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Supplement

Table I. Thermochemical data (taken from [38]) and calculated thresholds for the transitions observed experimentally. $\Delta_f H_g^{\circ}(X)$—standard enthalpy of formation of X in the gas phase, D(Y-X)—dissociation energy, E_{th}(X(A))—thermodynamic threshold energy of the appearance of fragment X in the state A.

$\Delta_f H_g^{\circ}(CH_4) = –74.87$ kJ/mol
$\Delta_f H_g^{\circ}(CH_3) = 145.69$ kJ/mol
$\Delta_f H_g^{\circ}(CH_2) = 386.39$ kJ/mol
$\Delta_f H_g^{\circ}(CH) = 594.13$ kJ/mol
$\Delta_f H_g^{\circ}(H) = 217.998 \pm 0.006$ kJ/mol
$\Delta_f H_g^{\circ}(C) = 716.68 \pm 0.45$ kJ/mol
$\Delta_f H_g^{\circ}(H_2) = 0$ kJ/mol

H excitation energies:
H(1→2) → 10.2 eV
H(2→3) → 1.9 eV
H(3→4) → 0.65 eV
H(4→5) → 0.31 eV
H(5→6) → 0.16 eV
H(6→7) → 0.103 eV
H(7→8) → 0.065 eV
H(8→9) → 0.045 eV

CH_3 + H
$\Delta_f H_g^{\circ}(CH_3) = \Delta_f H_g^{\circ}(CH_4) - \Delta_f H_g^{\circ}(H) + D(CH{+}H{+}H_2)$
145.69 kJ/mol = –74.87 kJ/mol – 217.998 kJ/mol + $D(CH{+}H{+}H_2)$
$D(CH_3{+}H)$=438.558 kJ/mol = 4.545 eV

CH_3(X) + H(n=3) → 16.645 eV
CH_3(X) + H(n=4) → 17.295 eV
CH_3(X) + H(n=5) → 17.605 eV
CH_3(X) + H(n=6) → 17.765 eV
CH_3(X) + H(n=7) → 17.868 eV
CH_3(X) + H(n=8) → 17.933 eV
CH_3(X) + H(n=9) → 17.978 eV

CH + H + H_2
$\Delta_f H_g^{\circ}(CH) = \Delta_f H_g^{\circ}(CH_4) - \Delta_f H_g^{\circ}(H) - \Delta_f H_g^{\circ}(H_2) + D(CH{+}H{+}H_2)$
594.13kJ/mol = –74.87kJ/mol – 217.998 KJ/mol + 0 kJ/mol + $D(CH{+}H{+}H_2)$
$D(CH{+}H{+}H_2)$ = 886.998 kJ/mol = 9.13 eV

CH(X) + H_2 + H(n=3) → 21.23 eV
CH(X) + H_2 + H(n=4) → 21.88 eV
CH(X) + H_2 + H(n=5) → 22.19 eV
CH(X) + H_2 + H(n=6) → 22.35 eV

$CH(X) + H_2 + H(n=7) \rightarrow 22.453$ eV
$CH(X) + H_2 + H(n=8) \rightarrow 22.518$ eV
$CH(X) + H_2 + H(n=9) \rightarrow 22.563$ eV

$CH(A) + H + H_2$ – 9.13 + 2.88(430 nm) =12.01 eV
$CH(B) + H + H_2$ – 9.13 + 3.20(387.2 nm) = 12.33 eV
$CH(C) + H + H_2$ – 9.13 + 3.95(314 nm) = 13.08 eV

CH + 3H
$\Delta_f H_g^{\circ}(CH) = \Delta_f H_g^{\circ}(CH_4)$-3. $\Delta_f H_g^{\circ}(H) + D(CH+3H)$
594.13kJ/mol = –74.87kJ/mol – 3x217.998 kJ/mol + 0 kJ/mol + $D(CH+3H)$
$D(CH+3H)$ = 1322.994 kJ/mol = 13.71 eV

$CH(A) + 3H \rightarrow 13.71 + 2.88$(430nm) = 16.59 eV
$CH(B) + 3H \rightarrow 13.71 + 3.20$(387.2nm) = 16.91 eV
$CH(C) + 3H \rightarrow 13.71 + 3.95$(314nm) = 17.66 eV

CH_2 + H + H
$\Delta_f H_g^{\circ}(CH_2) = \Delta_f H_g^{\circ}(CH_4) - 2\ \Delta_f H_g^{\circ}(H) + D(CH+H+H_2)$
594.13 kJ/mol = –74.87 kJ/mol – 2x217.998 KJ/mol + $D(CH+H+H_2)$
$D(CH_2+2H)$ = 897.256 kJ/mol = 9.299 eV

$CH_2(X) + H + H^*(n = 3) \rightarrow 21.399$ eV
$CH_2(X) + H + H^*(n = 4) \rightarrow 22.049$ eV
$CH_2(X) + H + H^*(n = 5) \rightarrow 22.359$ eV
$CH_2(X) + H + H^*(n = 6) \rightarrow 22.519$ eV
$CH_2(X) + H + H^*(n = 7) \rightarrow 22.622$ eV
$CH_2(X) + H + H^*(n = 8) \rightarrow 22.687$ eV
$CH_2(X) + H + H^*(n = 9) \rightarrow 22.732$ eV

CH^+
$E_{th}(CH^+(B)) \rightarrow E_{th}(CH(X)) + IE(CH) + E_{th}(CH(A)) + E_{th}(CH(B))$
$E_{th}(CH^+(B))$ = 9.13 + 10.64 + 2.94(422 nm) + 3.54(350 nm) eV= 26.25 eV

CI
$\Delta_f H_g^{\circ}(C) = \Delta_f H_g^{\circ}(CH_4) - 2\ \Delta_f H_g^{\circ}(H_2) + D(H_2+H_2)$
716.68= –74.87kJ/mol + $D(H_2+H_2)$
$D(H_2+H_2)$ = 716.68 + 74.87 = 791.55 kJ/mol = 8.20eV
E_{th}(CI ($3s(^1P^{\circ})$)) = 8.20 + 5.0 eV = 13.2 eV

$\Delta_f H_g^{\circ}(C) = \Delta_f H_g^{\circ}(CH_4) - 2\ \Delta_f H_g^{\circ}(H) + \Delta_f H_g^{\circ}(H_2) + D(2H+H_2)$
716.68 = –74.87 + 2x 217.998 + $D(2H+H_2)$ kJ/mol
$D(2H+H_2)$ = 716.68 + 74.87 + 2x217.98 = 1227.51 kJ/mol = 12.72eV
E_{th}(CI ($3s(^1P^{\circ})$)) = 12.72 + 5.0 eV = 17.72 eV

$\Delta_f H_g^{\circ}(C) = \Delta_f H_g^{\circ}(CH_4) - 4\ \Delta_f H_g^{\circ}(H) + D(4H)$

$716.68 = -74.87 kJ/mol + 2x\ 217.998 + D(4H)$
$D(4H) = 716.68 + 74.87 + 4 \times 217.98 = 1663.47$ kJ/mol= 17.24eV
$E_{th}(CI\ (3s(^1P^\circ))) = 17.24 + 5.0$ eV = 22.24 eV

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Figure I. Photon yield of transitions measured as a function of the initial electron energy not shown in the paper. Observed thresholds obtained using the fitting method in the measured energy range are indicated by arrows.