

Activation of Multiple C–H Bonds Promoted by Gold in AuNbO_3^+ Clusters**

Xiao-Nan Wu, Xiao-Na Li, Xun-Lei Ding, and Sheng-Gui He*

The success of generating more efficient catalysts lies in the improvement of their activity without sacrificing their selectivity, primarily through the identification of active sites and mechanisms that govern the reaction. The development of catalysts for the selective activation of carbon–hydrogen (C–H) bonds is a challenging task in chemistry.^[1] Earlier condensed-phase studies postulated that oxygen-centered radicals (O^\cdot)^[2] are active sites for the activation of C–H bonds of alkane molecules.^[3] Recent investigations on oxide clusters in the gas phase^[4] that can be handled under isolated, controlled, and reproducible conditions confirm that O^\cdot radicals are indeed very crucial for C–H activation of methane,^[5] ethane,^[6] *n*-butane,^[7] etc. under thermal collision conditions. The reported activations of alkane molecules by O^\cdot over atomic clusters usually produce products of single hydrogen atom abstraction (HAA; products: alkyl radicals). Herein, we report that when O^\cdot -containing clusters are doped with gold atoms, it is possible to observe activation of multiple (double and triple) C–H bonds of one alkane molecule with high selectivity. The activation of multiple C–H bonds is important as it directly generates alkenes, which are value-added products, from alkanes or alkenyl (other than alkyl) radicals, which can be intermediates for further chemical transformation.^[8]

Gold catalysts, such as Au^{I} and Au^{III} salts, are powerful for C–H activation,^[9] in which the $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ catalytic cycle is very likely to be involved.^[10] Gold species in different charge states (cationic, neutral, and anionic)^[11] are often identified in supported gold catalysts. These findings suggest that gold may switch its role between electron donor and electron acceptor in a chemical reaction. As a result, doping atomic clusters (metal oxide clusters in this study) with gold atoms may cause significant charge redistribution within the clusters and during reactions. The C–H activation, which depends heavily on the effects of local charges,^[12] can thus be effectively tuned by the introduction of gold into clusters.

Gold clusters and gold-containing heteroatomic systems^[13,14] in the gas phase have been extensively studied, and the bonding nature of gold, including the relativistic effect,^[15] was demonstrated. Investigations on gold-containing clusters of mixed oxides are very limited,^[16] but important in order to understand the mechanistic details of reactions catalyzed by oxide-supported gold, which have been under debate for many years.^[11,17] Taking into account that niobium oxides have extraordinary catalytic properties in selective oxidation reactions, including hydrocarbon conversions,^[18] we generated the mixed-oxide clusters $\text{Au}_x\text{Nb}_y\text{O}_z^+$ by laser ablation and studied their reactivity with small alkane molecules by mass spectrometry.

The mass spectra shown in Figure 1 indicate that AuNbO_3^+ cluster ($m/z = 338$) can abstract one, two, and three H atoms from methane, ethane, and *n*-butane, respectively:

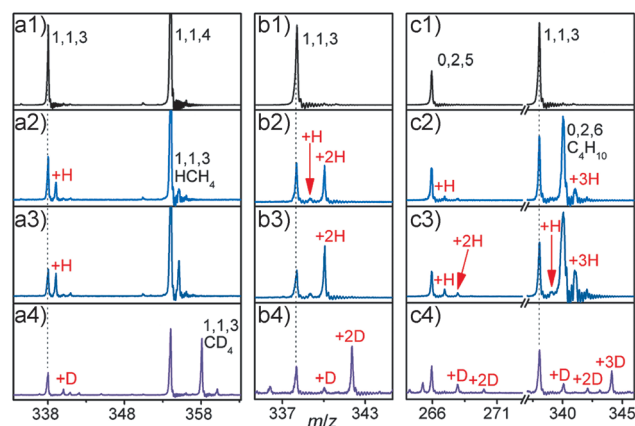
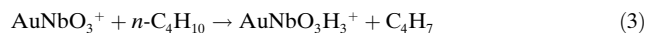
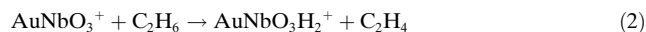
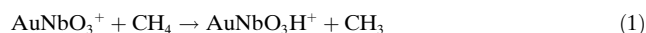


Figure 1. Selected time-of-flight mass spectra for interactions of $\text{Au}_x\text{Nb}_y\text{O}_z^+$ with a) methane, b) ethane, and c) *n*-butane. Reference spectra without hydrocarbons in the reaction cell are shown in a1, b1, and c1. The reactant gases in the cell are: a2) CH_4 (0.25 Pa), a3) CH_4 (0.35 Pa), a4) CD_4 (0.35 Pa); b2) C_2H_6 (0.17 Pa), b3) C_2H_6 (0.28 Pa), b4) C_2D_6 (0.28 Pa); and c2) *n*- C_4H_{10} (0.014 Pa), c3) *n*- C_4H_{10} (0.017 Pa), c4) *n*- C_4D_{10} (0.017 Pa). “x,y,z” denotes $\text{Au}_x\text{Nb}_y\text{O}_z^+$. The “+H”, “+D”, etc. mark the product signals with respect to AuNbO_3^+ or Nb_2O_5^+ . Most of the $\text{Au}_x\text{Nb}_y\text{O}_z^+$ clusters pick up the hydrocarbon molecules in the reaction cell (see the Supporting Information for complete spectra). The $\text{Nb}_2\text{O}_5\text{C}_4\text{H}_{10}^+$ signal overlaps with $\text{AuNbO}_3\text{H}_2^+$ (c2 and c3).

[*] Dr. X.-N. Wu, Dr. X.-N. Li, Dr. X.-L. Ding, Prof. Dr. S.-G. He
Beijing National Laboratory for Molecular Science, State Key
Laboratory for Structural Chemistry of Unstable and Stable Species,
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190 (P. R. China)
E-mail: shengguihe@iccas.ac.cn

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The above reactions were confirmed by isotopic labeling experiments (Figure 1, a4, b4, and c4). It is important to point out that production of $\text{AuNbO}_3\text{H}_2^+$ from ethane and $\text{AuNbO}_3\text{H}_3^+$ from *n*-butane are very selective, because product signals of AuNbO_3H^+ (with C_2H_6 and *n*- C_4H_{10}) and $\text{AuNbO}_3\text{D}_2^+$ (with *n*- C_4D_{10}) are relatively weak. The reaction of AuNbO_3^+ with propane (C_3H_8 , see Figure S3 in the Supporting Information) generates both the double and triple HAA products, thus indicating a transition from selective double (reaction (2)) to selective triple HAA (reaction (3)) reactivity. Figure 1c and Figures S2–S4 indicate that the double HAA from the C_2 – C_4 alkanes by homonuclear oxide cluster Nb_2O_5^+ ($m/z=266$)^[5e] can also be observed, although this is only a minor reaction pathway compared with the single HAA.

In addition to HAA, molecular association is also observed for the reactions of AuNbO_3^+ with alkane molecules. Table 1 lists the total and HAA rate constants.^[6c] The derived reaction efficiencies (ϕ)^[19] of AuNbO_3^+ with CD_4 , C_2H_6 , C_3D_8 , and *n*- C_4H_{10} are 0.49, 0.55, 0.78, and 3.0, respectively. Note that the ionic products of multiple HAAs

Table 1: Bimolecular rate constants (k_1 in $10^{-10} \text{ cm}^3 \text{ s}^{-1}$, with pseudo-first-order kinetic approximation) for total and HAA reactions of AuNbO_3^+ with small molecules.

Entry	Molecules ^[a]	k_1^{total}	k_1^{HAA}
1	CD_4	4.1	0.2
2	C_2H_6	5.0	2.9
3	C_3D_8	4.6	1.8
4	C_3D_8	6.6	4.0
5	<i>n</i> - C_4H_{10}	28	20

[a] Rate constants for reactions with CH_4 , C_3H_8 , and *n*- C_4D_{10} were not derived because AuNbO_4^+ , $\text{AuNbO}_4\text{N}_2^+$, and Nb_3O_8^+ signals overlap with $\text{AuNbO}_3\text{CH}_4^+$, $\text{AuNbO}_3\text{C}_3\text{H}_8^+$, and $\text{AuNbO}_3\text{C}_4\text{D}_{10}^+$, respectively (Figures 1, S3, and S4). The uncertainties of the relative k_1 values are within 30% and the absolute rate constants can be systematically under- or over-estimated by a factor of five.^[5e, 6a]

in reactions (2) and (3) are not a result of secondary reactions, such as $\text{AuNbO}_3\text{H}^+ + \text{C}_2\text{H}_6$ or $\text{AuNbO}_3\text{H}^+ + n\text{-C}_4\text{H}_{10}$, because the relative signal intensities of products of double or triple HAA with respect to AuNbO_3H^+ do not change when the concentration of the reactant gases is lowered.

The observation of the highly selective double HAA (reaction (2)) is interesting but not unexpected, because it terminates with the generation of a stable molecule (C_2H_4).^[20] However, the triple HAA (reaction (3)) is very surprising, because reaction (2) would suggest that $\text{AuNbO}_3^+ + n\text{-C}_4\text{H}_{10}$ should terminate with $\text{AuNbO}_3\text{H}_2^+ + \text{C}_4\text{H}_8$.

Density functional theory (DFT) calculations were performed for the structures of AuNbO_3^+ (Figure S7) and the reaction mechanisms with CH_4 , C_2H_6 , and *n*- C_4H_{10} (Figure 2b–d). The Au atom is terminally bonded with one O atom in the isomer of AuNbO_3^+ with the lowest energy, which contains an oxygen-centered radical O^- (Figure 2a). Such a radical can abstract one H atom from CH_4 , C_2H_6 , or *n*- C_4H_{10} very easily. The HAA from CH_4 terminates with the generation of a CH_3 radical ($\Delta H_{0K} = -0.75 \text{ eV}$) and the

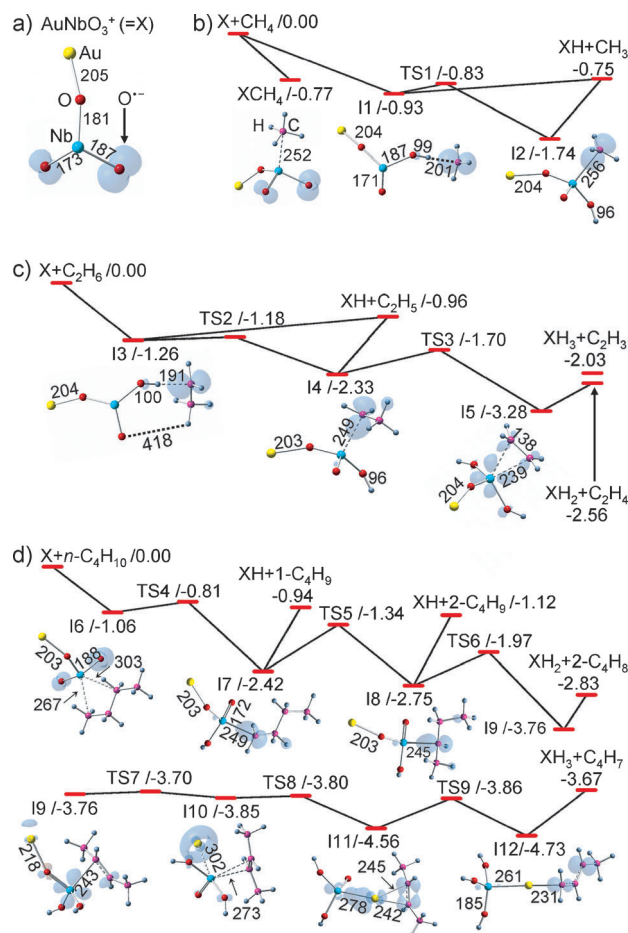


Figure 2. The DFT-calculated structure of AuNbO_3^+ (a) and potential energy profiles for reactions of AuNbO_3^+ (denoted as X) with CH_4 (b), C_2H_6 (c), and *n*- C_4H_{10} (d). The structures of the reaction intermediates (I1–I12) are given, those of the transition states (TS1–TS9) and products can be found in the Supporting Information (Figure S8–S10). The relative ΔH_{0K} energies (in eV), bond lengths (in pm), and profiles for unpaired spin densities are shown.

formation of double HAA species CH_2 is endothermic ($\Delta H_{0K} = 0.96 \text{ eV}$). The DFT study indicates that CH_4 can also be nondissociatively absorbed on AuNbO_3^+ (see XCH_4 in Figure 2b, where X denotes AuNbO_3^+), which can be confirmed by a collision-induced dissociation experiment (Figure S6).

For $\text{AuNbO}_3^+ + \text{C}_2\text{H}_6$ (Figure 2c), the C_2H_5 radical generated in the HAA by O^- tends to bind strongly with the Nb atom ($\text{I3} \rightarrow \text{TS2} \rightarrow \text{I4}$) rather than to form free C_2H_5 ($\text{I3} \rightarrow \text{XH} + \text{C}_2\text{H}_5$). The high energy that is released (2.33 eV) after formation of I4 drives the second HAA ($\text{I4} \rightarrow \text{TS3} \rightarrow \text{I5}$) from C_2H_5 by a non-radical O^{2-} ion, which finally leads to the highly exothermic double HAA (reaction (2), $\Delta H_{0K} = -2.56 \text{ eV}$). Because TS2 (−1.18 eV) is significantly lower in energy than $\text{XH} + \text{C}_2\text{H}_5$ (−0.96 eV), the double HAA can be highly selective with respect to the single HAA, which agrees with the experiments.

For $\text{AuNbO}_3^+ + n\text{-C}_4\text{H}_{10}$ (Figure 2d), formation of the double HAA intermediate I9 with the C_4H_8 moiety is more favorable than butyl generation ($\text{XH} + 1\text{-C}_4\text{H}_9$ and $\text{XH} + 2\text{-C}_4\text{H}_9$).

C_4H_9), which is similar to the favorable formation of I5 rather than $XH + C_2H_5$ (Figure 2c). After formation of I9, the Au atom is transferred from O to make chemical bonds with Nb and C atoms ($I9 \rightarrow TS7 \rightarrow I10 \rightarrow TS8 \rightarrow I11$). This process releases additional energy to break the third C–H bond ($I11 \rightarrow TS9 \rightarrow I12$). The energies of TS7–TS9 and $XH_3 + C_4H_7$ ($C_4H_7 = CH_2CHCHCH_3$) are well below that of $XH_2 + 2-C_4H_8$, so the triple HAA (reaction (3)) is the major pathway for $AuNbO_3^+ + n-C_4H_{10}$. This result agrees well with the experiments (Figure 1c). Note that H atom transfers starting from many other intermediates and alternative carbon sites were also tested (Figure S11), while Figure 2d provides the most favorable pathway for reaction (3).

The Au atom is transferred from O to Nb during reaction (3). Such a gold atom transfer (GAT) is crucial because it makes space on the O atom, which accepts the third H atom. The lowest lying isomer of $AuNbO_3H_3^+$ is a singlet with three OH^- groups and one Au–Nb chemical bond (Figure S13). Only formation of this $Au-Nb(OH)_3$ structure can satisfy the favorable thermodynamics to selectively produce the triple rather than the double HAA products:

$$\Delta H_{0K}(AuNbO_3H_3^+ + C_4H_7) \ll \Delta H_{0K}(AuNbO_3H_2^+ + 2-C_4H_8) \quad (4)$$

During reaction (3), Au atoms are involved in significant charge (Table 2) and spin (Figure 2d) transfers. The natural charge on Au decreases monotonically from 0.81 |e| in I6 to

Table 2: Natural charges (in |e|) on metal atoms in I6–I12 of Figure 2d.

Entry		First HAA		Second HAA			Third HAA	
		I6	I7	I8	I9	I10	I11	I12
1	Q_{Au}	0.81	0.78	0.77	0.40	0.28	0.27	0.16
2	Q_{Nb}	1.65	1.78	1.76	1.75	1.54	1.63	1.51
3	$Q_{Au} + Q_{Nb}$	2.46	2.56	2.53	2.15	1.82	1.90	1.67

0.16 |e| in I12. In contrast, the charge variation of the Nb atom is small. The gold atom in I6–I8 can be considered to be Au^{1+} ($5d^{10}6s^0$), which is consistent with no distribution of unpaired spin density (UPSD) on Au in these cluster species. Upon the second HAA and the GAT ($I9 \rightarrow I10$), more and more UPSD is transferred to Au and most of the UPSD ($\approx 1 \mu_B$) of I10 is localized on Au, which can be considered to be Au^0 ($5d^{10}6s^1$). This result is also consistent with loosely-bonded nature of Au in I10. Insertion of Au atom into Nb and C atoms ($I10 \rightarrow I11$) causes significant UPSD transfer from Au to C atoms. The third HAA ($I11 \rightarrow I12$) further eliminates the UPSD on Au and results in sharing of one pair of valence electrons between Au and Nb (Figure 3). For the free product $AuNb(OH)_3^+$, the total Au–Nb bond order amounts to 1.42 (Table 3) implying that this pair of electrons is well stored between the two metal atoms. Because of the strong relativistic effect,^[15] the Au atom has a contracted and stabilized 6s orbital, which tends to accept an electron.^[21] This result is consistent with a high percentage (62 %) of Au 6s in the highest occupied molecular orbital (HOMO, Figure 3, left) as well as significant (45 %) ionic bonding between Au and Nb (Table 3, last column).

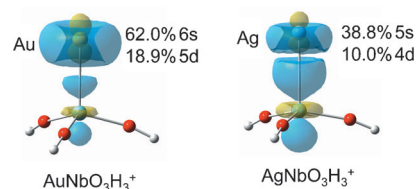


Figure 3: The HOMOs of $AuNbO_3H_3^+$ and $AgNbO_3H_3^+$ obtained through DFT calculations.

Table 3: M–Nb bond orders of $MNbO_3H_3^+$ (M = Au, Ag, and Cl) by natural bond orbital analysis.

Entry		Covalent	Ionic	Total	Ionic [%]
1	Au–Nb	0.78	0.64	1.42	45
2	Ag–Nb	0.65	0.32	0.97	33
3	Cl–Nb	0.48	1.07	1.55	69

During the second and the third HAA, the protons ($H = p^+ + e^-$) are transferred to non-radical O^{2-} sites and the electrons reduce metal atoms (Figure 2d, see entry 3 in Table 2). Such a process has been well described^[22] as proton-coupled electron transfer and was identified in reactions of many transition-metal complexes. Both the proton and electron are transferred to a radical O^- site during the first HAA ($I6 \rightarrow I7$), the barrier of which (0.25 eV) is much smaller than those of the second (0.78 eV) and third (0.70 eV) HAAs.

To further demonstrate that the multiple HAA reactivity is due to the unique property of gold, the reactivity of the silver-containing counterpart $AgNbO_3^+$ was considered theoretically and experimentally. In contrast to the highly localized HOMO (>80 % on Au) of $AuNbO_3H_3^+$, the HOMO of $AgNbO_3H_3^+$ is almost equally delocalized around Ag and Nb atoms. The bond order of Ag–Nb is much lower than that of Au–Nb (Table 3), and the calculated bond energy of $Ag-NbO_3H_3^+$ (1.87 eV) is also smaller than that of $Au-NbO_3H_3^+$ (2.35 eV). As a result, the triple HAA can be more exothermic than the double HAA for $AuNbO_3^+ + n-C_4H_{10}$ [equation (4)]. For the silver system, the tendency is reverse: $\Delta H_{0K}(AgNbO_3H_2^+ + 2-C_4H_8)$ (–2.80 eV) is more negative than $\Delta H_{0K}(AgNbO_3H_3^+ + C_4H_7)$ (–2.25 eV), a result that is consistent with our experiment that the triple HAA can not be observed for $AgNbO_3^+ + n-C_4H_{10}$. It can be concluded that the triple HAA reactivity (reaction (3)) is promoted by gold.

In $AuNbO_3^+ + C_2H_6$, the double HAA is highly selective with respect to the single HAA (Figure 1b). This observation is in sharp contrast with the result for $AgNbO_3^+ + C_2H_6$, in which the single HAA dominates the reaction (Figure S5). The reaction profile of $AgNbO_3^+ + C_2H_6$ is very similar to that of the gold system (Figure S9). However, the C_2H_5 radical generated from the first HAA is more loosely bounded in $AgNbO_3H \cdot C_2H_5^+$ (I3' in Figure 4) than in $AuNbO_3H \cdot C_2H_5^+$ (I3 in Figure 2c) because the former has lower binding energy (0.25 versus 0.30 eV) and longer $OH-C_2H_5$ distance (197 versus 191 pm). As a result, the C_2H_5 radical in $AgNbO_3H \cdot C_2H_5^+$ tends to dissociate into the single HAA products,

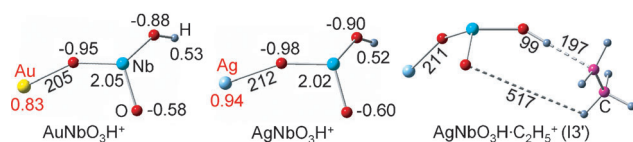


Figure 4. Natural charge (in |e|) distribution in MNbO_3H^+ ($\text{M} = \text{Au}/\text{Ag}$) and the structure of $\text{AgNbO}_3\text{H-C}_2\text{H}_5^+$. Bond lengths are given in pm.

while $\text{AuNbO}_3\text{H-C}_2\text{H}_5^+$ has more chance to trap C_2H_5 for further conversion into C_2H_4 , which interprets the experimental results. The net charge in AgNbO_3H^+ is mostly shifted onto Ag atom (0.94 |e|, Figure 4) and the NbO_3H moiety is almost neutral (0.06 |e|). In contrast, the ionization energy of Au (9.22 eV) is higher (because of the stabilized Au 6s orbital)^[15] than that of Ag (7.58 eV), so the Au atom in AuNbO_3H^+ is less charged (0.83 |e|) and the remaining NbO_3H moiety has a net charge of 0.17 |e|. Thus, when C_2H_5 approaches MNbO_3H^+ ($\text{M} = \text{Au}/\text{Ag}$) through the NbO_3H side (I3 in Figure 2c and I3' in Figure 4), the gold system will have relatively strong polarization^[19b,c] of C_2H_5 by NbO_3H and thus a good chance of trapping C_2H_5 for further chemical conversion. It can be concluded that the highly selective double HAA reactivity (reaction (2)) is also promoted by gold.

Great interests have been devoted to gold catalysts, such as Au/MgO , Au/TiO_2 , and many others that show excellent performances in important reactions, including CO oxidation^[11] and selective oxidation of organic molecules^[23] (e.g., alkenes, alkanes, etc.). The interpretation of gold oxidation states in the catalysts is often controversial. Some reports emphasized the importance of cationic gold,^[11a] while others, such as those based on theoretical studies, demonstrated the importance of anionic gold (e.g., in O_2 activation).^[11c] It is inappropriate to state that the oxidation state of Au in $\text{AuNbO}_3\text{H}_3^+$ (Figure 3) is anionic because Au carries a positive natural charge (0.18 |e|). However, the Au atom acts as electron acceptor during the triple HAA (Table 2, entry 1) and helps to store a pair of valence electrons between two metal atoms (Au and Nb). This pair of electrons may be released to activate and reduce O_2 (Figure S15). We thus propose that storage (starting from Au^{1+}) and release of a pair of valence electrons around an Au atom can be an important mechanism during gold-catalyzed oxidation reactions, particularly in cases when isolated mononuclear gold species^[11a,24] on oxides are prepared as catalysts.

It is interesting to point out that multiple HAAs with C_2H_6 or $n\text{-C}_4\text{H}_{10}$ (Figure 1 and 2) are initiated by highly reactive oxygen-centered radicals. Such radical initiation is often proposed for alkane transformations, such as the selective oxidation of cyclohexane to produce cyclohexanone and cyclohexanol over cobalt^[25] and gold^[23b,26] catalysts. The cluster reactions thus show similar behavior to condensed-phase systems and provide insights into the possible activation of multiple C–H bonds at the molecular level, which can be difficult in condensed-phase studies.

In conclusion, the highly selective activation of multiple C–H bonds initiated by oxygen-centered radicals and pro-

moted by gold is demonstrated. Gold acts as electron acceptor, and a pair of valence electrons can be stored between gold and metal (niobium) atoms in the triple HAA. This can be an important step to understand gold chemistry in many chemical processes.

Experimental Section

A reflectron time-of-flight mass spectrometer (TOF-MS) coupled with a laser ablation/supersonic expansion cluster source and a fast-flow reactor was used for the experiments (see Ref. [27] for details). The $\text{M}_x\text{Nb}_y\text{O}_z^+$ clusters ($\text{M} = \text{Au}$ or Ag) were generated by laser ablation of an M/Nb mixed metal disk (molar ratios: $\text{Au}:\text{Nb} = 3:7$ and $\text{Ag}:\text{Nb} = 1:5$) in the presence of O_2 (0.3%) seeded He carrier gas (8 atm). The generated clusters are reacted with CH_4 , C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, and their deuterated compounds (0.01–0.5 Pa) in the reaction cell for about 60 μs under thermal collision conditions. The reflectron TOF-MS is used to measure the cluster abundances before and after the reactions. A separated TOF/TOF-MS (tandem MS)^[28] employing a crossed He beam is used to study collision-induced dissociation for mass-selected $\text{AuNbO}_3\text{CD}_4^+$ from reaction of AuNbO_3^+ with CD_4 . The method to derive the rate constants (Table 1) is described in Ref. [6c]. The details of DFT calculations are given in the Supporting Information.

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