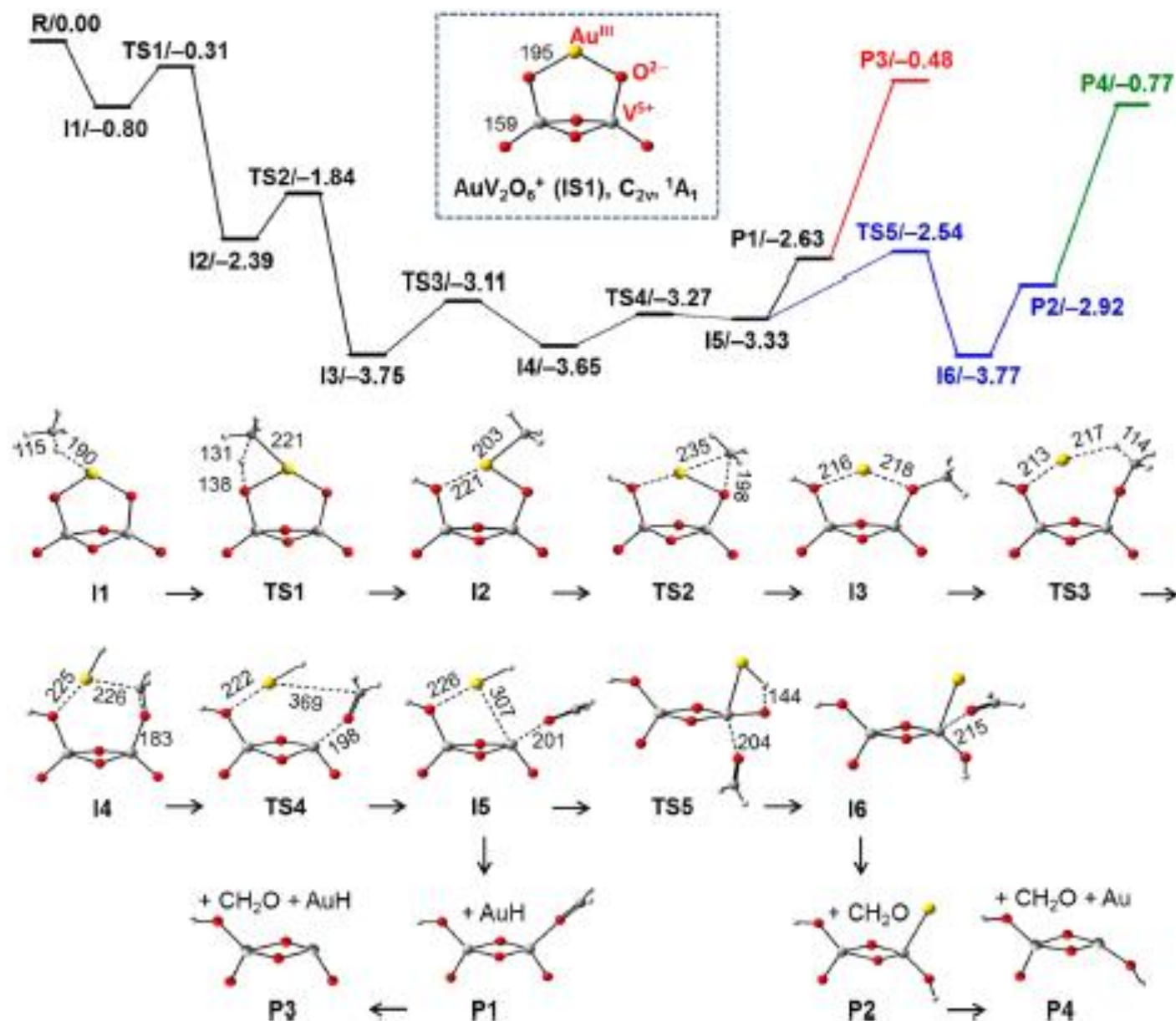
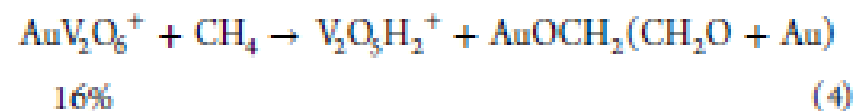
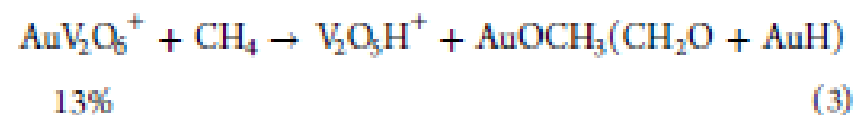


Figure 6. DFT calculated potential energy profile for reactions 1-4. The relative energies (in eV) of the reaction intermediates (I1-I6), transition states (TS1-TS5), and products (P1-P4) are with respect to the separate reactants (R). Some bond lengths (in pm) are given.

CONCLUSIONS:

- Combined with the structural characterizations and quantum chemistry calculations, it is revealed that the Au^{III} species with strong Lewis acid property is the active adsorption site and facilitates the C–H bond cleavage in collaboration with the adjacent O²⁻ anion through the mechanism of cooperative Lewis acid–base pairs.
- Such mechanism of cooperative effect of Lewis acid–base pairs has been proposed for methane activation in many condensed-phase systems including M^{II}–O²⁻ (M = Pt, Pd, Mg) and M^{III}–O²⁻ (M = Sc, Y, Ln, Al). However, it has been scarcely reported for methane activation by gas-phase clusters previously.
- This study enriches the Au^{III} chemistry at a strictly molecular level and provides a fundamental basis to transform methane under mild conditions. Transformation of the activated methane into formaldehyde has been identified.

THANK
YOU...