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which should be cited to refer to this work.

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.

$$\begin{aligned}\Delta_f H_g^\circ(\text{CH}_4) &= -74.87 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{CH}_3) &= 145.69 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{CH}_2) &= 386.39 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{CH}) &= 594.13 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{H}) &= 217.998 \pm 0.006 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{C}) &= 716.68 \pm 0.45 \text{ kJ/mol} \\ \Delta_f H_g^\circ(\text{H}_2) &= 0 \text{ kJ/mol}\end{aligned}$$

H excitation energies:

$$\begin{aligned}\text{H}(1 \rightarrow 2) &\rightarrow 10.2 \text{ eV} \\ \text{H}(2 \rightarrow 3) &\rightarrow 1.9 \text{ eV} \\ \text{H}(3 \rightarrow 4) &\rightarrow 0.65 \text{ eV} \\ \text{H}(4 \rightarrow 5) &\rightarrow 0.31 \text{ eV} \\ \text{H}(5 \rightarrow 6) &\rightarrow 0.16 \text{ eV} \\ \text{H}(6 \rightarrow 7) &\rightarrow 0.103 \text{ eV} \\ \text{H}(7 \rightarrow 8) &\rightarrow 0.065 \text{ eV} \\ \text{H}(8 \rightarrow 9) &\rightarrow 0.045 \text{ eV}\end{aligned}$$

CH₃ + H

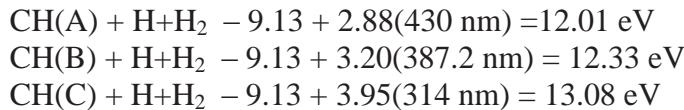
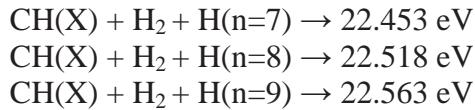
$$\begin{aligned}\Delta_f H_g^\circ(\text{CH}_3) &= \Delta_f H_g^\circ(\text{CH}_4) - \Delta_f H_g^\circ(\text{H}) + D(\text{CH}+\text{H}+\text{H}_2) \\ 145.69 \text{ kJ/mol} &= -74.87 \text{ kJ/mol} - 217.998 \text{ kJ/mol} + D(\text{CH}+\text{H}+\text{H}_2) \\ D(\text{CH}_3+\text{H}) &= 438.558 \text{ kJ/mol} = 4.545 \text{ eV}\end{aligned}$$

$$\begin{aligned}\text{CH}_3(\text{X}) + \text{H}(\text{n}=3) &\rightarrow 16.645 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=4) &\rightarrow 17.295 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=5) &\rightarrow 17.605 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=6) &\rightarrow 17.765 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=7) &\rightarrow 17.868 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=8) &\rightarrow 17.933 \text{ eV} \\ \text{CH}_3(\text{X}) + \text{H}(\text{n}=9) &\rightarrow 17.978 \text{ eV}\end{aligned}$$

CH + H + H₂

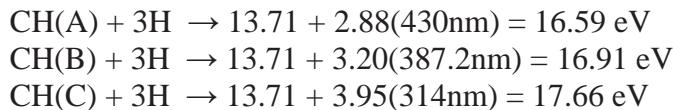
$$\begin{aligned}\Delta_f H_g^\circ(\text{CH}) &= \Delta_f H_g^\circ(\text{CH}_4) - \Delta_f H_g^\circ(\text{H}) - \Delta_f H_g^\circ(\text{H}_2) + D(\text{CH}+\text{H}+\text{H}_2) \\ 594.13 \text{ kJ/mol} &= -74.87 \text{ kJ/mol} - 217.998 \text{ kJ/mol} + 0 \text{ kJ/mol} + D(\text{CH}+\text{H}+\text{H}_2) \\ D(\text{CH}+\text{H}+\text{H}_2) &= 886.998 \text{ kJ/mol} = 9.13 \text{ eV}\end{aligned}$$

$$\begin{aligned}\text{CH}(\text{X}) + \text{H}_2 + \text{H}(\text{n}=3) &\rightarrow 21.23 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(\text{n}=4) &\rightarrow 21.88 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(\text{n}=5) &\rightarrow 22.19 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(\text{n}=6) &\rightarrow 22.35 \text{ eV}\end{aligned}$$



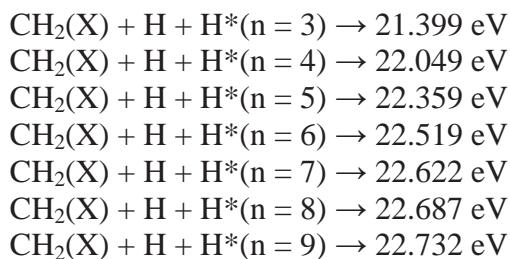
CH + 3H

$$\begin{aligned} \Delta_f H_g^\circ(\text{CH}) &= \Delta_f H_g^\circ(\text{CH}_4) - 3 \cdot \Delta_f H_g^\circ(\text{H}) + D(\text{CH}+3\text{H}) \\ 594.13 \text{ kJ/mol} &= -74.87 \text{ kJ/mol} - 3 \times 217.998 \text{ kJ/mol} + 0 \text{ kJ/mol} + D(\text{CH}+3\text{H}) \\ D(\text{CH}+3\text{H}) &= 1322.994 \text{ kJ/mol} = 13.71 \text{ eV} \end{aligned}$$



CH₂ + H + H

$$\begin{aligned} \Delta_f H_g^\circ(\text{CH}_2) &= \Delta_f H_g^\circ(\text{CH}_4) - 2 \cdot \Delta_f H_g^\circ(\text{H}) + D(\text{CH}+\text{H}+\text{H}_2) \\ 594.13 \text{ kJ/mol} &= -74.87 \text{ kJ/mol} - 2 \times 217.998 \text{ kJ/mol} + D(\text{CH}+\text{H}+\text{H}_2) \\ D(\text{CH}_2+2\text{H}) &= 897.256 \text{ kJ/mol} = 9.299 \text{ eV} \end{aligned}$$



CH⁺

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

CI

$$\begin{aligned} \Delta_f H_g^\circ(\text{C}) &= \Delta_f H_g^\circ(\text{CH}_4) - 2 \cdot \Delta_f H_g^\circ(\text{H}_2) + D(\text{H}_2+\text{H}_2) \\ 716.68 &= -74.87 \text{ kJ/mol} + D(\text{H}_2+\text{H}_2) \\ D(\text{H}_2+\text{H}_2) &= 716.68 + 74.87 = 791.55 \text{ kJ/mol} = 8.20 \text{ eV} \\ E_{th}(\text{CI } (3s(^1\text{P}^o))) &= 8.20 + 5.0 \text{ eV} = 13.2 \text{ eV} \end{aligned}$$

$$\begin{aligned} \Delta_f H_g^\circ(\text{C}) &= \Delta_f H_g^\circ(\text{CH}_4) - 2 \cdot \Delta_f H_g^\circ(\text{H}) + \Delta_f H_g^\circ(\text{H}_2) + D(2\text{H}+\text{H}_2) \\ 716.68 &= -74.87 + 2 \times 217.998 + D(2\text{H}+\text{H}_2) \text{ kJ/mol} \\ D(2\text{H}+\text{H}_2) &= 716.68 + 74.87 + 2 \times 217.98 = 1227.51 \text{ kJ/mol} = 12.72 \text{ eV} \\ E_{th}(\text{CI } (3s(^1\text{P}^o))) &= 12.72 + 5.0 \text{ eV} = 17.72 \text{ eV} \end{aligned}$$

$$\Delta_f H_g^\circ(\text{C}) = \Delta_f H_g^\circ(\text{CH}_4) - 4 \cdot \Delta_f H_g^\circ(\text{H}) + D(4\text{H})$$

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

Supplement

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.

