

Electronic Supplementary Information

Reaction of nitric oxide molecules

on transition-metal-doped silver cluster cations:

Size- and dopant-dependent reaction pathways

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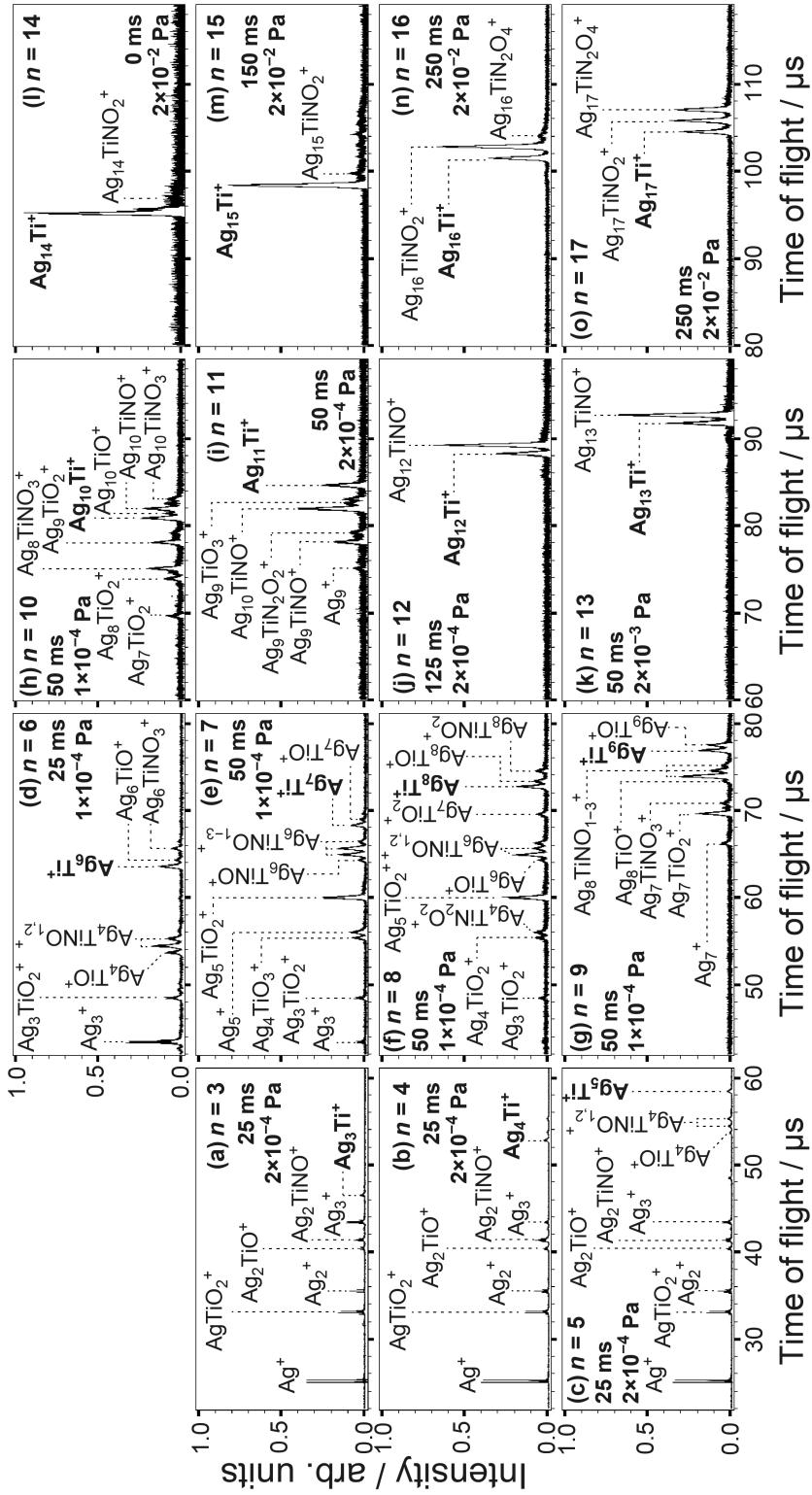


Figure S1. Mass spectra of ions produced from Ag_nTi^+ reacting with NO molecules for $n = 3\text{--}17$ in panels a–o, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

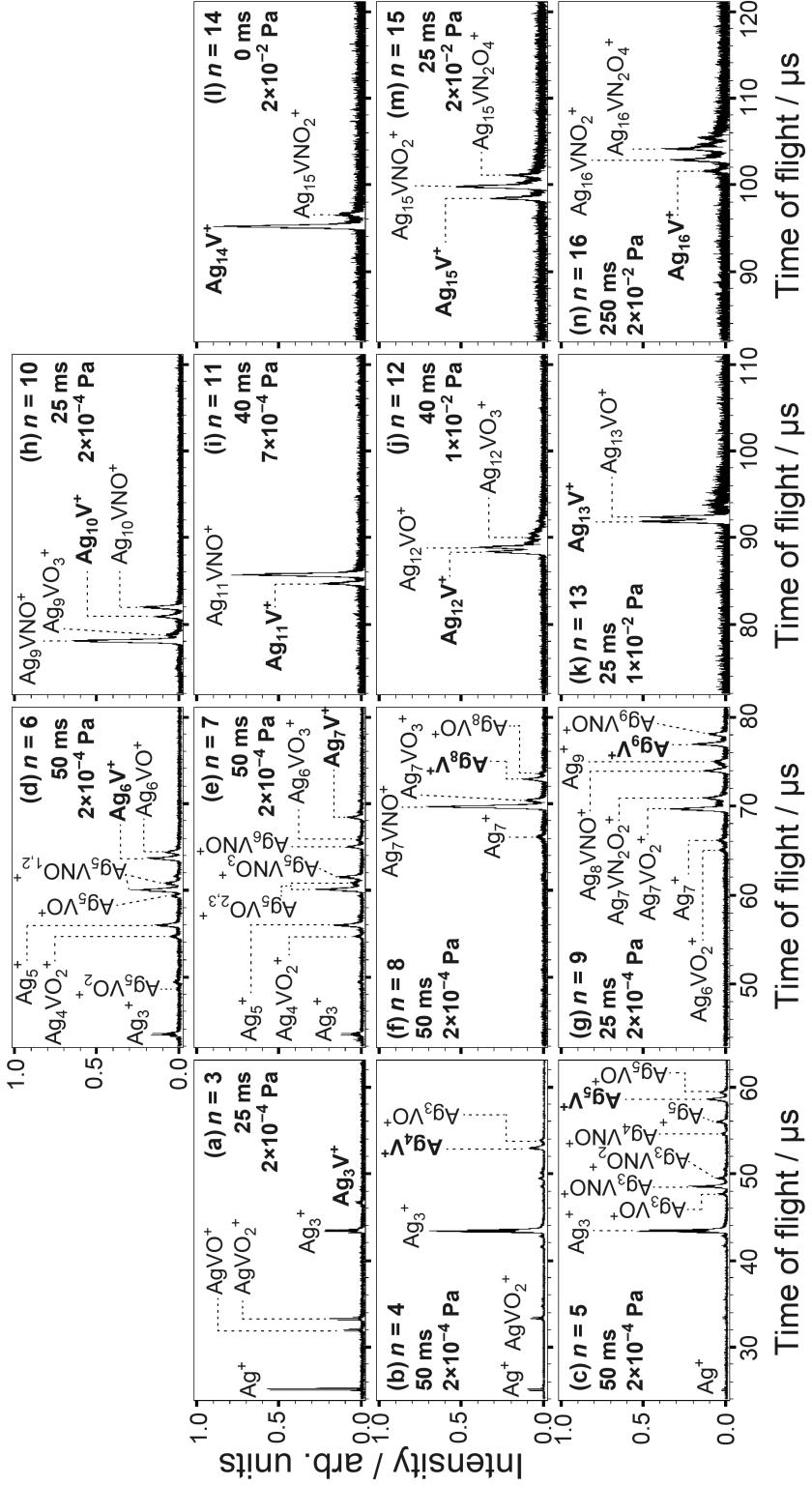


Figure S2. Mass spectra of ions produced from $\text{Ag}_n \text{V}^+$ reacting with NO molecules for $n = 3\text{--}16$ in panels a–n, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

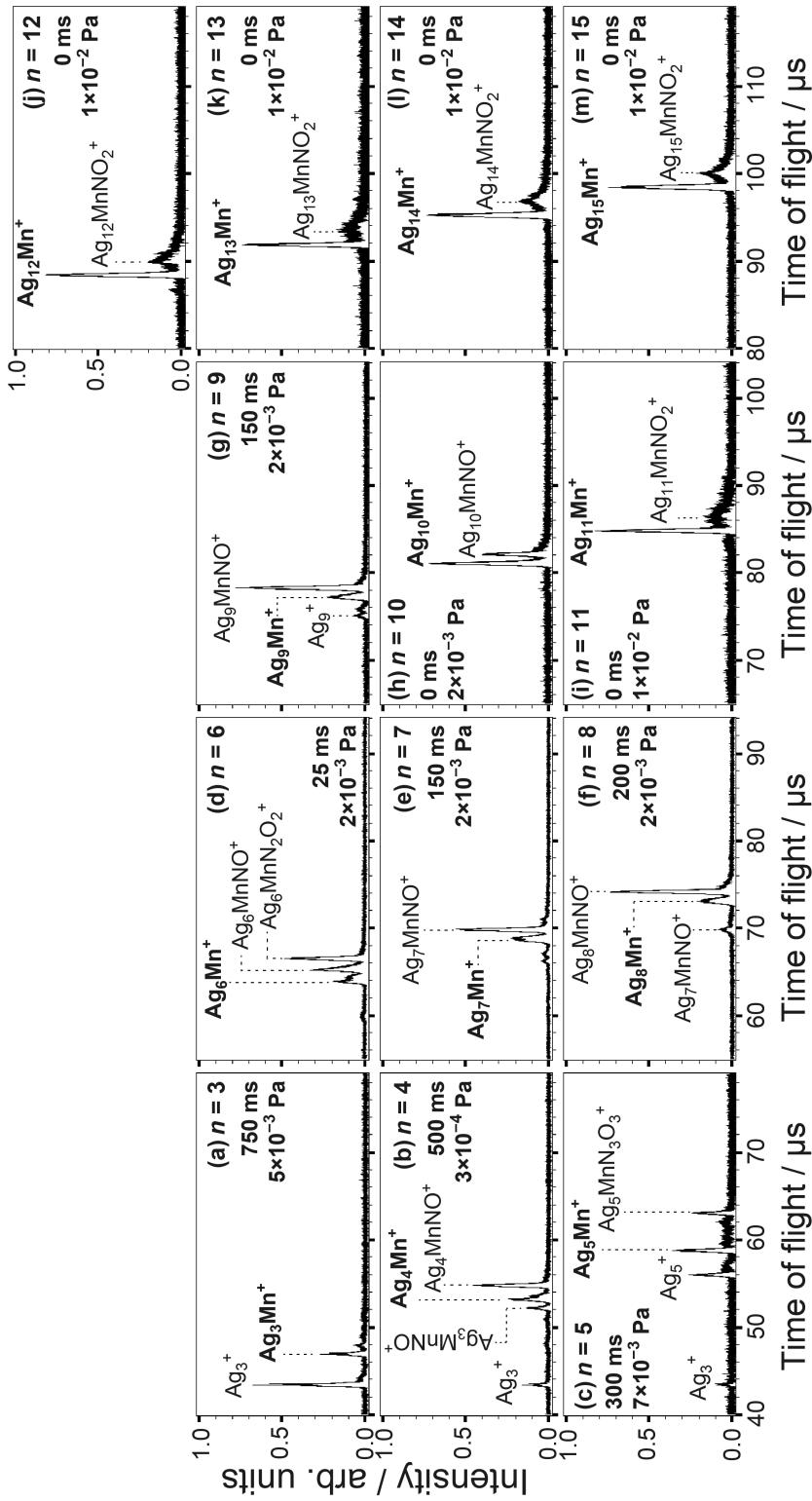


Figure S3. Mass spectra of ions produced from Ag_nMn^+ reacting with NO molecules for $n = 3–15$ in panels a–m, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

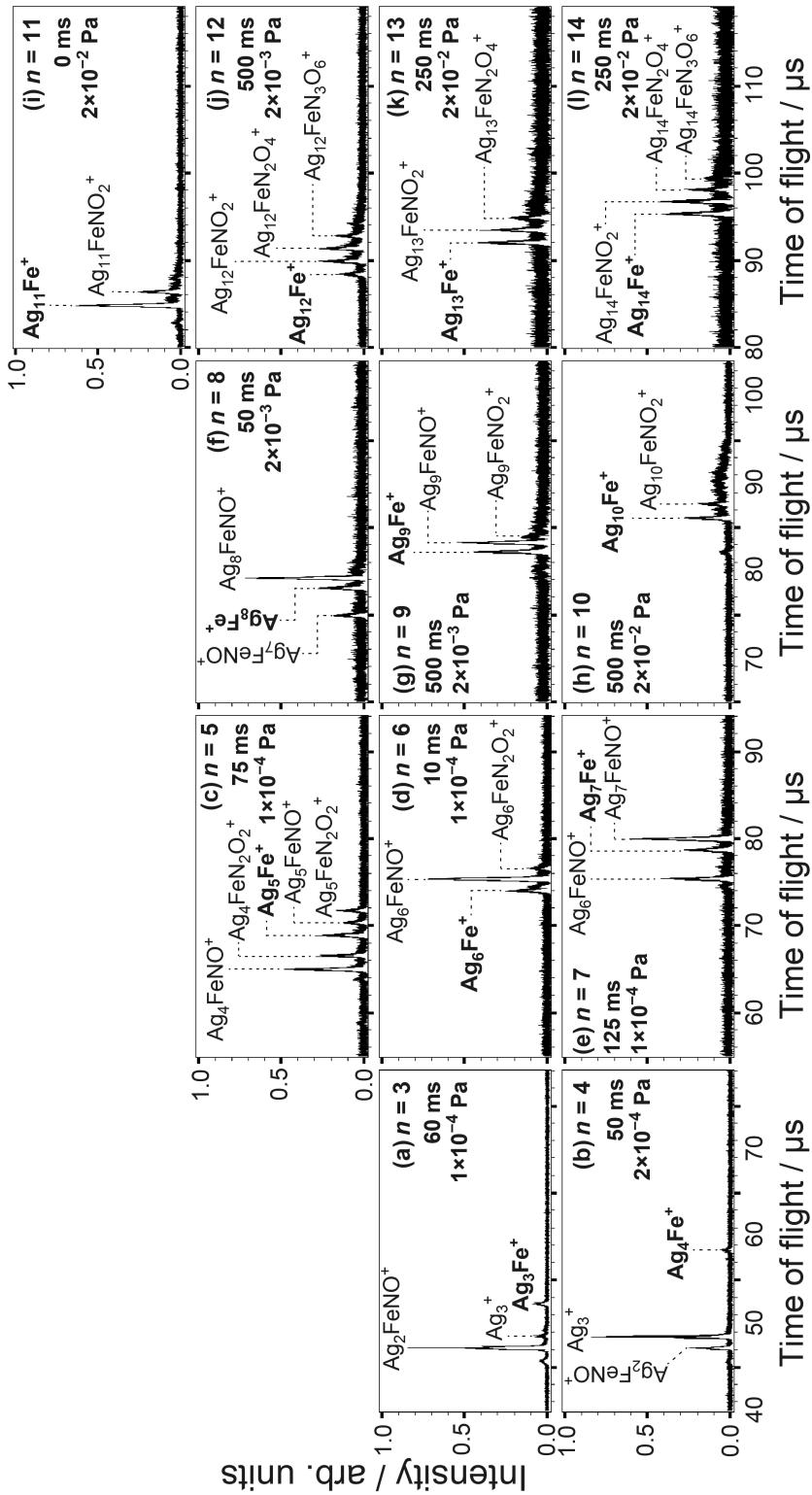


Figure S4. Mass spectra of ions produced from Ag_nFe^+ reacting with NO molecules for $n = 3\text{--}14$ in panels a–l, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

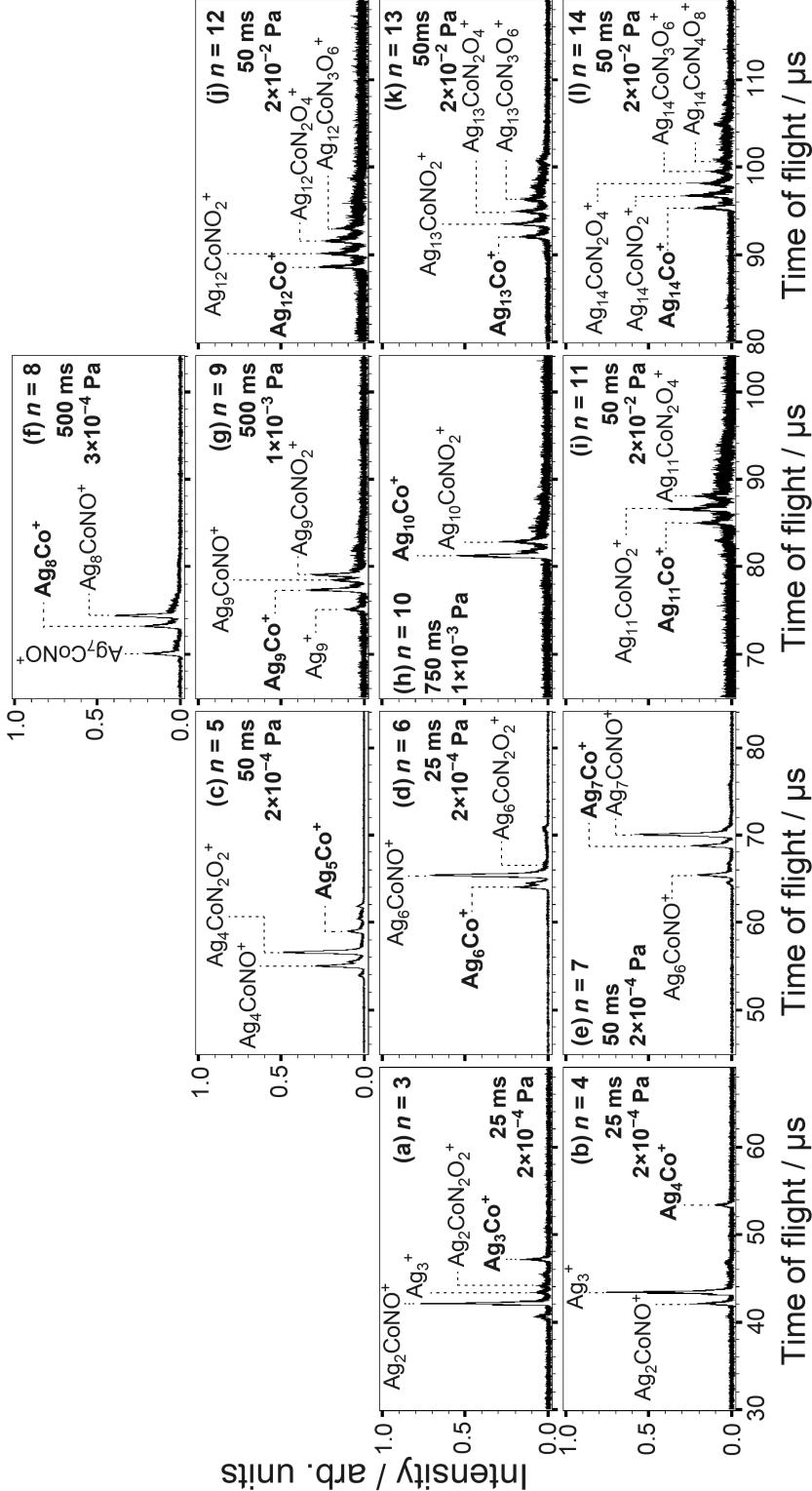


Figure S5. Mass spectra of ions produced from Ag_nCo^+ reacting with NO molecules for $n = 3\text{--}14$ in panels a–l, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

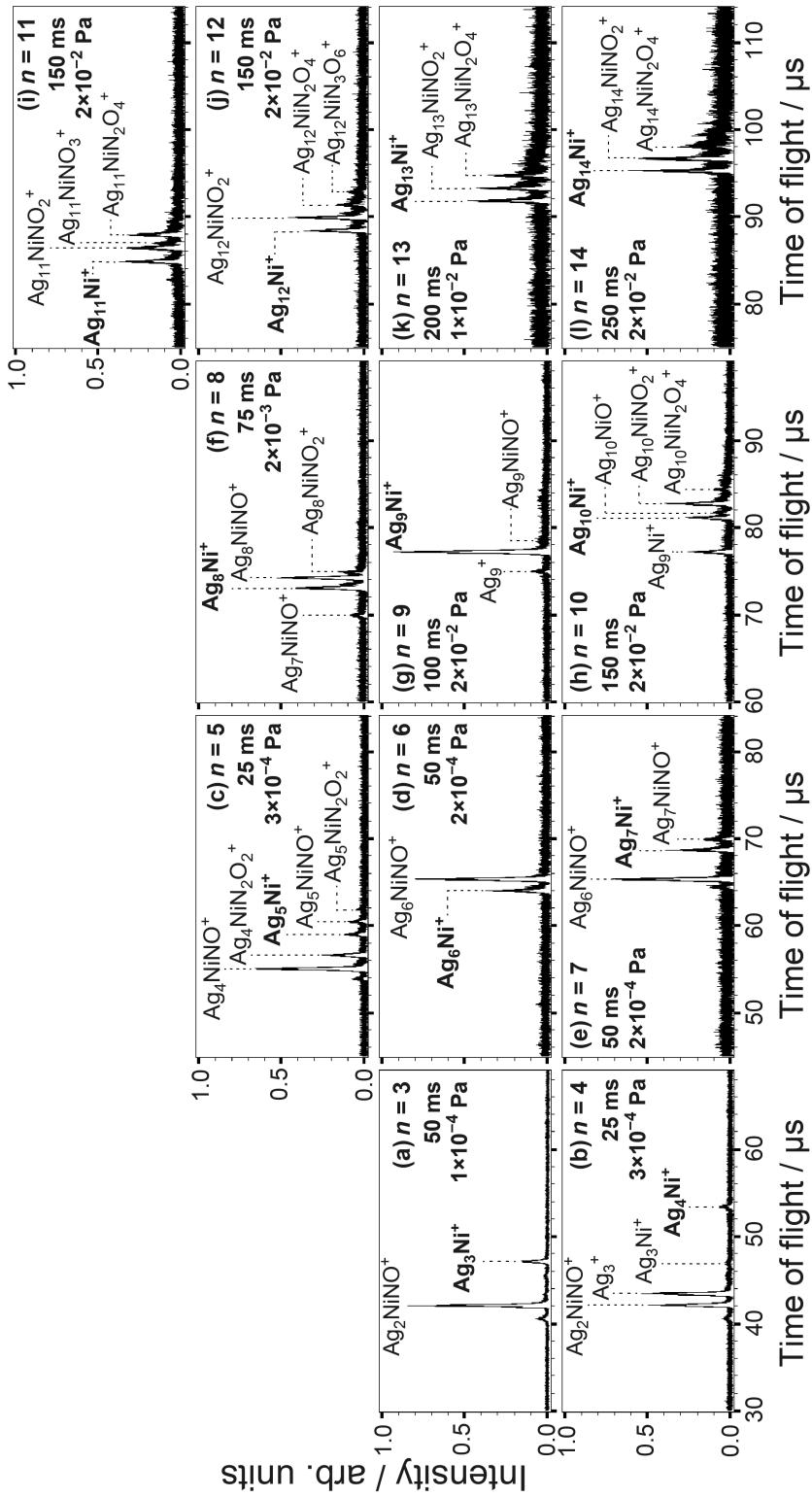


Figure S6. Mass spectra of ions produced from Ag_nNi^+ reacting with NO molecules for $n = 3$ – 14 in panels a–l, respectively. The partial pressure of NO, P_{NO} , and the storage time, t , are given in each panel.

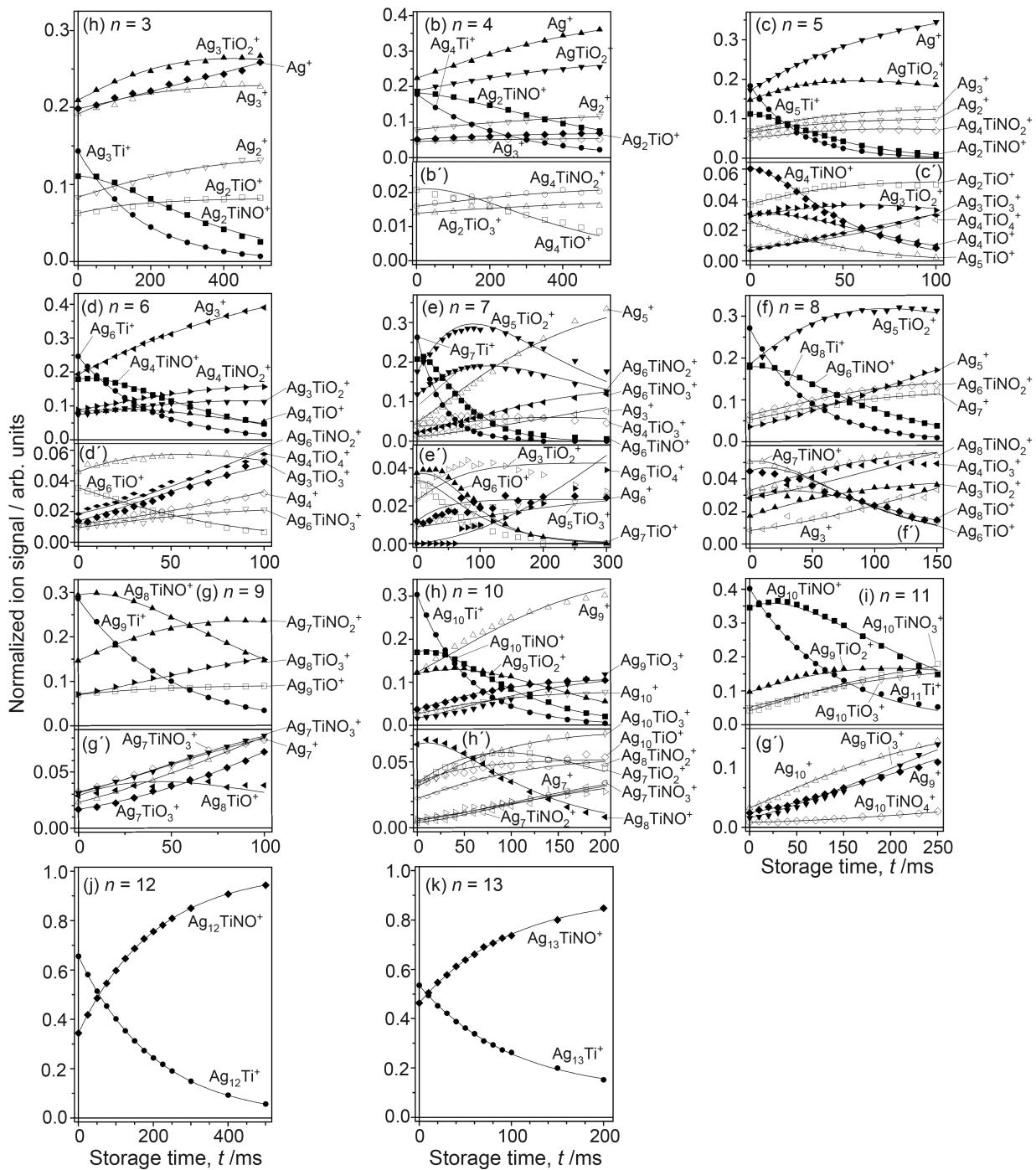


Figure S7. Reaction kinetics of Ag_nTi^+ interacting with NO. (a)–(k) for $n = 3$ –13, respectively. For $n = 4$ –11, minor products are displayed in a magnified scale in b'–i'. The ion signals are normalized so that the total signal of all the ions is unity at each storage time. Solid lines are fitting curves to pseudo-first-order rate equations based on the reaction pathway shown in Scheme S1. P_{NO} was 2×10^{-4} Pa for $n = 3$ –5, 11, and 12, 1×10^{-4} Pa for $n = 6$ –10, and 2×10^{-3} Pa for $n = 13$.

Scheme S1. Reaction pathways of Ag_nTi^+ interacting with NO. (a)–(k) for $n = 3$ –13, respectively. Reaction rate constants obtained under $P_{\text{NO}} = 2 \times 10^{-4}$ Pa for $n = 3$ –5, 11, and 12, 1×10^{-4} Pa for $n = 7$ –10, 2×10^{-3} Pa for $n = 13$, and 2×10^{-2} Pa for $n = 14$ –17 are given in the unit of s⁻¹.

