Electronic supplementary information for the PCCP paper

Capture and dissociation in the complex-forming CH(v=0,1) + D_2 → CHD + D, CD_2 + H, CD + HD reactions and comparison with CH(v=0,1) + H_2

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For the CH($v = 0, 1$) + D_2 and CH($v = 1$) + H_2 systems, QCT capture rate coefficients (Tables 1S, 2S, and 3S), QCT capture probabilities (Figure 1S), QCT dissociation probabilities (Tables 4S, 5S, and 6S and Figures 2S and 3S), QCT total reaction rate coefficients (Tables 7S, 8S and 9S and Figures 4S, 5S and 6S) QCT abstraction rate coefficients (Tables 10S, 11S and 12S and Figures 7S, 8S and 9S), QCT abstraction-exchange rate coefficients (Tables 13S and 14S, and Figures 10S and 11S), and QCT exchange rate coefficients (Tables 15S, 16S and 17S, and Figures 12S, 13S and 14S). From Table 7S to Table 17S the QCT-C2 and QCT-C2e results are reported, and from Figure 4S to Figure 14S the QCT reaction rate coefficients and those obtained with all ZPE treatments analyzed are presented.

Table 1S: QCT capture rate coefficients* for the CH($v = 0$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_c^{QCT}	179.6	157.7	143.4	133.5	126.4	118.7	114.0	112.0

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

Table 2S: QCT capture rate coefficients* for the CH($v = 1$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_c^{QCT}	300.2	268.7	240.4	218.4	201.0	177.3	163.7	155.0

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

Table 3S: QCT capture rate coefficients* for the CH($v = 1$) + H_2 reaction

T /K	200	300	400	500	600	800
k_c^{QCT}	405.3	365.1	327.3	298.6	274.8	242.3

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

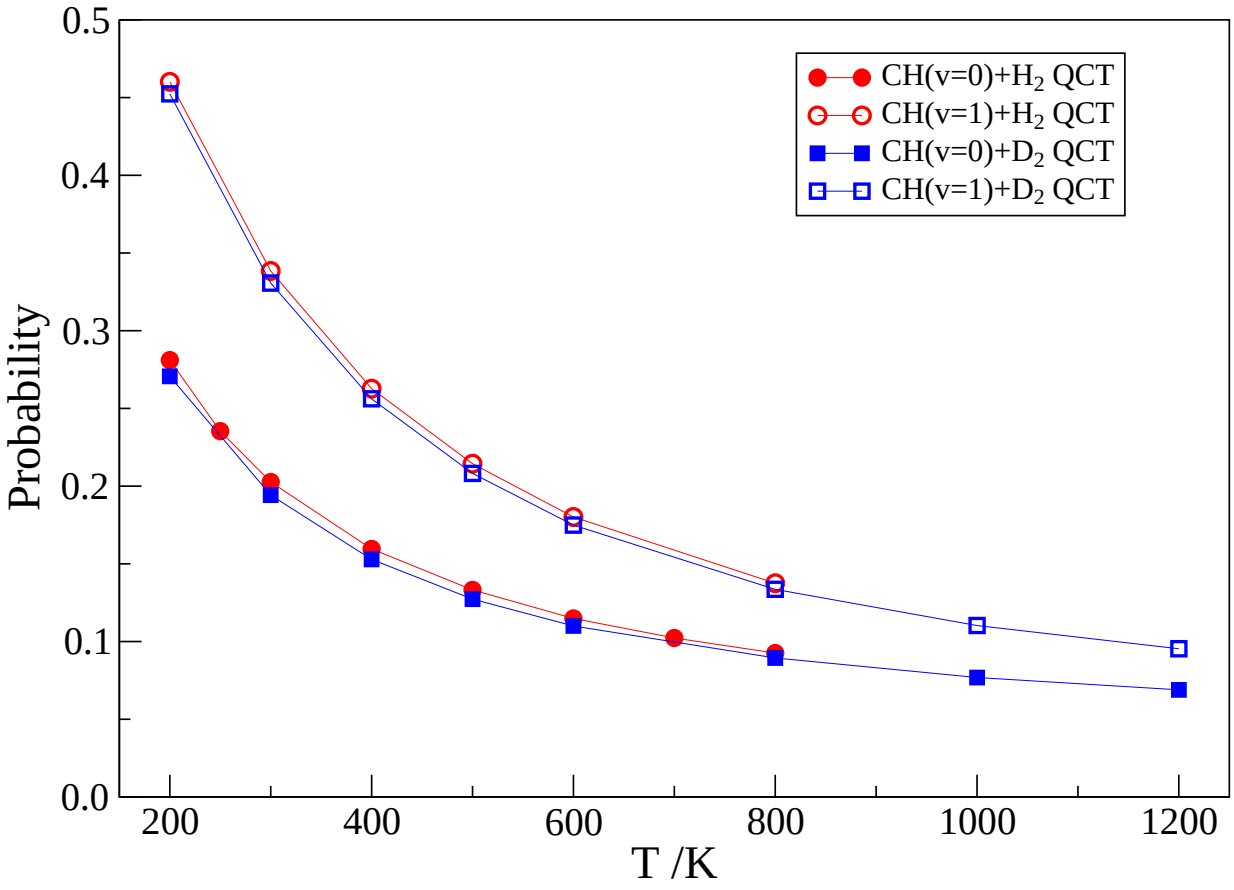

Figure 1S: QCT capture probabilities for CH(v=0,1) + D_2 → CHD_2 and CH(v=0,1) + H_2 → CH_3 plotted as a function of temperature. QCT errors are smaller than the size of the symbols.

Table 4S: Dissociation probabilities of the CHD_2 complex formed in the $CH(v = 0) + D_2$ reaction for the different types of processes (i, inelastic; e, exchange; a, abstraction; ae, abstraction-exchange).

Channel		200 K	300 K	400 K	500 K	600 K	800 K	1000 K	1000 K
$CH_b + D_cD_d$	(i)	0.265	0.261	0.255	0.250	0.243	0.235	0.225	0.217
$CD_c + H_bD_d$	(e)	0.315	0.306	0.298	0.290	0.283	0.267	0.251	0.239
$CD_d + H_bD_c$	(e)	0.313	0.305	0.298	0.290	0.281	0.268	0.256	0.239
$CH_bD_c + D_d$	(a)	0.029	0.036	0.042	0.049	0.057	0.068	0.080	0.091
$CH_bD_d + D_c$	(a)	0.030	0.036	0.043	0.048	0.056	0.068	0.080	0.092
$CD_cD_d + H_b$	(ae)	0.047	0.055	0.063	0.071	0.080	0.093	0.109	0.123

Table 5S: Dissociation probabilities of the CHD_2 complex formed in the $CH(v = 1) + D_2$ reaction for the different types of processes (i, inelastic; e, exchange; a, abstraction; ae, abstraction-exchange).

Channel		200 K	300 K	400 K	500 K	600 K	800 K	1000 K	1000 K
$CH_b + D_cD_d$	(i)	0.206	0.203	0.201	0.198	0.194	0.193	0.189	0.184
$CD_c + H_bD_d$	(e)	0.235	0.232	0.229	0.225	0.222	0.214	0.209	0.206
$CD_d + H_bD_c$	(e)	0.235	0.231	0.228	0.224	0.222	0.215	0.206	0.202
$CH_bD_c + D_d$	(a)	0.088	0.092	0.096	0.099	0.102	0.105	0.114	0.117
$CH_bD_d + D_c$	(a)	0.088	0.091	0.095	0.098	0.102	0.107	0.113	0.117
$CD_cD_d + H_b$	(ae)	0.147	0.150	0.152	0.156	0.159	0.166	0.170	0.173

Table 6S: Dissociation probabilities of the CH_2 complex formed in the $CH(v = 1) + H_2$ reaction for the different types of processes (i, inelastic; e, exchange; a, abstraction).

Channel		200 K	300 K	400 K	500 K	600 K	800 K
$CH_b + H_cH_d$	(i)	0.218	0.217	0.215	0.211	0.210	0.206
$CH_c + H_bH_d$	(e)	0.214	0.211	0.209	0.207	0.203	0.200
$CH_d + H_bH_c$	(e)	0.216	0.211	0.208	0.206	0.205	0.198
$CH_bH_c + H_d$	(a)	0.117	0.119	0.122	0.125	0.127	0.131
$CH_bH_d + H_c$	(a)	0.117	0.121	0.123	0.125	0.127	0.132
$CH_cH_d + H_b$	(a)	0.117	0.121	0.123	0.126	0.129	0.133

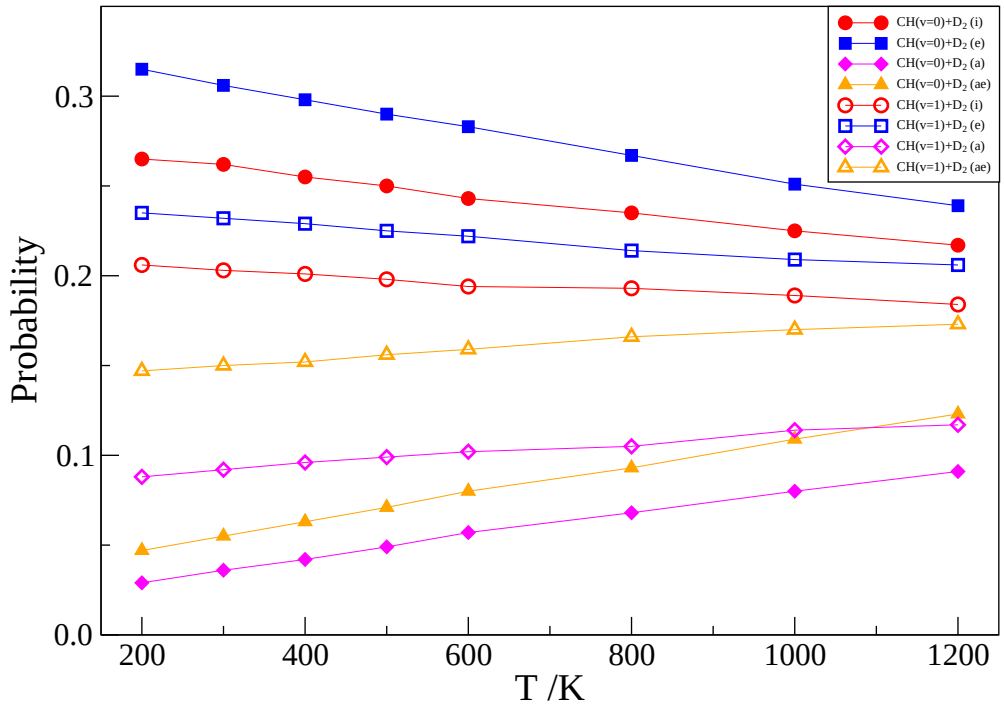

Figure 2S: Dissociation probabilities of the CHD_2 complex formed in the $CH(v = 0, 1) + D_2$ reactions plotted as a function of temperature.

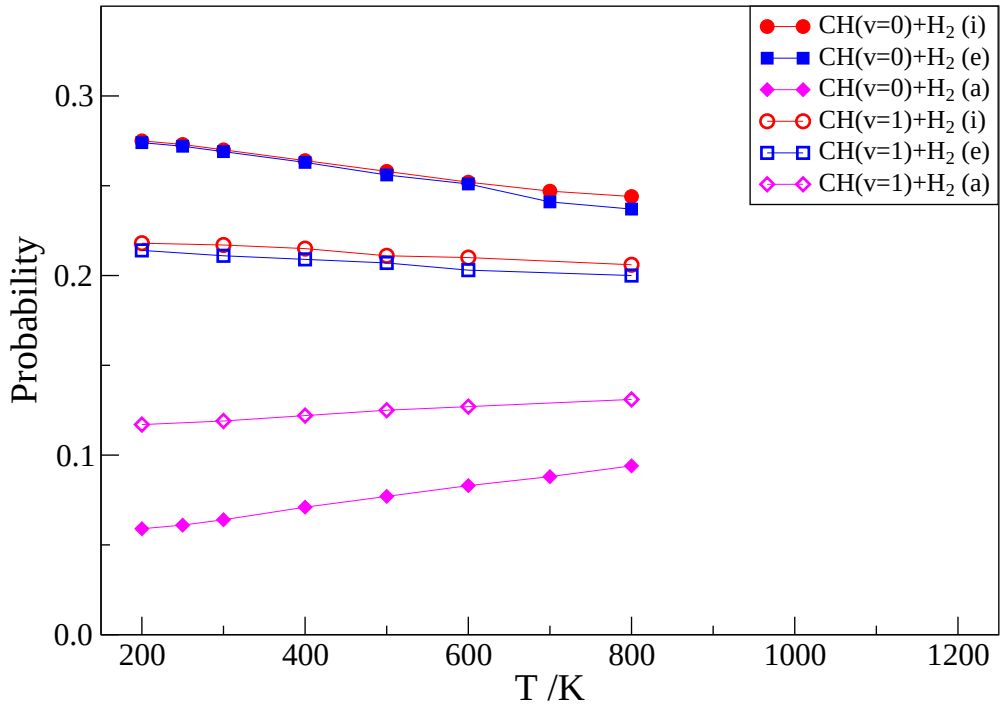

Figure 3S: Dissociation probabilities of the CH_3 complex formed in the $CH(v = 0, 1) + H_2$ reactions plotted as a function of temperature.

Table 7S: QCT-C2 and QCT-C2e total reaction rate coefficients* for the CH($v = 0$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
$k_{\rm all}^{\rm QCT-C2}$	7.167	12.99	21.59	33.52	51.01	82.85	123.9	155.0
$k_{\rm all}^{\rm QCT-C2e}$	7.824	17.47	33.10	53.34	79.68	120.8	165.3	198.8

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

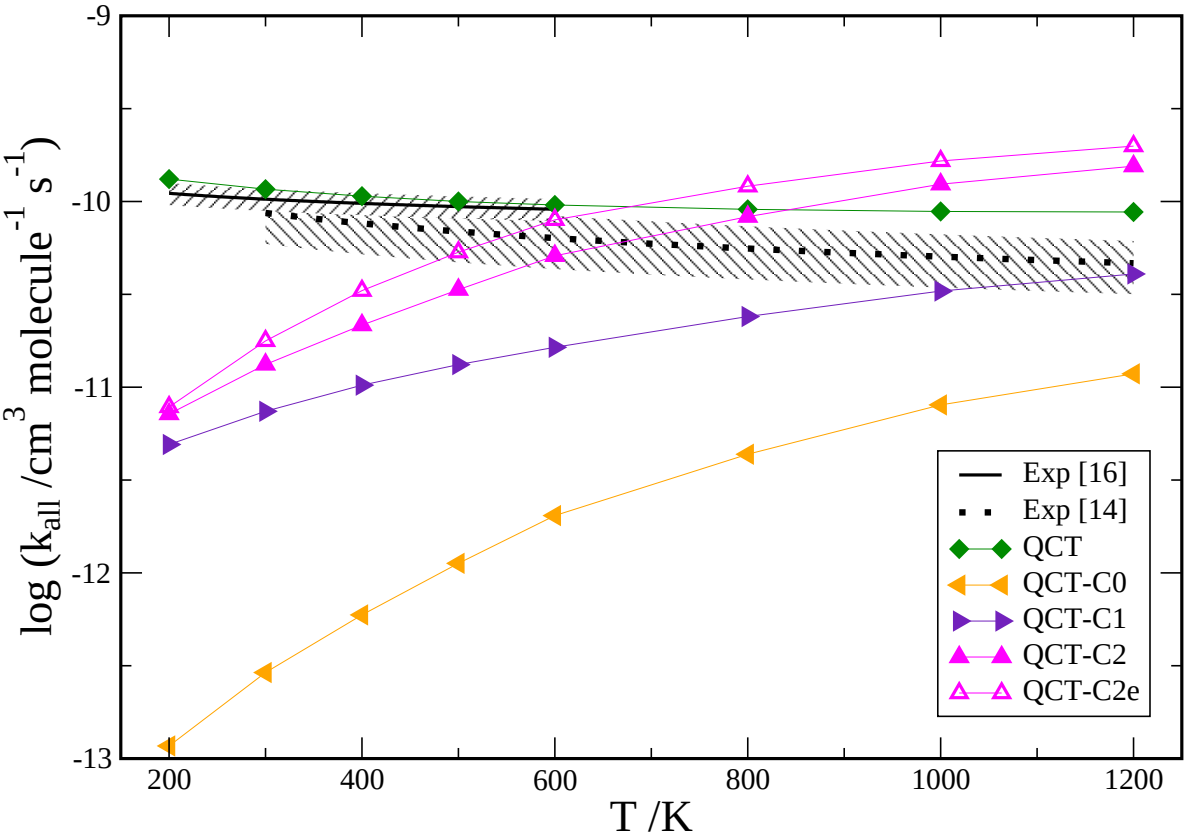

Figure 4S: QCT total reaction rate coefficients for the CH($v = 0$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Experimental values (with the related error margins) [14, 16] are also plotted. QCT errors are smaller than the size of the symbols.

The C0 criterion to treat the ZPE problem consists in discarding the trajectories of a given reaction channel with products vibrational energy below the ZPE. Namely, when determining the number of trajectories of a given reaction channel, only will be accepted the trajectories satisfying: a) $E_{\rm vib}({\rm CHD}) > {\rm E}_{\rm zpe}({\rm CHD})$ for abstraction; b) $E_{\rm vib}({\rm CD_2}) > {\rm E}_{\rm zpe}({\rm CD_2})$ for abstraction-exchange; c) $E_{\rm vib}({\rm CD}) + {\rm E}_{\rm vib}({\rm HD}) > {\rm E}_{\rm zpe}({\rm CD}) + {\rm E}_{\rm vib}({\rm HD})$ for exchange. The C1 criterion, in addition to C0, also takes into account restrictions to determine the number of trajectories leading to the other channels (reactive or not), according to what is indicated in C0 for them and discarding also the inelastic trajectories that do not satisfy $E_{\rm vib}({\rm CH}) + {\rm E}_{\rm vib}({\rm D_2}) > {\rm E}_{\rm zpe}({\rm CH}) + {\rm E}_{\rm vib}({\rm D_2})$.

Table 8S: QCT-C2 and QCT-C2e total reaction rate coefficients* for the CH($v = 1$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
$k_{\rm all}^{\rm QCT-C2}$	104.4	92.48	86.14	84.14	83.31	84.44	87.91	91.83
$k_{\rm all}^{\rm QCT-C2e}$	139.9	122.8	111.9	106.4	103.6	101.0	102.3	104.6

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

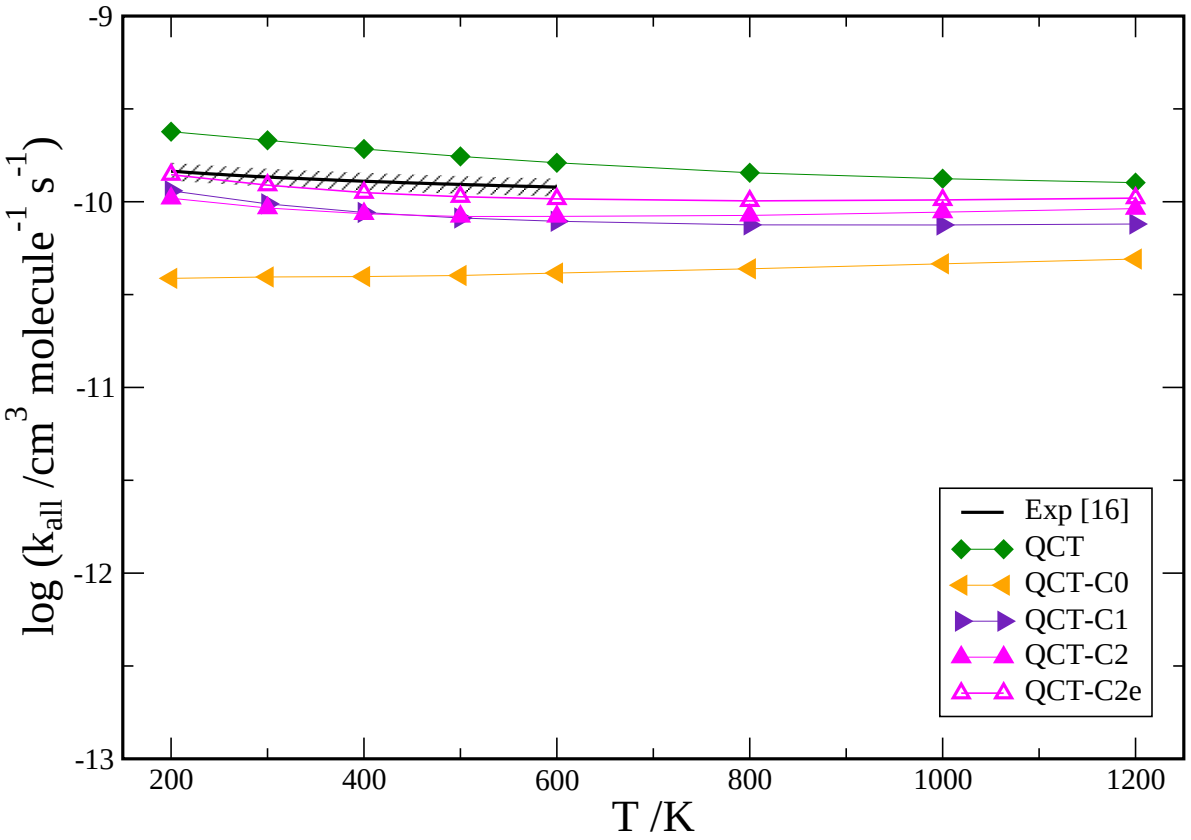

Figure 5S: QCT total reaction rate coefficients for the CH($v = 1$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Experimental values (with the related error margins) [16] are also plotted. QCT errors are smaller than the size of the symbols.

Table 9S: QCT-C2 and QCT-C2e total reaction rate coefficients* for the CH($v = 1$) + H_2 reaction

T /K	200	300	400	500	600	800
$k_{\rm all}^{\rm QCT-C2}$	118.5	107.1	103.5	103.7	104.1	109.0
$k_{\rm all}^{\rm QCT-C2e}$	168.5	150.0	140.8	137.4	133.6	133.8

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

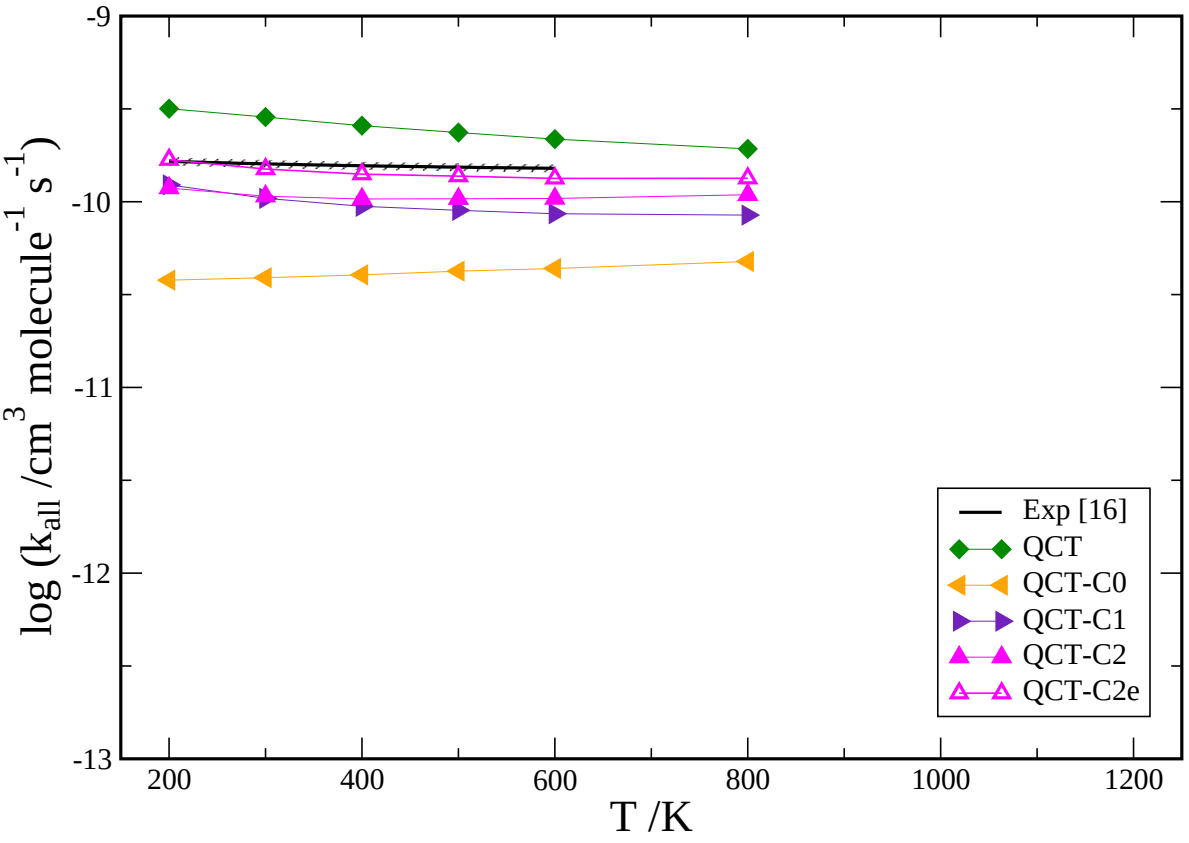

Figure 6S: QCT total reaction rate coefficients for the CH($v = 1$) + H_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Experimental values (with the related error margins) [16] are also plotted. QCT errors are smaller than the size of the symbols.

The C0 criterion to treat the ZPE problem consists in discarding the trajectories of a given reaction channel with products vibrational energy below the ZPE. Namely, when determining the number of trajectories of a given reaction channel, only will be accepted the trajectories satisfying: a) $E_{\rm vib}(CH_2) > E_{\rm zpe}(CH_2)$ for abstraction; b) $E_{\rm vib}(CH) + E_{\rm vib}(H_2) > E_{\rm zpe}(CH) + E_{\rm vib}(H_2)$. The C1 criterion, in addition to C0, also takes into account restrictions to determine the number of trajectories leading to the other channels (reactive or not), according to what is indicated in C0 for them and discarding also the inelastic trajectories that do not satisfy $E_{\rm vib}(CH)+E_{\rm vib}(H_2) > E_{\rm zpe}(CH)+E_{\rm vib}(H_2)$.

Table 10S: QCT-C2 and QCT-C2e abstraction rate coefficients* for the CH($v = 0$) + D_2 reaction

T /K	300	400	500	600	800	1000	1200
k_a^{QCT-C2}	0.1136	0.8653	3.210	8.868	21.98	41.73	58.39
$k_a^{QCT-C2e}$	0.9977	3.754	9.443	20.14	39.78	61.29	81.39

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

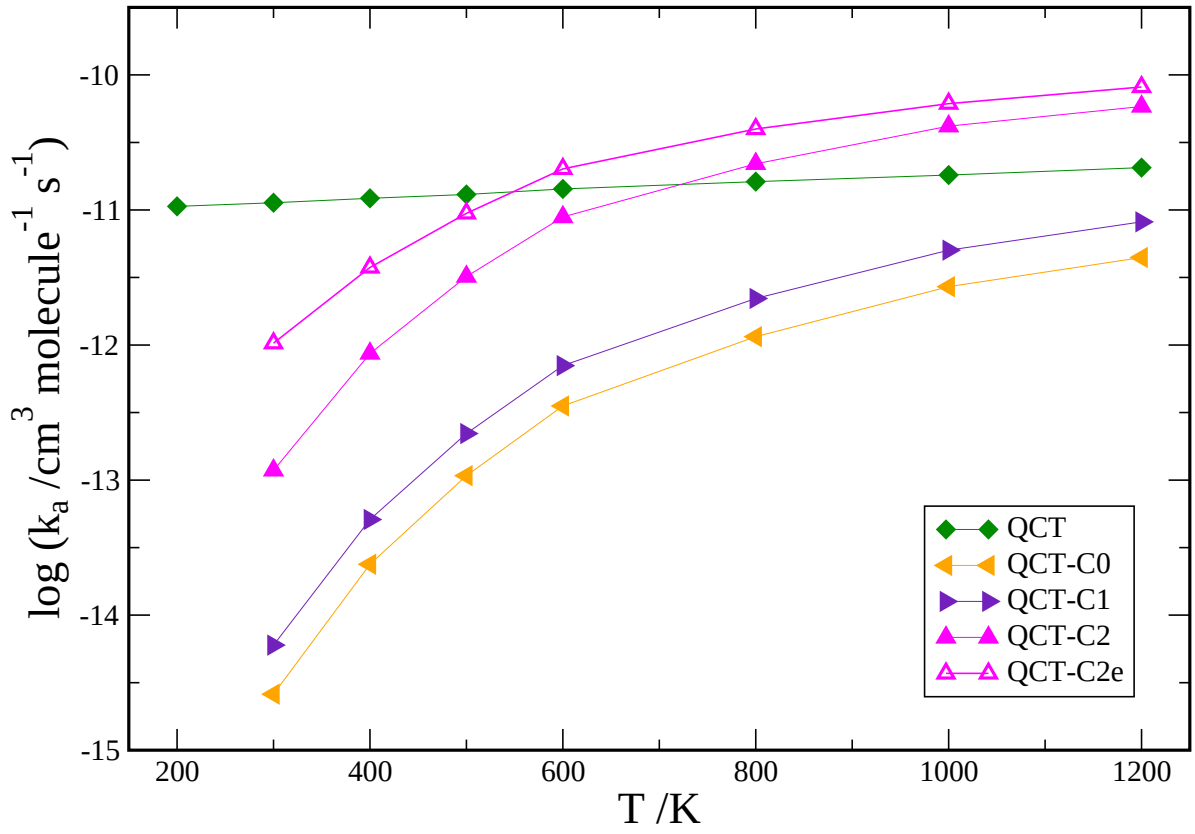

Figure 7S: QCT abstraction rate coefficients for the CH($v = 0$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. QCT errors are smaller than the size of the symbols.

Table 11S: QCT-C2 and QCT-C2e abstraction rate coefficients* for the CH($v = 1$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_a^{QCT-C2}	27.83	27.38	27.80	28.24	29.46	31.73	35.92	37.95
$k_a^{QCT-C2e}$	47.96	44.26	42.19	41.45	41.05	41.54	44.42	45.55

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

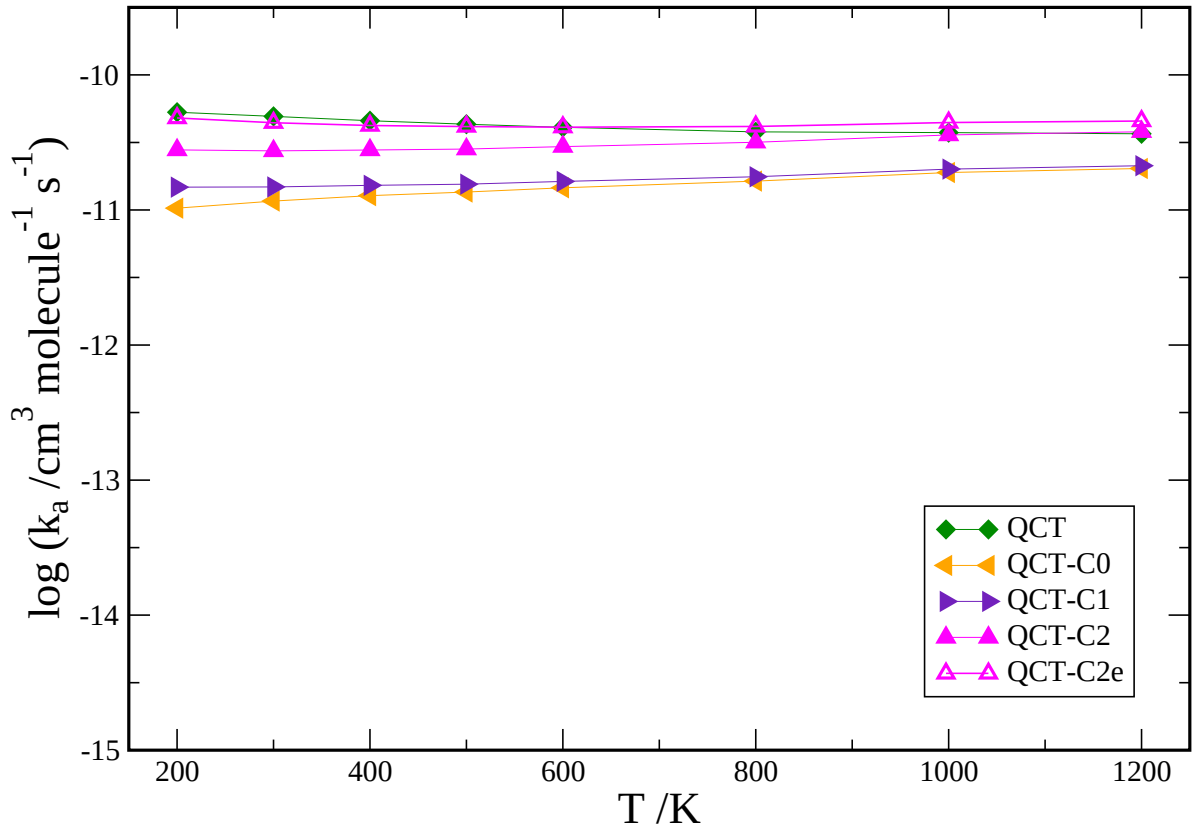

Figure 8S: QCT abstraction rate coefficients for the CH($v = 1$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. QCT errors are smaller than the size of the symbols.

Table 12S: QCT-C2 and QCT-C2e abstraction rate coefficients* for the CH($v = 1$) + H_2 reaction

T /K	200	300	400	500	600	800
k_a^{QCT-C2}	85.79	79.82	79.26	80.02	81.22	87.27
$k_a^{QCT-C2e}$	137.9	123.9	117.3	114.3	111.2	112.3

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

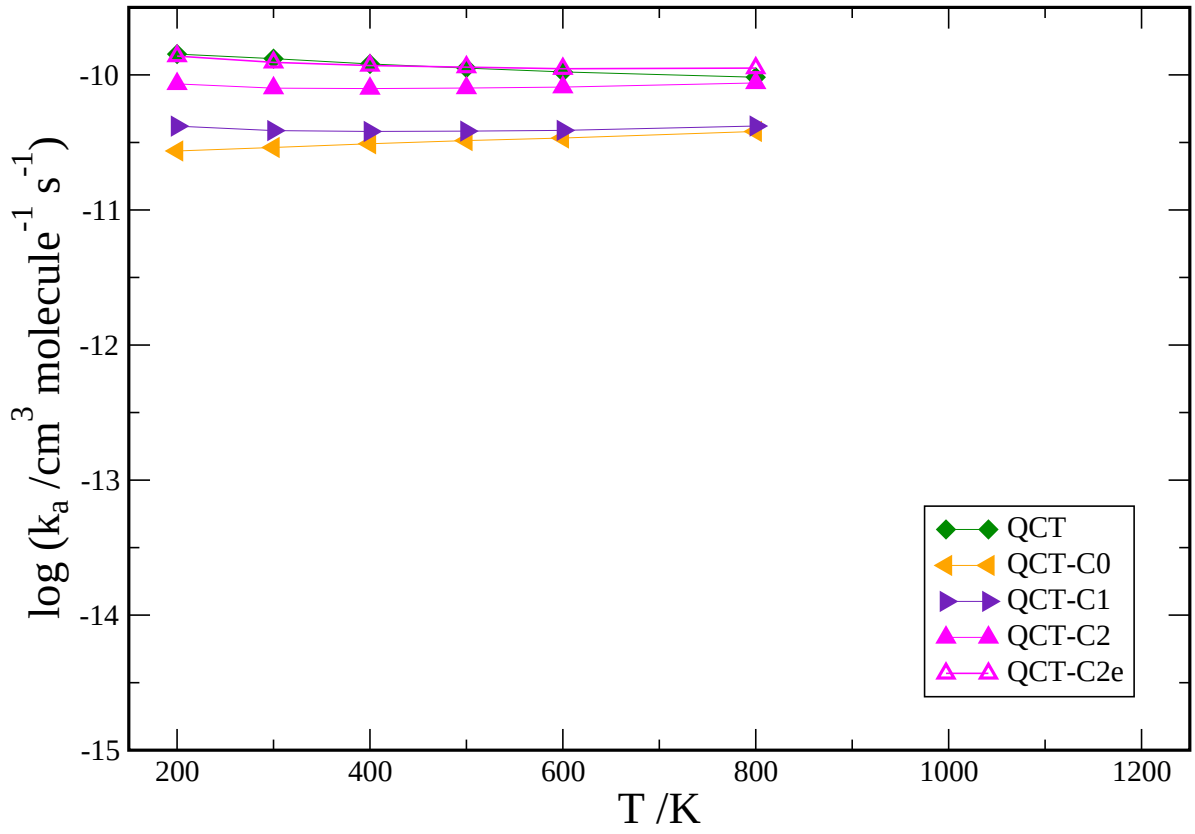

Figure 9S: QCT abstraction rate coefficients for the CH($v = 1$) + H_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. QCT errors are smaller than the size of the symbols.

Table 13S: QCT-C2 and QCT-C2e abstraction-exchange rate coefficients* for the CH($v = 0$) + D_2 reaction

T /K	300	400	500	600	800	1000	1200
k_{ae}^{QCT-C2}	0.7572	3.498	8.403	15.05	28.11	43.61	52.75
$k_{ae}^{QCT-C2e}$	4.418	12.33	22.41	33.16	49.27	66.70	74.86

* 10^{-12} cm^3 $molecule^{-1}$ mol^{-1}

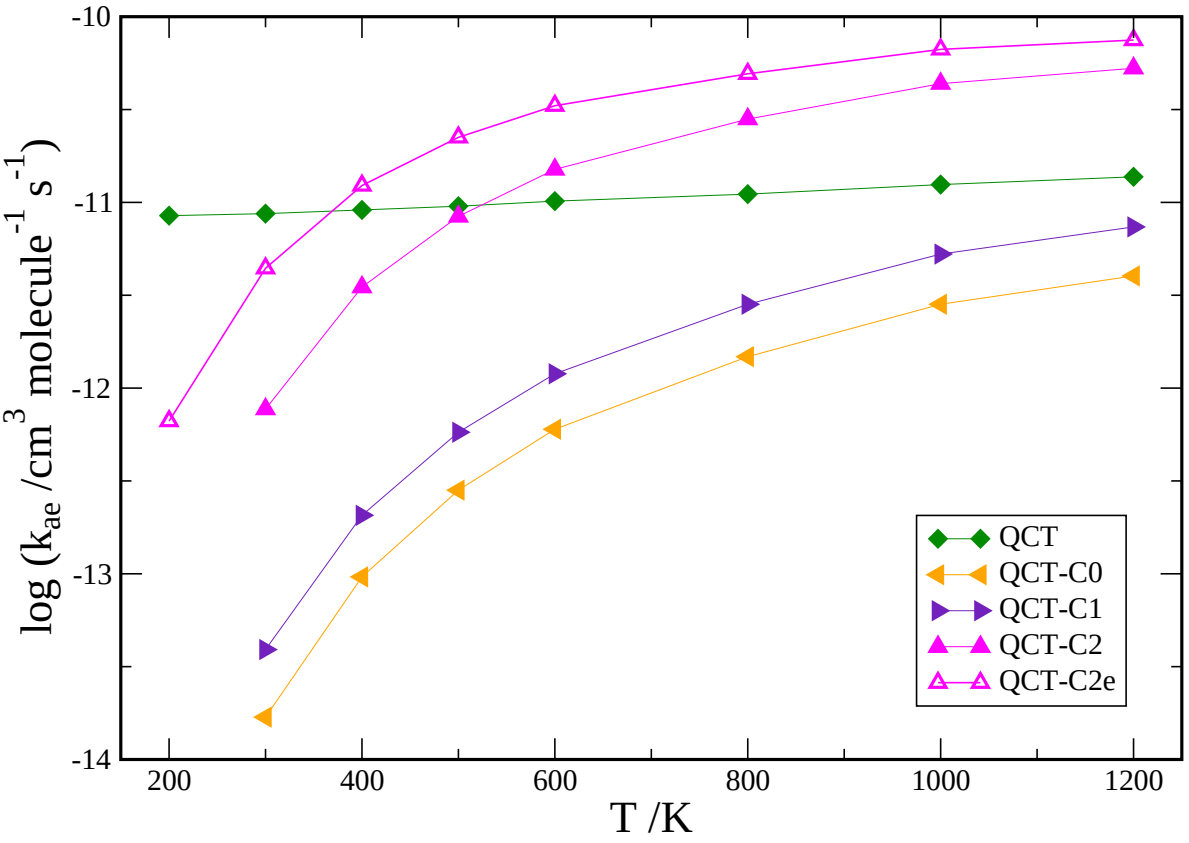

Figure 10S: QCT abstraction-exchange rate coefficients for the CH($v = 0$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. QCT errors are smaller than the size of the symbols.

Table 14S: QCT-C2 and QCT-C2e abstraction-exchange rate coefficients* for the CH($v = 1$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_{ae}^{QCT-C2}	43.83	37.85	34.41	33.32	32.29	32.27	32.08	33.41
$k_{ae}^{QCT-C2e}$	61.33	52.44	46.52	43.67	41.36	39.34	38.17	38.71

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

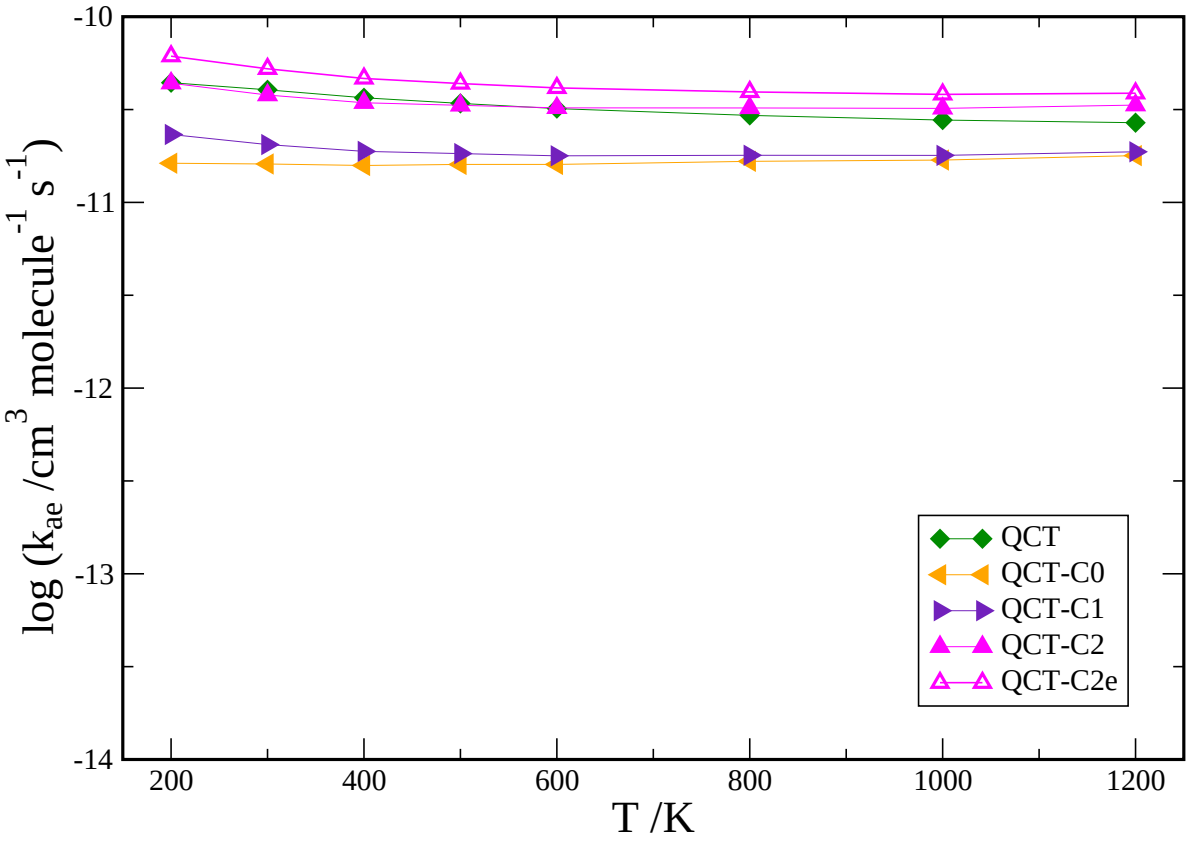

Figure 11S: QCT abstraction-exchange rate coefficients for the CH($v = 1$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. QCT errors are smaller than the size of the symbols.

Table 15S: QCT-C2 and QCT-C2e exchange rate coefficients* for the CH($v = 0$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_e^{QCT-C2}	7.167	12.05	17.23	21.91	27.09	32.76	38.51	43.89
$k_e^{QCT-C2e}$	7.160	12.12	17.01	21.48	26.38	31.76	37.33	42.58

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

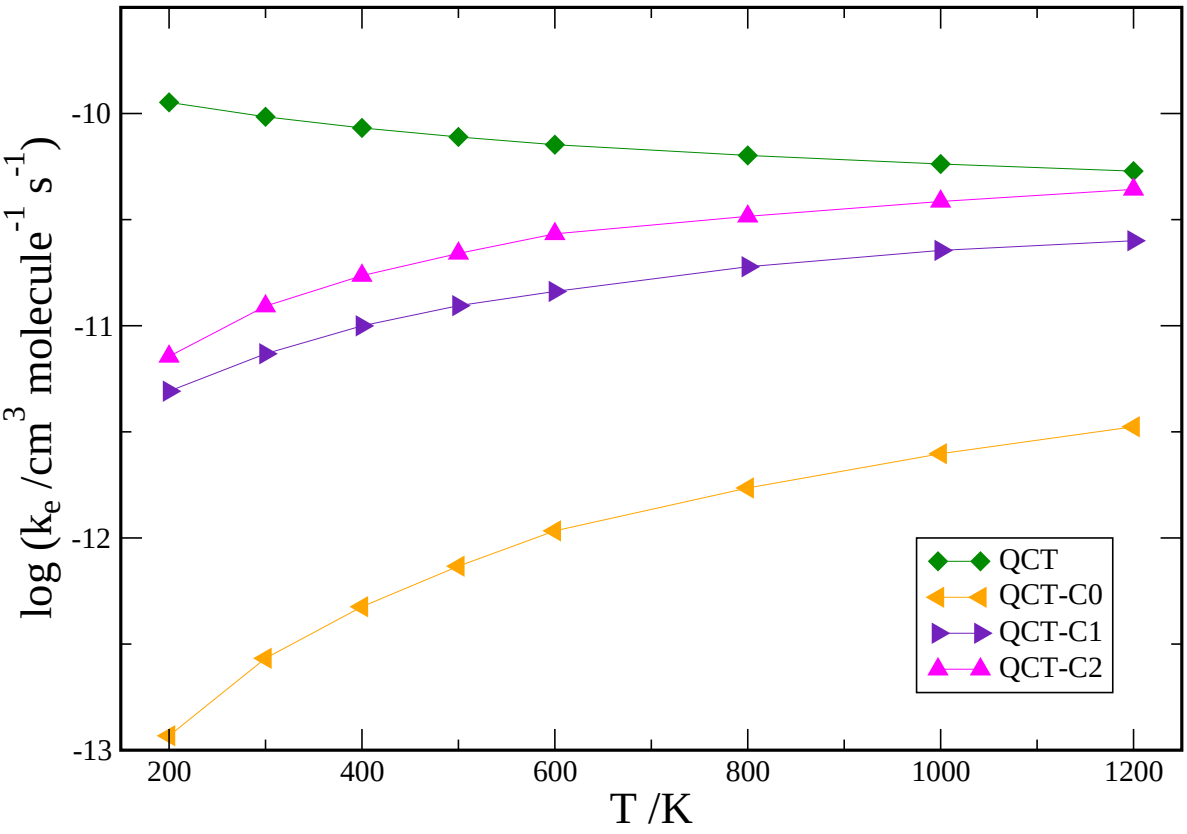

Figure 12S: QCT exchange rate coefficients for the CH($v = 0$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Values for the QCT-C2e criterion are almost coincident with those for the QCT-C2 one. QCT errors are smaller than the size of the symbols.

Table 16S: QCT-C2 and QCT-C2e exchange rate coefficients* for the CH($v = 1$) + D_2 reaction

T /K	200	300	400	500	600	800	1000	1200
k_e^{QCT-C2}	32.71	27.25	23.93	21.75	21.59	20.44	19.91	20.47
$k_e^{QCT-C2e}$	30.63	26.10	23.21	21.23	21.18	20.17	19.71	20.30

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

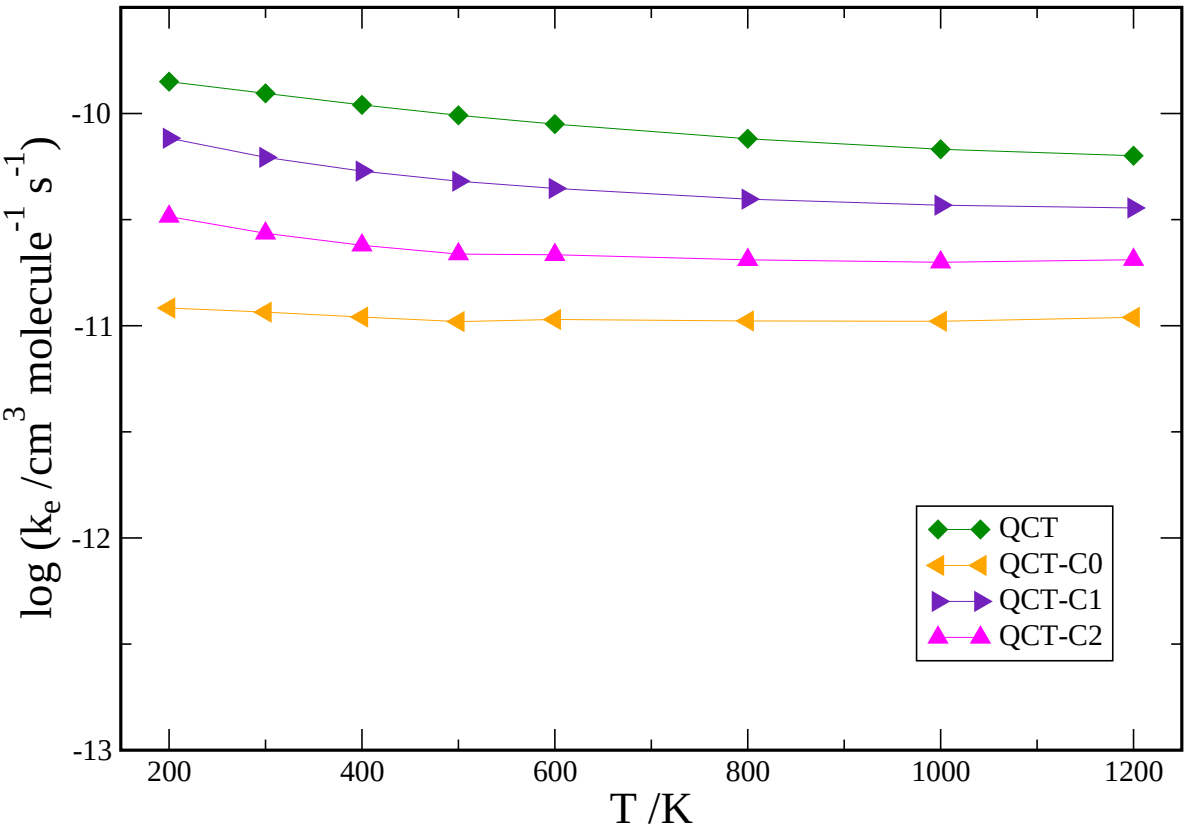

Figure 13S: QCT exchange rate coefficients for the CH($v = 1$) + D_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Values for the QCT-C2e criterion are almost coincident with those for the QCT-C2 one. QCT errors are smaller than the size of the symbols.

Table 17S: QCT-C2 and QCT-C2e exchange rate coefficients* for the CH($v = 1$) + H_2 reaction

T /K	200	300	400	500	600	800
k_e^{QCT-C2}	32.73	27.31	24.27	23.71	22.88	21.77
$k_e^{QCT-C2e}$	30.59	26.11	23.48	23.09	22.41	21.44

* 10^{-12} cm^3 molecule^{-1} mol^{-1}

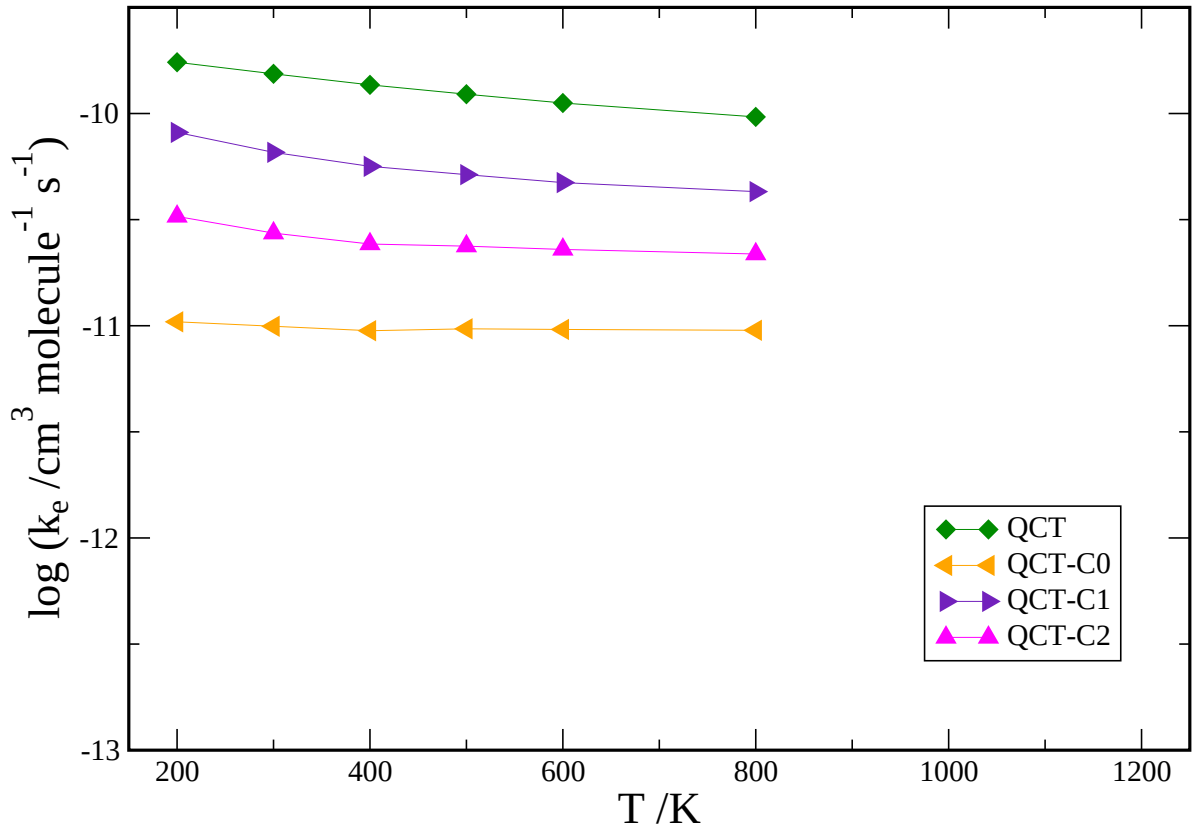

Figure 14S: QCT exchange rate coefficients for the CH($v = 1$) + H_2 reaction plotted as a function of temperature. Several treatments of the ZPE violation problem are taken into account. Values for the QCT-C2e criterion are almost coincident with those for the QCT-C2 one. QCT errors are smaller than the size of the symbols.