IR spectroscopic characterization of 3d transition metal carbene cations, FeCH₂⁺ and CoCH₂⁺: Periodic Trends and A Challenge for DFT approaches

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Supporting Information



Figure S1: Product mass distributions of the reaction between ethylene oxide and a) Fe⁺ ($\Delta M = m/z - 55.937$) and b) Co⁺ ($\Delta M = m/z - 58.935$). Some artifacts resulting from electrical noise pickup are denoted by an asterisk (*).



Figure S2: Observed ion intensities of $[M,C,2H]^+$ (black trace), MC⁺ (red) and M⁺ (green) normalized to their sum as a function of IR wavenumber for M = Fe (panel a) and Co (panel b). Bright versus light colors indicate measurements with different FEL settings. The signal increase in the Fe⁺ channel around 1100 cm⁻¹ is attributed to fragmentation of an unwanted [Fe,C,3H]⁺ reaction product that was not mass-ejected prior to irradiation.



Figure S3: Observed ion intensities of $[M,C,2H]^+$ (black trace), [MC,3H] (red), MC^+ (green) and M^+ (blue) during one single scan (panel a), and each channel normalized to the sum of all four (panel b); resulting IR fragmentation yield for $[Fe,C,2H]^+$ calculated using Fe^+ and FeC^+ as fragments.



Figure S4: Experimental IRMPD spectra of $[Fe,C,2H]^+$ (panel a) and $[Co,C,2H]^+$ (panel c). Comparison of the spectra calculated at the MP2(full)/def2-TZVPPD level (panel b) $FeCH_2^+$ (⁴B₁, black) and (⁴B₂, red) and (panel d) $CoCH_2^+$ (³A₁, black) and (³A₂, red).



Figure S5: Experimental IRMPD spectra of $[Fe,C,2H]^+$ (panel a) and $[Co,C,2H]^+$ (panel c). Comparison of the spectra calculated at the CCSD/def2-TZVPPD level with rovibrational simulations for (panel b) $FeCH_2^+$ (⁴B₁, black) and (⁴B₂, red) and (panel d) $CoCH_2^+$ (³A₁, black) and (³A₂, red).

| Species | State | $E_{Rel} (eV)$ | Occupation |
|--------------------------------|------------------------|----------------|--|
| $\mathrm{FeCH}_{2^{+}}$ | ${}^{4}\text{B}_{1}$ | 0.000 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1$ |
| | ${}^{4}\text{B}_{2}$ | 0.013 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^2(3a_1)^1(1b_2)^1$ |
| | $^{4}A_{2}$ | 0.179 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^1(3a_1)^1(1b_2)^2$ |
| | ${}^{4}B_{1}$ | 0.635 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^1(3a_1)^2(1b_2)^1$ |
| | $^{4}A_{1}$ | 1.009 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^1(3a_1)^1(1b_2)^1(2b_1)^1$ |
| | ${}^{6}\mathrm{B}_{1}$ | 0.826 | $(1a_1)^2(1b_1)^1(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1(2b_1)^1$ |
| | $^{2}A^{\prime\prime}$ | 1.038 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1$ |
| | $^{2}B_{1}$ | 1.052 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1$ |
| | ${}^{2}A_{2}$ | 1.061 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^0(1b_2)^2$ |
| | ${}^{2}\mathbf{B}_{1}$ | 1.328 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1$ |
| | ${}^{2}A_{2}$ | 1.419 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^0(1b_2)^2$ |
| | ${}^{2}A_{1}$ | 2.008 | |
| | ${}^{2}A_{1}$ | 2.367 | |
| HFeCH ⁺ | ⁶ A ′′ | 3.323 | |
| $(H_2)FeC^+$ | $^{2}A'$ | 2.695 | |
| | ⁴ A'' | 3.595 | |
| | ⁶ A′ | 4.371 | |
| HHFeC ⁺ | ⁴ A'' | 5.544 | |
| | | | |
| CoCH ₂ ⁺ | $^{3}A_{2}$ | 0.000 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^2$ |
| | ${}^{3}A_{1}$ | 0.050 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^2(3a_1)^1(1b_2)^2$ |
| | ${}^{3}B_{1}$ | 0.412 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^2(1b_2)^1$ |
| | ${}^{3}B_{2}$ | 0.898 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^2(3a_1)^1(1b_2)^1$ |
| | ${}^{3}A_{1}$ | 1.068 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^1(2b_1)^1$ |
| | ${}^{3}A_{1}$ | 1.906 | |
| | ${}^{1}A_{1}$ | 0.714 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^2(3a_1)^1(1b_2)^2$ |
| | ${}^{1}A_{2}$ | 0.771 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^1(3a_1)^1(1b_2)^2$ |
| | ${}^{1}A_{1}$ | 0.851 | $(1a_1)^2(1b_1)^2(2a_1)^1(1a_2)^2(3a_1)^1(1b_2)^2$ |
| | ${}^{1}A_{1}$ | 1.711 | $(1a_1)^2(1b_1)^2(2a_1)^2(1a_2)^2(3a_1)^0(1b_2)^2$ |
| | ${}^{1}A_{1}$ | 2.877 | |
| | ${}^{1}A_{1}$ | 3.005 | |
| | ⁵ A′ | 0.860 | |
| | ⁵ A'' | 0.943 | |
| | ${}^{5}\text{B}_{2}$ | 1.409 | |
| $\mathrm{HCoCH^{+}}$ | ⁵ A′ | 3.258 | |
| | $^{1}A'$ | 3.670 | |
| $(H_2)CoC^+$ | $^{1}A'$ | 3.086 | |
| - | ³ A′ | 3.414 | |
| | ${}^{5}B_{1}$ | 4.220 | |

Table S1: Ground and excited electronic states for $[M,C,2H]^+$ isomers with electronic occupation for selected states calculated at the B3LYP/def2-TZVPPD level. The 0 K relative energy E_{Rel} is given with respect to the lowest energy isomer for the metal involved.

| MCH_{2}^{+} | State | Intensity (mode)/Intensity (CH ₂ wag) x 100 | | |
|--------------------------------|------------------------|--|-------------|--------------------------|
| | | CH ₂ rock | M-C stretch | CH ₂ scissors |
| FeCH ₂ ⁺ | ${}^{4}\mathrm{B}_{1}$ | 35/42 | 5/41 | 1/1 |
| RuCH_2^+ | ${}^{4}\mathrm{B}_{1}$ | 4/12 | 0/0.1 | 0/1 |
| OsCH_{2}^{+} | ${}^{4}\mathrm{B}_{1}$ | 5/18 | 0.4/0.3 | 1/0.1 |
| $\mathrm{CoCH_2^+}$ | $^{3}A_{2}$ | 41/41 | 0.05/25 | 3/23 |
| $RhCH_2^{+a}$ | $^{1}A_{1}$ | 0/1 | 24/30 | 8/22 |
| $RhCH_2^{+a}$ | $^{3}A_{2}$ | 9/6 | 23/23 | 6/2 |
| IrCH_{2}^{+} | $^{3}A_{2}$ | 15/15 | 35/24 | 13/4 |

Table S2. Intensities of vibrational modes relative to those for the CH_2 wag (in %) calculated at the B3LYP/CCSD level. Notable differences are bolded.

^a CCSD values are from EOM-SF_CCSD calculations provided in Wensink, F. J.; Smink, C. E.; Steele, R. P.; Armentrout, P. B.; Bakker, J. M. *Phys. Chem. Chem. Phys.*, submitted for publication.