Supporting Information

A Reaction-Induced Localization of Spin Density Enables Thermal C–H Bond Activation of Methane by Pristine FeC$_4^+$

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1. Experimental Details

The ion/molecule reactions were performed with a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source as described elsewhere.\textsuperscript{1-3} In brief, FeC\textsubscript{4}\textsuperscript{+} was generated by laser ablation of a compressed iron/graphite powder (1:4; molar ratio) disk using a Nd:YAG laser operating at 532 nm; helium served as a cooling and carrier gas. Using a series of potentials and ion lenses, the ions were transferred into the ICR cell, which is positioned in the bore of a 7.05 T superconducting magnet. After thermalization by pulses of argon (ca. 2×10\textsuperscript{-6} mbar), the reactions of mass-selected FeC\textsubscript{4}\textsuperscript{+} were studied by introducing isotopologues of methane, i.e., CH\textsubscript{4}, CD\textsubscript{4}, \textsuperscript{13}CH\textsubscript{4}, and a mixture of CH\textsubscript{4} and CD\textsubscript{4} (CH\textsubscript{4} : CD\textsubscript{4} = 1:2) via leak valves at stationary pressures. A temperature of 298 K was assumed for the thermalized clusters.\textsuperscript{1-3}

2. Computational Details

The calculations of the electronic structures were performed with Gaussian 16 and ORCA.\textsuperscript{4,5} To locate the most stable structure of FeC\textsubscript{4}\textsuperscript{+}, a Fortran-based genetic algorithm\textsuperscript{6} to generate initial guess structures of FeC\textsubscript{4}\textsuperscript{+}, followed by density functional theory (DFT) calculations, were conducted; these results point to A01 as the most stable species (Figure S1), in agreement with a previous study.\textsuperscript{7} The most stable structure of FeC\textsubscript{4}\textsuperscript{+} corresponds to a linear arrangement of these five atoms with the iron atom located at one end of the carbon chain.

To elucidate whether the ground state of A01 corresponds to a sextet or a quartet state, quite elaborate multireference (MR) calculations were conducted. The state-specific complete active space self-consistent field (CASSCF)\textsuperscript{8} approach in conjunction with def2-TZVP (TZ) basis set,\textsuperscript{9,10} as implemented in ORCA 4, was employed to optimize the geometries of A01. An active space (17e,15o) is considered in these MR calculations; for selection of the active space, see Figure S4. Finally, \textit{n}-electron valence perturbation theory (NEVPT2)\textsuperscript{11} single-point energy (SPE) calculations were performed by using the def2-QZVP (QZ) basis set.\textsuperscript{9,10}
We used the ωB97 density functional in combination with the TZ basis set for structural optimization to model the potential energy surfaces of the reaction.\textsuperscript{12,13} Harmonic vibrational frequencies were computed to verify the nature of the stationary points. The minimum structures reported in this paper show only positive eigenvalues of the Hessian matrix, whereas the transition states (TSs) have only one negative eigenvalue. Intrinsic reaction coordinate (IRC)\textsuperscript{14-17} calculations were also performed to confirm that the transition states correlate between designated intermediates. The thermodynamic functions (ΔH) were estimated within the ideal gas, rigid-rotor, and harmonic oscillator approximations at 298 K and 1 atm.

We also conducted further calculations for structural optimization by using the BH\&HLYP,\textsuperscript{18} MN15-L,\textsuperscript{19} MN15,\textsuperscript{20} ωB97XD\textsuperscript{12} functionals combined with TZ basis set for 4,6TS1 and 4,6TS2; these structures are shown in Tables S1 and S2.

As commonly accepted, the geometries of molecular structures are less dependent on the level of theory than their energies. For further energetic refinements, SPE calculations at the ωB97XD/QZ level of theory were performed on the structures optimized with ωB97 functional.

As suggested by Perdew and co-workers,\textsuperscript{21} the electron density distributions and atomic charges were calculated at the CASSCF(19e,17o)/TZ level of theory to avoid physically meaningless electron density obtained by DFT method.
3. Figures

Figure S1. Most stable isomers of FeC₄⁺ as calculated at the ωB97/TZ level of theory. Selected geometric parameters are also provided. Bond lengths are given in Å. The superscripts refer to the respective spin states. The symmetries and relative enthalpies (kJ mol⁻¹) are given in parentheses. Color codes: sextet state, black; quartet state, blue.
Figure S2. Transition states related to active sites of $C_\beta$ and $C_\gamma$. Relative energies ($\Delta H$ in kJ mol$^{-1}$) are also provided in parentheses. Selected geometric parameters are also provided. Charges are omitted for the sake of clarity. Bond lengths are given in Å and angles in degrees. The relative enthalpies (kJ mol$^{-1}$) are given in parentheses. Color codes: sextet state, black; quartet state, blue.
Figure S3. Simplified potential energy profiles calculated at the ωB97XD/QZ//ωB97/TZ level of theory with geometric structures (a, b and c; ΔH_{298K} in kJ mol\(^{-1}\)) for the reactions of FeC_4^* with CH_4. Charges are omitted for the sake of clarity.
Figure S4. The selected active spaces considered in the NEVPT2(17e,15o)/QZ//CASSCF(17e,15o)/TZ calculations. Natural orbital partial occupation numbers are given.
Figure S5. Schematic orbital diagrams represented by a frontier orbital analysis for the selected points in path D obtained by CASSCF(19e,17o) calculations. Natural orbital partial occupation numbers are also given.

Note, the orbitals of 27 and 31 are two individual singly-occupied orbitals but with significant overlaps to each other.
Figure S6. The evolution of the spin density of C$_5$ (red) and C$_{CH_4}$ (black) along the sextet (a) and quartet (b) states reaction coordinates of the first C–H bond activation of methane.
4. Tables

**Table S1.** Selected geometric parameters for $^{4,6}$TS1 obtained by DFT methods combined with TZ basis set. Bond lengths are given in Angstrom.

![Diagram of $^{4,6}$TS1]

|        | $^{6}$TS1 | $^{4}$TS1 |
|--------|-----------|-----------|
|        | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ |
| $\omega$B97 | 1.60 | 1.39 | 1.90 | 2.06 | 1.50 | 1.40 | 1.75 | 1.95 |
| $\omega$B97XD | 1.58 | 1.40 | 1.91 | 2.08 | 1.56 | 1.40 | 1.95 | 2.08 |
| MN15   | 1.60 | 1.39 | 1.89 | 2.07 | 1.58 | 1.39 | 1.95 | 2.08 |
| MN15-L | 1.61 | 1.44 | 1.85 | 2.08 | 1.56 | 1.38 | 1.85 | 2.08 |
| BH&HLYP | 1.53 | 1.40 | 1.98 | 2.12 | 1.47 | 1.37 | 1.89 | 2.03 |
Table S2. Selected geometric parameters for $^{4,6}\text{TS2}$ obtained by DFT methods combined with TZ basis set. Bond lengths are given in Angstrom and angles in degree.

![Diagram of TS2](image)

|       | $r_1$ | $r_2$ | $r_3$ | $r_4$ | $a_1$ | $a_2$ | $a_3$ |
|-------|-------|-------|-------|-------|-------|-------|-------|
| $^{6}\text{TS2}$ |       |       |       |       |       |       |       |
| $\omega B97$ | 1.12  | 1.82  | 1.28  | 1.33  | 139   | 114   | 166   |
| $\omega B97 XD$ | 1.14  | 1.68  | 1.29  | 1.30  | 156   | 114   | 166   |
| MN15    | 1.18  | 1.49  | 1.28  | 1.32  | 155   | 120   | 168   |
| MN15-L  | 1.27  | 1.36  | 1.29  | 1.32  | 160   | 123   | 167   |
| BH&HLYP | 1.10  | 1.92  | 1.26  | 1.33  | 144   | 114   | 165   |

|       | $r_1$ | $r_2$ | $r_3$ | $r_4$ | $a_1$ | $a_2$ | $a_3$ |
|-------|-------|-------|-------|-------|-------|-------|-------|
| $^{4}\text{TS2}$ |       |       |       |       |       |       |       |
| $\omega B97$ | 1.12  | 1.84  | 1.29  | 1.32  | 135   | 108   | 165   |
| $\omega B97 XD$ | 1.10  | 2.37  | 1.29  | 1.31  | 115   | 106   | 168   |
| MN15    | 1.10  | 2.30  | 1.30  | 1.31  | 112   | 105   | 168   |
| MN15-L  | 1.12  | 1.99  | 1.32  | 1.31  | 131   | 105   | 167   |
| BH&HLYP | 1.11  | 1.79  | 1.27  | 1.32  | 147   | 111   | 165   |
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6. Coordinates

$^6[\text{FeC}_4]^+$

| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Fe   | 0.000012| 0.000002| -1.762661|
| C    | 0.000012| 0.000002| 0.043415 |
| C    | 0.000012| 0.000002| 1.323592 |
| C    | 0.000012| 0.000002| 2.610154 |
| C    | 0.000012| 0.000002| 3.920822 |

$^4[\text{FeC}_4]^+$

| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Fe   | -3.725367| 1.417683| -0.003878|
| C    | -1.929177| 1.161795| -0.000308|
| C    | -0.676105| 0.983331| 0.002184 |
| C    | 0.618433 | 0.798923| 0.004759 |
| C    | 1.907586 | 0.615612| 0.007326 |

$^4\text{EC1}$

| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Fe   | -1.152887| 0.076986| 0.111841 |
| C    | 0.679815 | 0.042045| 0.063209 |
| C    | 1.937601 | 0.015588| 0.018971 |
| C    | 3.252168 | -0.012175| -0.026254|
| C    | 4.546878 | -0.041500| -0.075470|
| H    | -3.119757| 0.497333| 0.947699 |
| C    | -3.358621| 0.022386| -0.024032|
| H    | -3.058324| -1.039019| -0.085695|
| H    | -4.447603| 0.011695| -0.059159|
| H    | -3.048785| 0.621098| -0.899386|

$^8\text{EC1}$

| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Fe   | -4.085773| 1.172472| -1.465921|
| C    | -3.032606| 2.277156| -2.486693|
| C    | -2.324187| 3.023037| -3.167927|
| C    | -1.543057| 3.845595| -3.919346|
| C    | -0.846556| 4.578971| -4.589450|
| H    | -6.022828| 0.370453| -0.782170|
| C    | -5.295917| -0.053676| -0.065067|
| H    | -4.816301| 0.704939| 0.578268 |
| H    | -4.580045| -0.759309| -0.525618|
| H    | -5.894411| -0.664848| 0.609521 |

$^4\text{EC2}$

| Atom | $x$     | $y$     | $z$     |
|------|---------|---------|---------|
| Fe   | -2.375010| -0.181659| 0.000077 |
| C    | -0.618253| 0.245184| 0.000302 |
| C    | 0.604089 | 0.557795| 0.000810 |
| C    | 1.878255 | 0.881534| 0.001350 |
| C    | 3.034172 | 1.468368| 0.002022 |
| H    | 4.457517 | -0.172915| -0.001325|
\begin{verbatim}
C  4.152182 -1.229541 -0.000920  
H  5.065572 -1.825344  0.001121  
H  3.573232 -1.453678  0.895678  
H  3.576206 -1.454869 -0.899115  

\textbf{6EC2}  
Fe  1.714699  0.867878 -0.000279  
C  0.130052  0.000251  0.000817  
C  -0.992004  0.614520 -0.001610  
C  -2.120029 -1.233600  0.002444  
C  -3.258946 -1.882952  0.003349  
H  -4.951732  0.213799 -0.003614  
C  -4.390763  1.150877 -0.000794  
H  -3.767765  1.210570 -0.895508  
H  -3.772660  1.208150 -0.897462  
H  -5.094418  1.982950 -0.001574  

\textbf{4TS1}  
Fe  3.272100 -1.762843 -0.058476  
C  3.210144 -0.060326  0.358064  
C  3.048781  1.163727  0.672046  
C  2.957252  2.402370  1.037836  
C  2.842530  3.642515  1.396846  
H  2.374478 -0.585551 -0.638466  
C  1.591428 -1.803119 -1.046344  
H  1.976002 -2.535649 -1.773832  
H  1.007719 -1.056426 -1.588414  
H  0.966706 -2.250892 -0.262274  

\textbf{6TS1}  
Fe  3.265681 -1.886558  0.088923  
C  3.210521 -0.036331  0.497474  
C  3.103465  1.214025  0.724121  
C  3.008716  2.483994  0.964235  
C  2.915421  3.759320  1.206659  
H  2.245636 -0.610904 -0.325328  
C  1.584795 -1.849586 -1.093333  
H  2.018260 -2.260015 -2.014649  
H  0.901819 -1.048286 -1.383457  
H  0.992828 -2.610119 -0.567661  

\textbf{4TS2}  
Fe  2.484526  0.347050 -0.000773  
C  0.730766 -0.075154 -0.000373  
C  -0.487154 -0.393297 -0.000089  
C  -1.764991 -0.724143  0.000207  
C  -2.883252 -1.366049  0.000572  
\end{verbatim}
|       |       |       |       |
|-------|-------|-------|-------|
| H     | -4.265461 | -0.146656 | 0.000419 |
| C     | -4.343935  | 0.966052  | 0.000103  |
| H     | -3.879848  | 1.367801  | -0.899421 |
| H     | -3.879570  | 1.368331  | 0.899248  |
| H     | -5.414637  | 1.173752  | 0.000208  |

**6^TS2**

|       |       |       |       |
|-------|-------|-------|-------|
| Fe    | 2.637545  | 0.248567  | -0.001089 |
| C     | 0.810894   | -0.130292 | -0.000479 |
| C     | -1.700250  | -0.697238 | 0.000381  |
| C     | -0.405968  | -0.404413 | -0.000064 |
| C     | -2.842414  | -1.276530 | 0.000945  |
| H     | -4.251414  | -0.124745 | 0.000688  |
| C     | -4.431941  | 0.979636  | 0.000065  |
| H     | -4.001756  | 1.416859  | -0.899583 |
| H     | -4.001229  | 1.417964  | 0.899222  |
| H     | -5.517023  | 1.087882  | 0.000316  |

**4^I2**

|       |       |       |       |
|-------|-------|-------|-------|
| Fe    | 3.060188  | -1.292866 | 0.001366 |
| C     | 1.294852   | -0.861788 | -0.000168 |
| C     | 0.096856   | -0.566748 | 0.000191  |
| C     | -1.226568  | -0.241068 | 0.000443  |
| C     | -2.397807  | 0.047128  | 0.000638  |
| H     | -3.447853  | 0.305652  | 0.000835  |
| C     | -5.637925  | 0.847468  | 0.000190  |
| H     | -5.585640  | 1.377875  | -0.942286 |
| H     | -5.582270  | 1.402773  | 0.928010  |
| H     | -5.973626  | -0.181808 | 0.014502  |

**6^I2**

|       |       |       |       |
|-------|-------|-------|-------|
| Fe    | 2.974912  | -1.204093 | 0.012031 |
| C     | 1.212983   | -0.764972 | 0.006417 |
| C     | 0.015007   | -0.466299 | 0.003563 |
| C     | -1.306127  | -0.136859 | 0.001109 |
| C     | -2.477328  | 0.155204  | -0.000765 |
| H     | -3.528550  | 0.417298  | -0.002416 |
| C     | -5.677026  | 0.951689  | -0.003816 |
| H     | -5.647189  | 1.411901  | -0.983495 |
| H     | -5.607135  | 1.574749  | 0.878999  |
| H     | -6.016409  | -0.071979 | 0.092994  |