

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

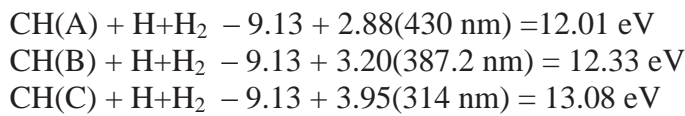
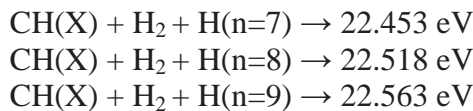
$$\begin{aligned}\Delta_f H_g^\circ(\text{CH}_3) &= \Delta_f H_g^\circ(\text{CH}_4) - \Delta_f H_g^\circ(\text{H}) + D(\text{CH}+\text{H}+\text{H}_2) \\ 145.69 \text{ kJ/mol} &= -74.87 \text{ kJ/mol} - 217.998 \text{ kJ/mol} + D(\text{CH}+\text{H}+\text{H}_2) \\ D(\text{CH}_3+\text{H}) &= 438.558 \text{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

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

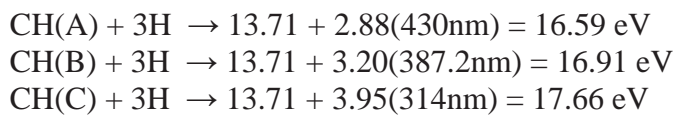
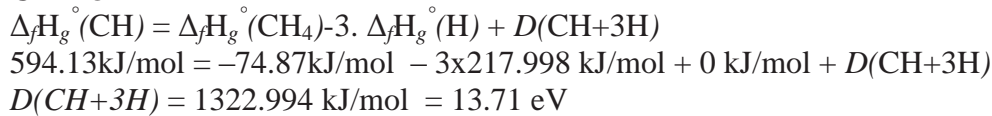
CH + H + H₂

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

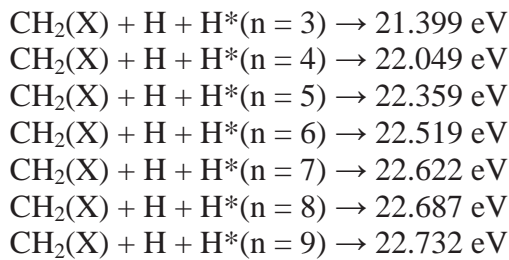
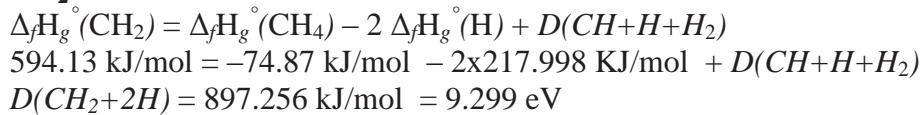
$$\begin{aligned}\text{CH}(\text{X}) + \text{H}_2 + \text{H}(n=3) &\rightarrow 21.23 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(n=4) &\rightarrow 21.88 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(n=5) &\rightarrow 22.19 \text{ eV} \\ \text{CH}(\text{X}) + \text{H}_2 + \text{H}(n=6)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



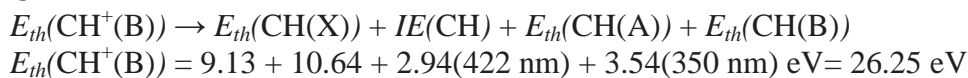
CH + 3H



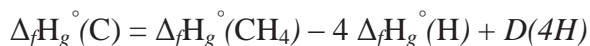
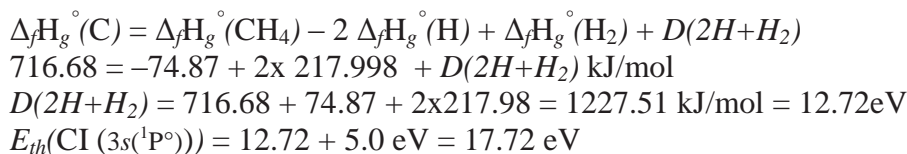
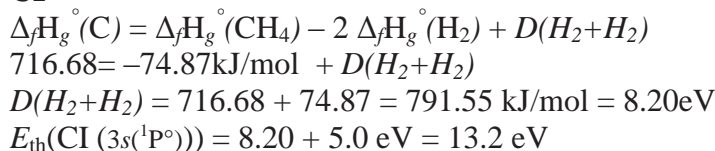
CH₂ + H + H



CH⁺



CI



$$716.68 = -74.87 \text{ kJ/mol} + 2 \times 217.998 + D(4H)$$

$$D(4H) = 716.68 + 74.87 + 4 \times 217.98 = 1663.47 \text{ kJ/mol} = 17.24 \text{ eV}$$

$$E_{th}(\text{CI}(3s(^1P^o))) = 17.24 + 5.0 \text{ eV} = 22.24 \text{ eV}$$

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.

