Supporting information for

Vacuum Ultraviolet Ionization-Induced Reaction of Neutral $Au_2Al_2O_3$ Clusters with Methane

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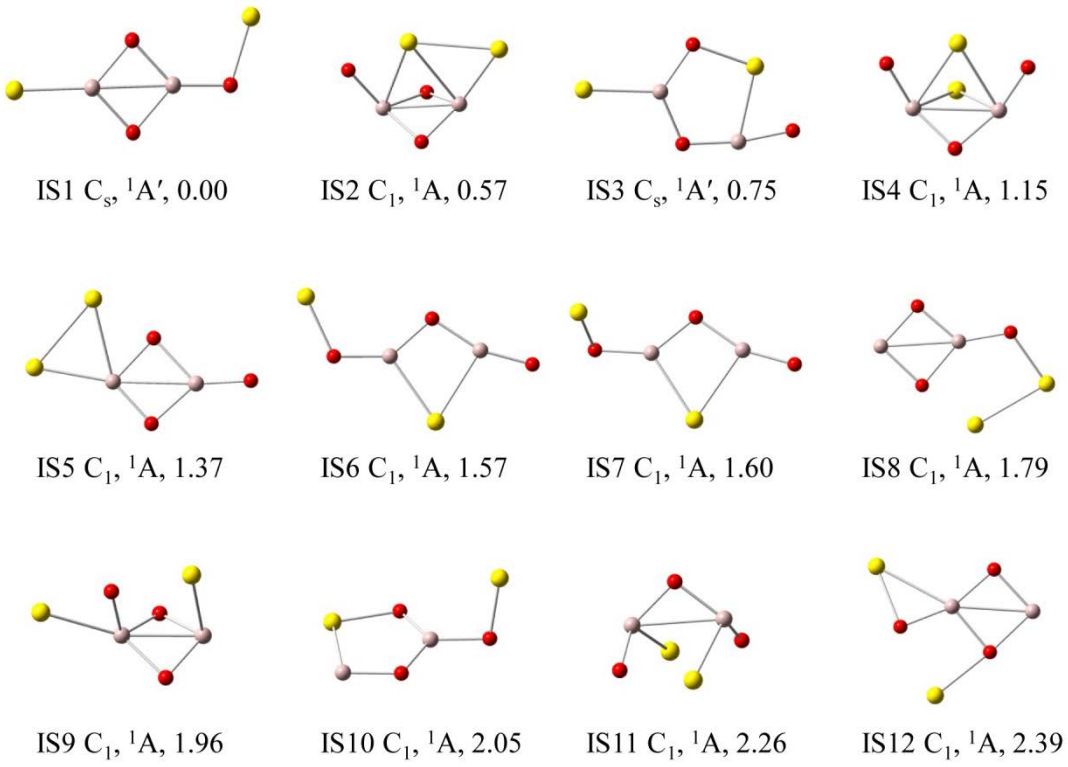

Figure S1. The DFT optimized structural isomers of neutral $Au_2Al_2O_3$ cluster. The symmetry, electronic state, and relative energies (in eV, with zero-point vibrational energy correction) are listed below each structure.

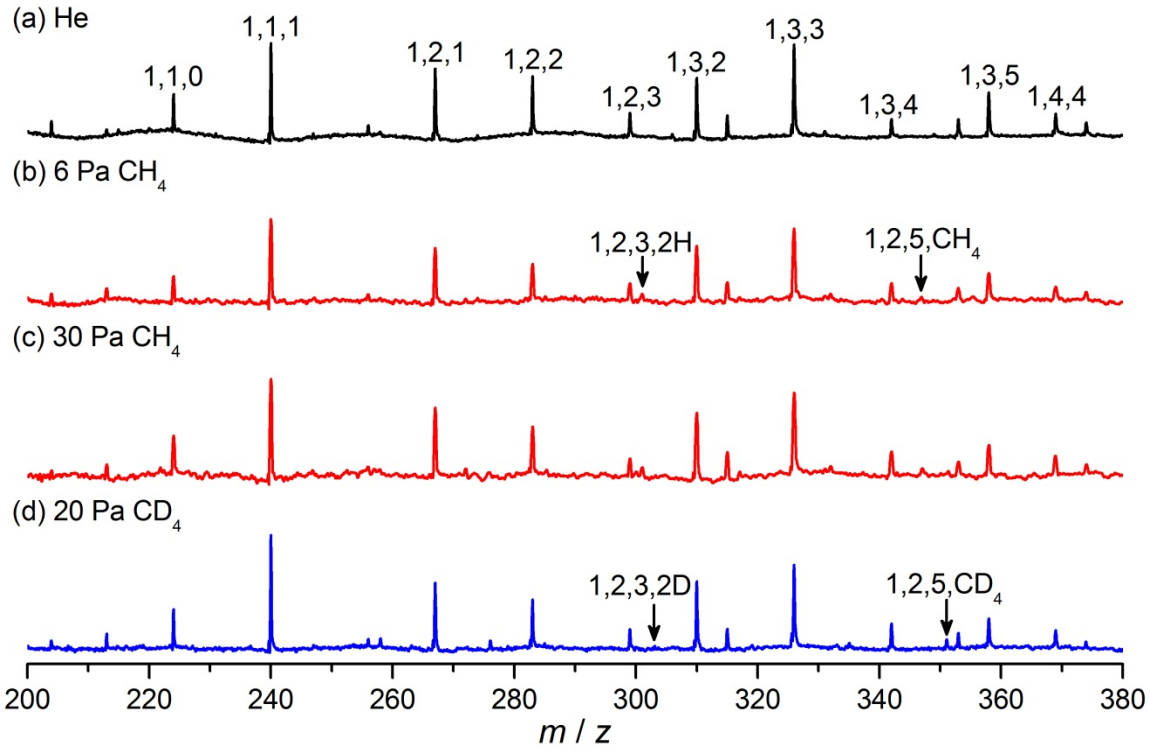

Figure S2. TOF mass spectra for the reactions of neutral $Au_xAl_yO_z$ clusters (a) with CH_4 (b, c), and CD_4 (d). The reactant gas pressures are shown. $Au_xAl_yO_z$ is denoted as *x*, *y*, *z* and $Au_xAl_yO_zX$ is denoted as *x*, *y*, *z*, X (X = H, D, CH_4, CD_4).

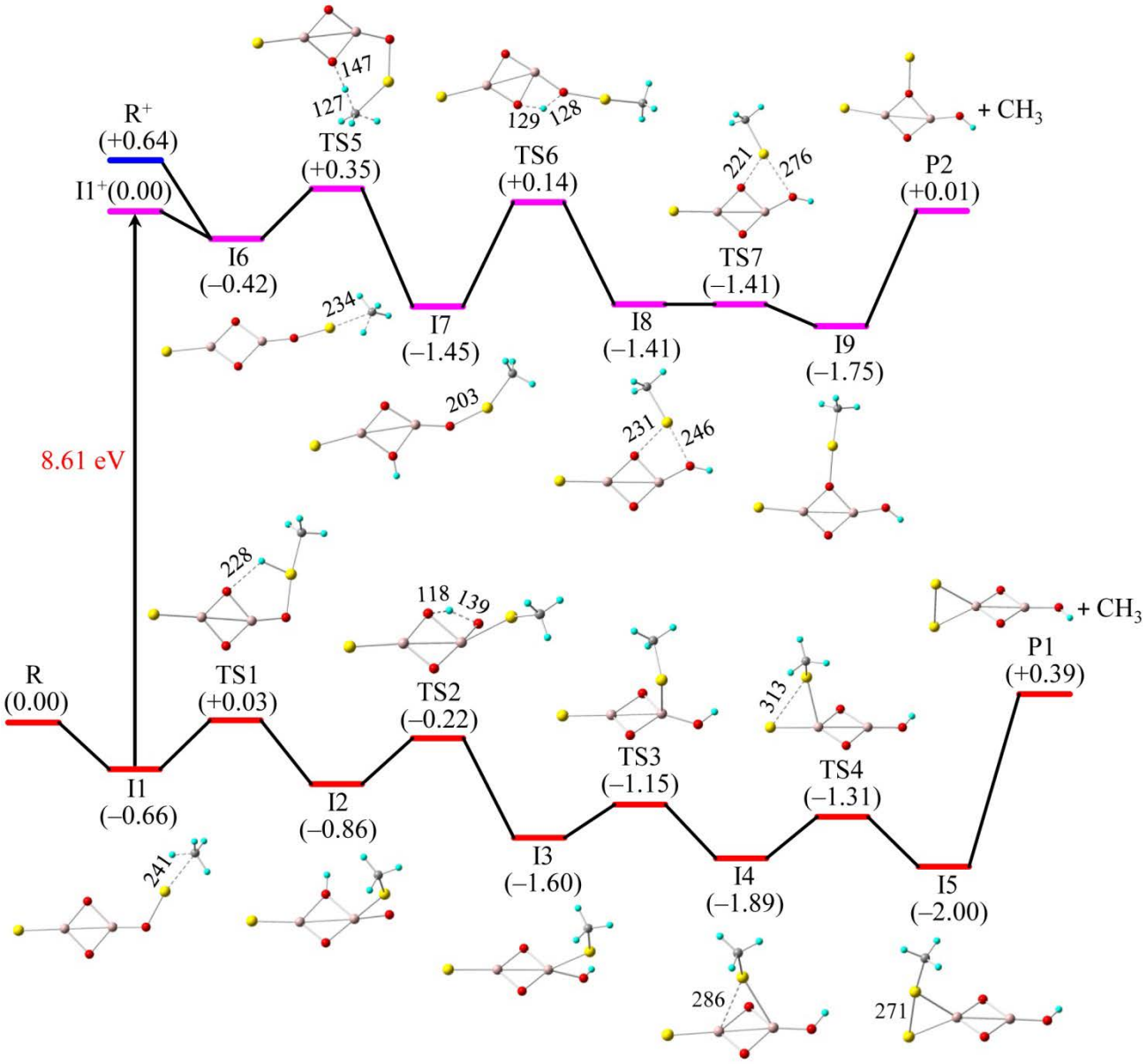

Figure S3. DFT-calculated potential-energy profile for VUV ionization induced reaction of neutral $Au_2Al_2O_3$ cluster with CH_4 (R). The structures of the intermediates (I1−I9), transition states (TS1−TS7), and products (P1 and P2) are shown. The relative energies (eV) of the reaction intermediates (I1–I5), transition states (TS1–TS4), and products (P1) are with respect to the separated reactants (R). The relative energies (eV) of the separated reactants (R^+: $Au_2Al_2O_3^+$ and CH_4), reaction intermediates (I6–I9), transition states (TS5–TS7), and products (P2) are with respect to $I1^+$. The vertical ionization energy of I1 and the bond lengths (in pm) are also shown.

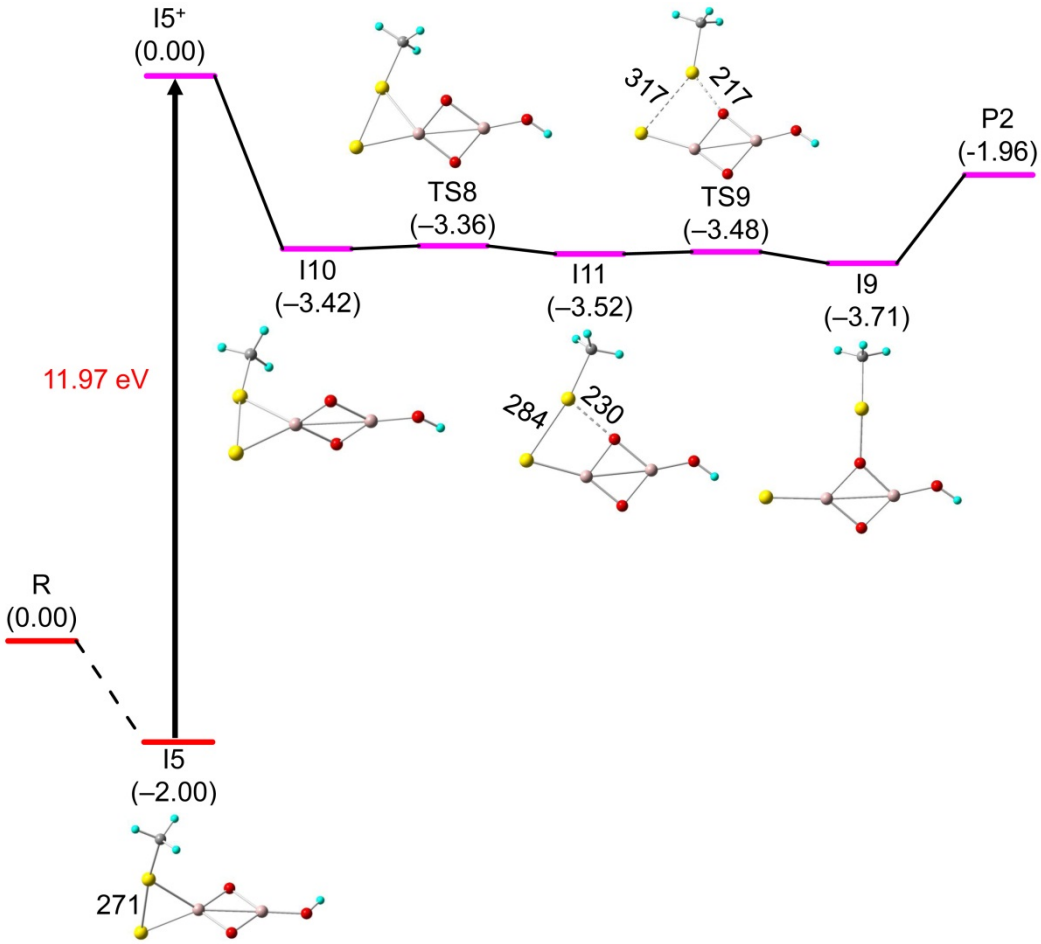

Figure S4. DFT-calculated potential-energy profile for VUV ionization of I5 to generate $CH_3^{\bullet}$. The relative energies (eV) of reaction intermediates (I9–I11), transition states (TS8 and TS9), and products (P2) are with respect to $I5^+$. The vertical ionization energy of I5 and the bond lengths (in pm) are also shown.

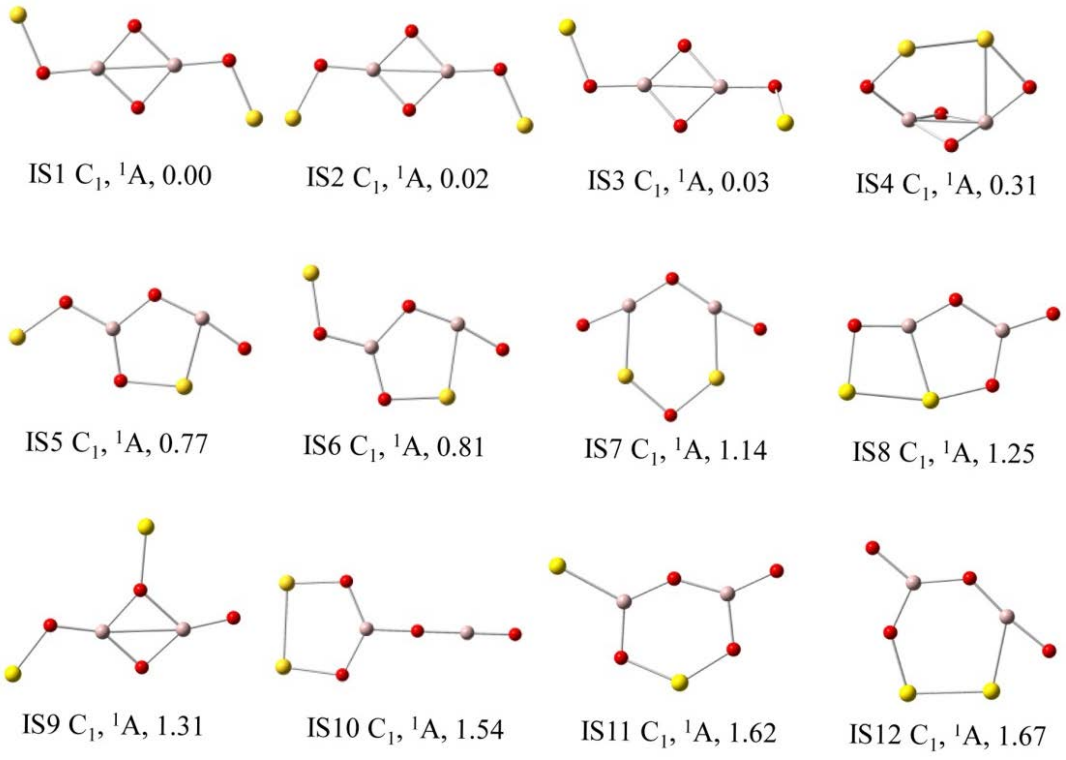

Figure S5. The DFT optimized structural isomers of neutral $Au_2Al_2O_4$ cluster. The symmetry, electronic state, and relative energies (in eV, with zero-point vibrational energy correction) are listed below each structure.

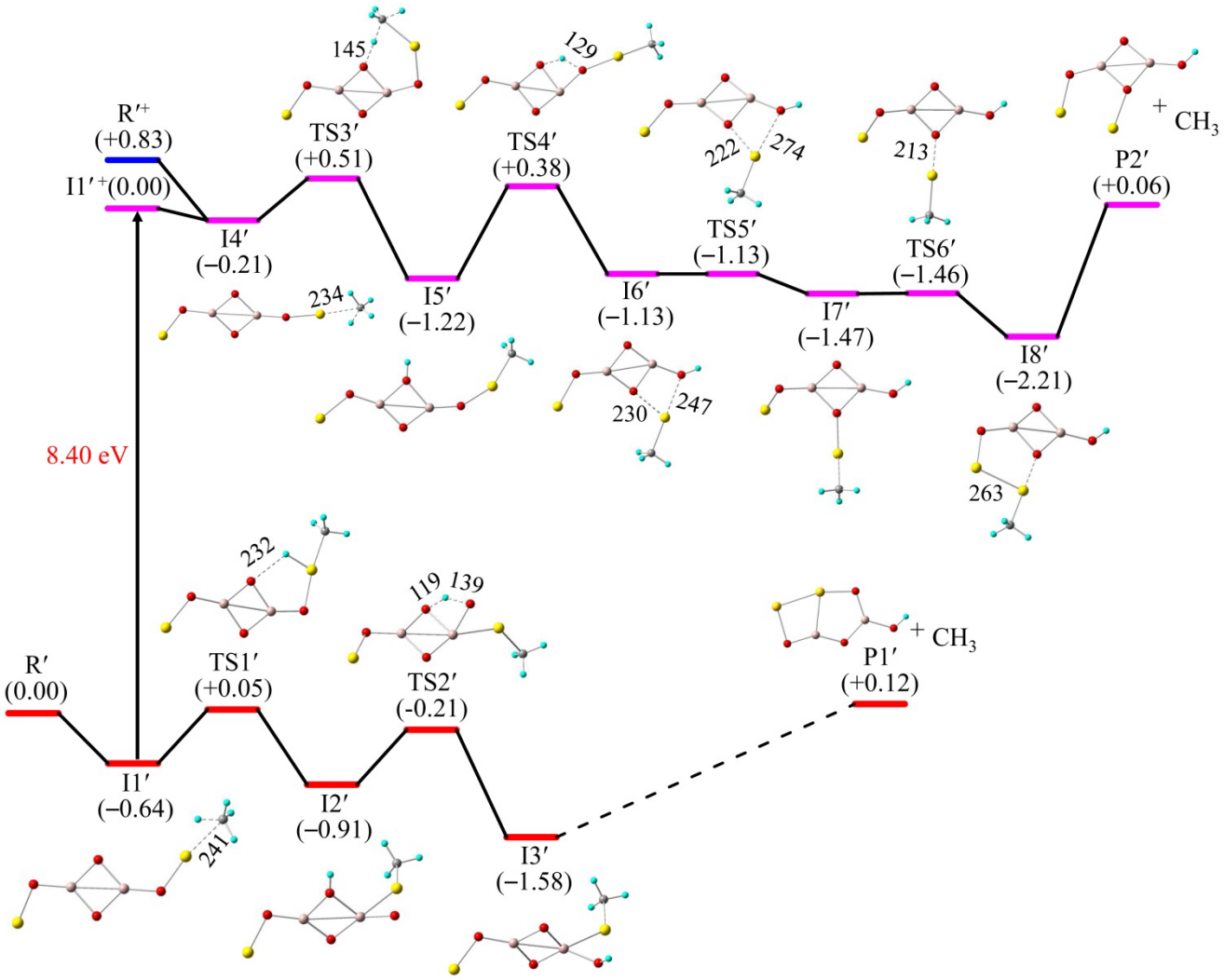

Figure S6. DFT-calculated potential-energy profile for VUV ionization induced reaction of neutral $Au_2Al_2O_4$ cluster with CH_4 (R′). The structures of the intermediates (I1′−I8′), transition states (TS1′−TS6′), and products (P1′ and P2′) are shown. The relative energies (eV) of the reaction intermediates (I1′–I3′), transition states (TS1′–TS2′), and products (P1′) are with respect to the separated reactants (R′). The relative energies (eV) of the separated reactants (R′$^+$: $Au_2Al_2O_4^+$ and CH_4), reaction intermediates (I4′–I8′), transition states (TS3′–TS6′), and products (P2′) are with respect to I1′$^+$. The vertical ionization energy of I1 and the bond lengths (in pm) are also shown.

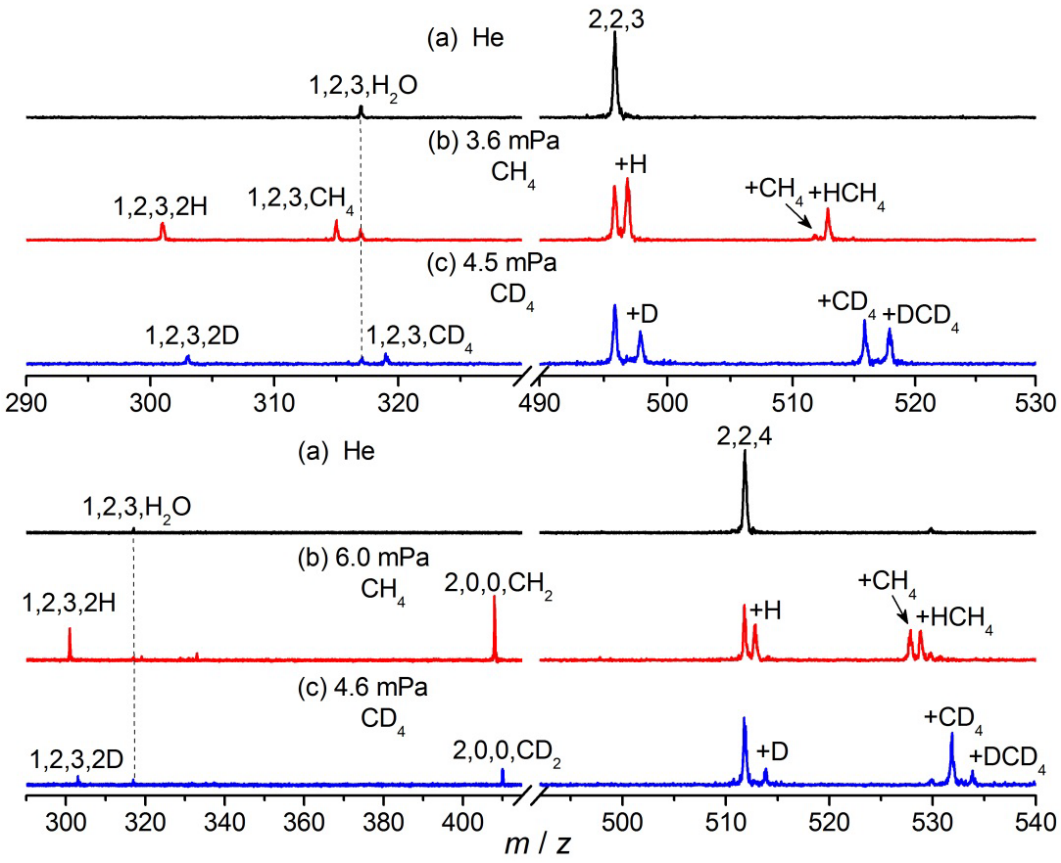

Figure S7. The TOF mass spectra for the reactions of mass-selected $Au_2Al_2O_3^+$ and $Au_2Al_2O_4^+$ clusters (a) with CH_4 (b) and CD_4 (c) in an ion trap reactor for about 1.9 ms. The reactant gas pressures are shown. $Au_xAl_yO_z^+$ is denoted as *x*, *y*, *z* and $Au_xAl_yO_zX^+$ is denoted as *x*, *y*, *z*, X (X = H, D, CH_4, CD_4, etc.). The label + X denotes $Au_2Al_2O_{3,4}\ X^+$ (X = H, D, CH_4, CD_4, etc.).

Figure S7 shows the time-of-flight mass spectra for the interactions of mass-selected $Au_2Al_2O_3^+$ (*m*/*z* = 496) and $Au_2Al_2O_4^+$ (*m*/*z* = 512) clusters with CH_4 and CD_4. The experimental details of $Au_2Al_2O_4^+$ cluster reaction system are similar to that of $Au_2Al_2O_3^+$.[1] It is noticeable that the both of the two clusters can react with a trace amount of H_2O impurity in the gas-handling system to generate $AuAl_2O_3H_2O^+$ ($Au_2Al_2O_3^+ + H_2O \rightarrow AuAl_2O_3H_2O^+ + Au$ and $Au_2Al_2O_4^+ + H_2O \rightarrow AuAl_2O_3H_2O^+ + AuO$). The product peaks assigned as $Au_2Al_2O_3H^+$, $Au_2Al_2O_3CH_4^+$, $AuAl_2O_3H_2^+$, and $AuAl_2O_3CH_4^+$ were observed for the reaction of $Au_2Al_2O_3^+$ cluster with CH_4,[1] suggesting the following reaction channels [Eq.(S1)-(S4)]:

$$Au_2Al_2O_3^+ + CH_4 \rightarrow Au_2Al_2O_3H^+ + CH_3 \qquad 57\% \text{ (S1)}$$

$$Au_2Al_2O_3^+ + CH_4 \rightarrow Au_2Al_2O_3CH_4^+ \quad 2\% \text{ (S2)}$$

$$Au_2Al_2O_3^+ + CH_4 \rightarrow AuAl_2O_3H_2^+ + AuCH_2 \quad 27\% \text{ (S3)}$$

$$Au_2Al_2O_3^+ + CH_4 \rightarrow AuAl_2O_3CH_4^+ + Au \quad 14\% \text{ (S4)}$$

Similarly, the product peaks assigned as $Au_2Al_2O_4H^+$, $Au_2Al_2O_4CH_4^+$, $AuAl_2O_3H_2^+$, and $AuCH_2^+$ were observed for the reaction of $Au_2Al_2O_4^+$ cluster with CH_4, as shown below [Eq.(S5)-(S8)]:

$$Au_2Al_2O_4^+ + CH_4 \rightarrow Au_2Al_2O_4H^+ + CH_3 \quad 39\% \text{ (S5)}$$

$$Au_2Al_2O_4^+ + CH_4 \rightarrow Au_2Al_2O_4CH_4^+ \quad 16\% \text{ (S6)}$$

$$Au_2Al_2O_4^+ + CH_4 \rightarrow AuAl_2O_3H_2^+ + AuOCH_2 \quad 14\% \text{ (S7)}$$

$$Au_2Al_2O_4^+ + CH_4 \rightarrow Au_2CH_2^+ + Al_2O_4H_2 \quad 31\% \text{ (S8)}$$

It is clear that the branching ratio of association channel (16%) for generation of $Au_2Al_2O_4CH_4^+$ is larger than that (2%) of $Au_2Al_2O_3CH_4^+$.

References

(1) Zhou, X.-H.; Li, Z.-Y.; Jiang, L.-X.; He, S.-G.; Ma, T.-M. Methane Activation Mediated by Dual Gold Atoms Doped in Aluminium Oxide Cluster Cations $Au_2Al_2O_3^+$. *Chemistryselect* **2017**, *2*, 991-996.