

## Electronic Supplementary Information

### **Reaction of size-selected iron-oxide cluster cations with methane:**

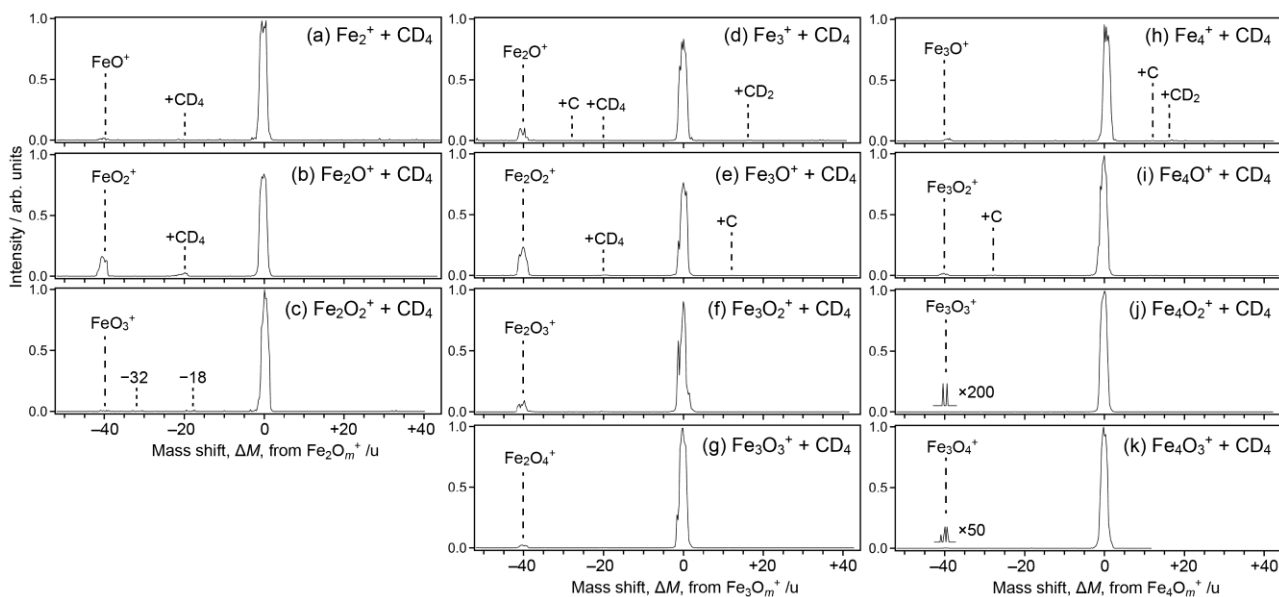
### **A model study of rapid methane loss in the Mars' atmosphere**

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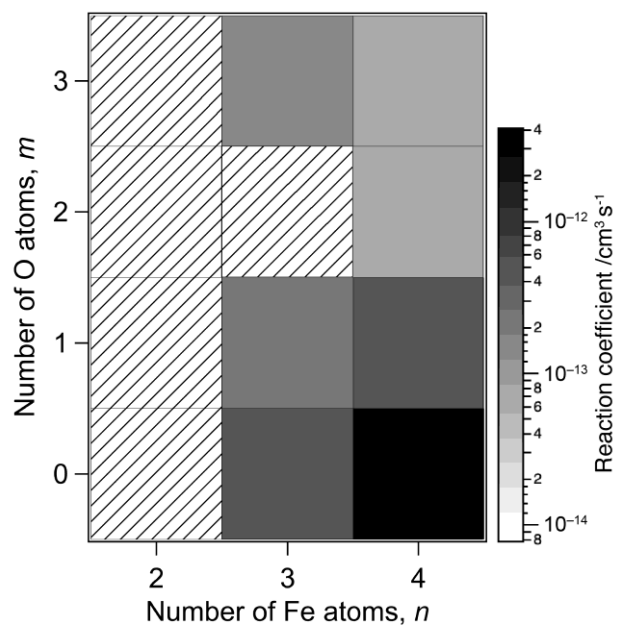
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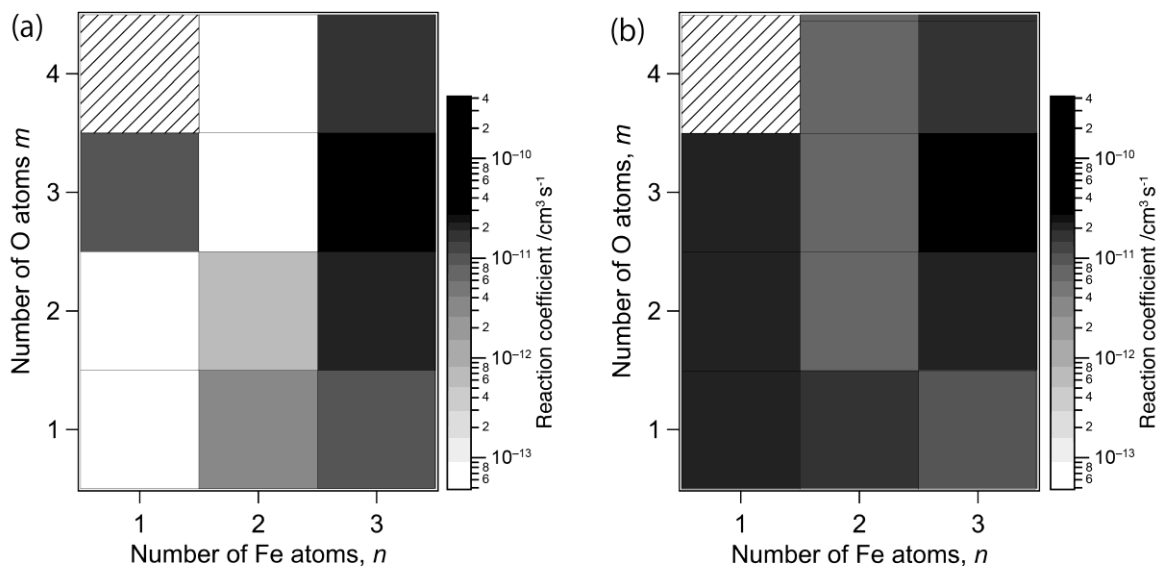
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**Figure S1.** Mass spectra of ions produced from the reaction of  $\text{Fe}_n\text{O}_m^+$  and  $\text{Fe}_{n-1}\text{O}_{m+1}\text{Ar}^+$  ( $n = 2, 3$  and 4) with  $\text{CD}_4$ , which were recorded in the low-sensitivity mode that should be compared with Fig. 1. Reactant ions are (a–c)  $n = 2, m = 0–2$ ; (d–g)  $n = 3, m = 0–3$ ; (h–k)  $n = 4, m = 0–3$ . The abscissa shows a mass shift,  $\Delta M$ , from  $\text{Fe}_n\text{O}_m^+$ . Peaks are assigned to adducts to  $\text{Fe}_n\text{O}_m^+$  in the  $\Delta M \geq 0$  region, while adducts to  $\text{Fe}_{n-1}\text{O}_{m+1}^+$  after desorption of Ar in the  $\Delta M < 0$  region.



**Figure S2.** Rate coefficients of activation of  $\text{CH}_4$  by  $\text{Fe}_n\text{O}_m^+$  as a function of the numbers of iron,  $n$ , and oxygen atoms,  $m$ . The hatched pixels represent unexamined compositions.



**Figure S3.** Rate coefficients obtained for  $\text{Fe}_n\text{O}_m\text{Ar}^+$  as a function of the numbers of iron,  $n$ , and oxygen atoms,  $m$ . The reaction channel is: (a) dehydrogenation of  $\text{CD}_4$  and (b) adsorption of  $\text{CD}_4$ . The hatched pixel at  $(n, m) = (1, 4)$  represents an unexamined composition. Note that the rate coefficients are much larger than those for  $\text{Fe}_n\text{O}_m^+$  presented in Fig. 3 by about two orders of magnitude, indicating the role of the Ar atom in stabilizing methane adducts by exchanging the ligand.