

1 Addition 2: Capture-auto-dissociation of CH_y^+

Electron capture to a doubly excited dissociative state of CH produces, after auto-dissociation, the same reaction products $C^+ + H$ as the direct DE process. This capture-auto ionization dissociative (CAD) channel was considered in subsection 2.3.2 of the original report. $\sigma_{CAD}(C^+)$ is significantly larger than $\sigma_{DE}(C^+)$ [47].

It is not possible to make a more accurate judgment about the CAD cross sections of CH_y^+ ions with $y = 2 - 4$. However, if the magnitude of the resonant structures in the dissociative recombination cross sections of CH_y^+ ions (see sub-section 2.5) is taken as a measure of the relative role of processes proceeding via the doubly excited dissociative CH_y^{**} states, then, with increasing y in CH_y^+ the CAD cross section should rapidly decrease (approximately by a factor of two for each decrease of y by one). This can be also inferred from the rapid decrease of the electron capture cross section to the doubly excited state of CH_y with increasing “vertical” transition energy from the bottom of ground electronic state of CH_y^+ to the dissociative potential curve of CH_y^{**} (which increases when y increases).

Taking these considerations as guidance the total cross sections for capture-auto-dissociation of CH_y^+ ($y = 1-4$) ions by electron impact, can probably be represented by the analytic expression

$$\sigma_{CAD}^{tot}(CH_y^+) = \frac{20.6}{2^{y-1}} \left(1 - \frac{E_{th}}{E}\right)^{2.5} \frac{1}{E(1+aE)^\gamma} \ln(e + 0.9E) \quad (\times 10^{-16} cm^2) \quad (1)$$

where E_{th} and E are the threshold and collision energy, expressed in eV, and $e = 2.71828\dots$. The fit parameters a and γ are given in Table 5a, and E_{th} is taken as the minimum of the “threshold” energies of all reaction channels for any particular CH_y^+ ion, as listed in Table 5b.

The partial cross sections of the individual dissociative excitation channels are given by

$$R_{CAD}(A^+/CH_y^+) = \frac{\sigma_{CAD}(A^+/CH_y^+)}{\sigma_{CAD}^{tot}(CH_y^+)} \quad (2)$$

For the branching ratio we suggest to assume $R_{CAD} = R_{DR}$, and the energy of products $E_{K,CAD}^{(0)}$ may be set to (see Table 5a below):

$$\overline{E}_{K,CAD}^{(0)} = \overline{E}_{K,DR}^{(0)} - \overline{E}_{exc}(A^*) \quad (3)$$

and the “threshold energy” $E_{th} \approx \overline{E}_{exc}(A^*)$ as estimated with the energy of appearance of oscillations in σ_{DR} .

2 Tables

Table 5a

Fitting parameters for total capture-auto-dissociation (CAD) cross sections of CH_y^+ hydrocarbon ions.

	a	γ	E_{th} (eV)
CH_4^+	0.52	1.25	0.54
CH_3^+	1.20	0.60	0.54
CH_2^+	1.35	0.65	1.25
CH^+	0.45	0.75	2.5

Table 5b

Capture-auto-dissociation (CAD) channels in $e + CH_y^+$ collisions, their branching ratios, R_{CAD} , “threshold” energies E_{th} and total kinetic energy $E_K^{(0)}$ of the products.

Reaction Channel	R_{CAD}	E_{th} (eV)	$E_{K,CAD}^{(0)}$ (eV)	Mediating excited states
$e + CH_4^+ \rightarrow CH_3^+ + H + e$	0.21	5.73	2.44	$CH_3^*(3s^2A'_1)$
$\rightarrow CH_2^+ + H_2 + e$	0.09	3.58	4.26	$CH_2^*(c)$
$\rightarrow CH_2^+ + H + H + e$	0.43	0.91	2.36	$CH_2^*(a; b)$
$\rightarrow CH^+ + H_2 + H + e$	0.25	0.54	2.58	$CH^*(a; A)$
$\rightarrow C^+ + H_2 + H_2 + e$	0.02	1.97	2.46	$C^*(^1D; ^1S)$
$e + CH_3^+ \rightarrow CH_2^+ + H + e$	0.40	1.80	3.17	$CH_2^*(a; b; c)$
$\rightarrow CH^+ + H_2 + e$	0.14	2.51	2.59	$CH^*(A; B; C)$
$\rightarrow CH^+ + H + H + e$	0.16	0.54	0.10	$CH^*(a; A)$
$\rightarrow C^+ + H_2 + H + e$	0.30	1.25	0.31	$C^*(^1D)$
$e + CH_2^+ \rightarrow CH^+ + H + e$	0.25	2.51	3.49	$CH^*(A; B; C)$
$\rightarrow C^+ + H_2 + e$	0.12	3.43	3.57	$C^*(^1S; ^5S_2^0)$
$\rightarrow C^+ + H + H + e$	0.63	1.25	1.16	$C^*(^1D)$
$e + CH^+ \rightarrow C^+ + H + e$	1.00	2.50	4.47	$C^*(^1D; ^1S; ^5S_2^0)$