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Quantum versus Classical Unimolecular Fragmentation Rate Constants and Activation Energies at Finite Temperature from Direct Dynamics Simulations

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S1 Algorithm

Here we report the details of the algorithm used to propagate RPMD trajectories, as discussed by Ceriotti and co-workers in their original work.[1]

$$p_i^j \leftarrow p_i^j - \Delta t \frac{\partial V(q_1^j..q_N^j)}{\partial q_i^j} \tag{1}$$

$$\widetilde{p}_i^k = \sum_{j=1}^{P} p_i^j C_{jk} \quad \widetilde{q}_i^k = \sum_{j=1}^{P} q_i^j C_{jk} \tag{2}$$

$$\begin{bmatrix} \widetilde{p}_i^k \\ \widetilde{q}_i^k \end{bmatrix} \leftarrow \begin{bmatrix} \cos\omega_k \frac{\Delta t}{2} & -m_i\omega_k \sin\omega_k \frac{\Delta t}{2} \\ [\frac{1}{m_i\omega_k}] \sin\omega_k \frac{\Delta t}{2} & \cos\omega_k \frac{\Delta t}{2} \end{bmatrix} \begin{bmatrix} \widetilde{p}_i^k \\ \widetilde{q}_i^k \end{bmatrix} \tag{3}$$

$$\widetilde{p}_i^k \leftarrow c_1^k \widetilde{p}_i^k + \sqrt{\frac{m_i}{\beta_P}} c_2^k \eta_i^k \tag{4}$$

$$\begin{bmatrix} \widetilde{p}_i^k \\ \widetilde{q}_i^k \end{bmatrix} \leftarrow \begin{bmatrix} \cos\omega_k \frac{\Delta t}{2} & -m_i\omega_k \sin\omega_k \frac{\Delta t}{2} \\ [\frac{1}{m_i\omega_k}] \sin\omega_k \frac{\Delta t}{2} & \cos\omega_k \frac{\Delta t}{2} \end{bmatrix} \begin{bmatrix} \widetilde{p}_i^k \\ \widetilde{q}_i^k \end{bmatrix} \tag{5}$$

$$p_i^j = \sum_{k=0}^{P-1} C_{jk} \widetilde{p}_i^k \quad q_i^j = \sum_{k=0}^{P-1} C_{jk} \widetilde{q}_i^k \tag{6}$$

Where η is a random gaussian number and:

$$c_1^k = e^{-\Delta t \gamma^k} \tag{7}$$

$$c_2^k = \sqrt{1 - [c_1^k]^2} \tag{8}$$

S2 Temperature Correlation Function

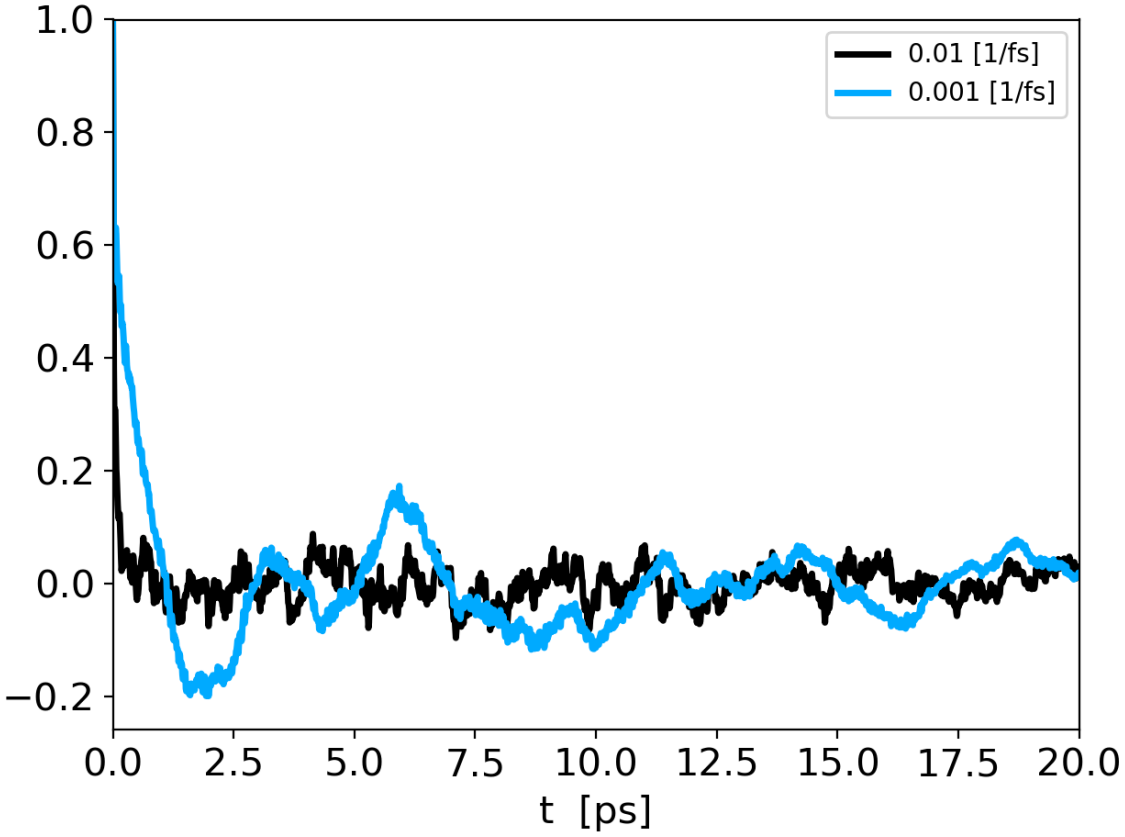

Figure S1: Temperature autocorrelation function obtained from LMD simulations at 3000 K with potential C for two different values of γ: 0.01 fs $^{-1}$ in black and 0.001 fs $^{-1}$ in blue.

S3 Rate constants

S3.1 1-D Morse model

Table S1: Lifetimes in ps for the 1D-Morse as a function of temperature (in K).

Method	700	800	900	1000	1100	1200
Classical Sum-of-States	33.07	13.76	7.03	4.15	2.72	1.93
Quantum Sum-of-States	23.78	5.75	3.54	2.39	1.74	10.67
LMD ($\gamma = 0.01$)	48±1	21.9±0.6	11.8±0.3	7.8±0.2	5.0±0.1	3.63±0.08
RPMD ($\gamma = 0.01$)	34.1±0.8	15.8±0.4	9.2±0.2	6.3±0.2	4.3±0.1	3.21±0.09
QTB ($\gamma = 0.01$)	1.32±0.06	1.22±0.05	1.18±0.06	1.08±0.05	1.03±0.05	0.85±0.03
LMD ($\gamma = 0.045$)	48±1	20.5±0.5	10.3±0.3	5.9±0.1	3.88±0.09	2.64±0.07
RPMD ($\gamma = 0.045$)	34.3±0.8	15.5±0.4	8.3±0.2	5.1±0.1	3.41±0.08	2.41±0.06
QTB ($\gamma = 0.045$)	1.18±0.05	1.01±0.05	0.90±0.04	0.85±0.04	0.75±0.03	0.69±0.03
LMD ($\gamma = 0.3$)	149±4	62±2	32.0±0.9	17.9±0.4	10.9±0.2	8.1±0.2
RPMD ($\gamma = 0.3$)	-	48±1	26.6±0.7	15.3±0.4	9.9±0.2	7.0±0.2
QTB ($\gamma = 0.3$)	20±1	12.5±0.8	9.3±0.5	6.9±0.4	4.7±0.2	3.6±0.2

Table S2: Rate constants in ps^{-1} for the 1D-Morse potential as a function of temperature (in K).

Method	700	800	900	1000	1100	1200
Classical SoS	0.03	0.07	0.14	0.24	0.37	0.52
Quantum SoS	0.04	0.17	0.28	0.42	0.57	0.09
LMD ($\gamma = 0.01$)	0.0207	0.0456	0.0847	0.128	0.199	0.275
RPMD ($\gamma = 0.01$)	0.0293	0.0633	0.109	0.158	0.234	0.311
QTB ($\gamma = 0.01$)	0.756	0.819	0.849	0.924	0.965	1.17
LMD ($\gamma = 0.045$)	0.0207	0.0488	0.0968	0.168	0.258	0.379
RPMD ($\gamma = 0.045$)	0.0292	0.0644	0.121	0.1958	0.293	0.415
QTB ($\gamma = 0.045$)	0.845	0.989	1.109	1.18	1.336	1.441
LMD ($\gamma = 0.3$)	0.00669	0.0161	0.0312	0.0559	0.0914	0.123
RPMD ($\gamma = 0.3$)	-	0.0209	0.0376	0.06538	0.100	0.143
QTB ($\gamma = 0.3$)	0.049	0.0796	0.108	0.143	0.2099	0.280

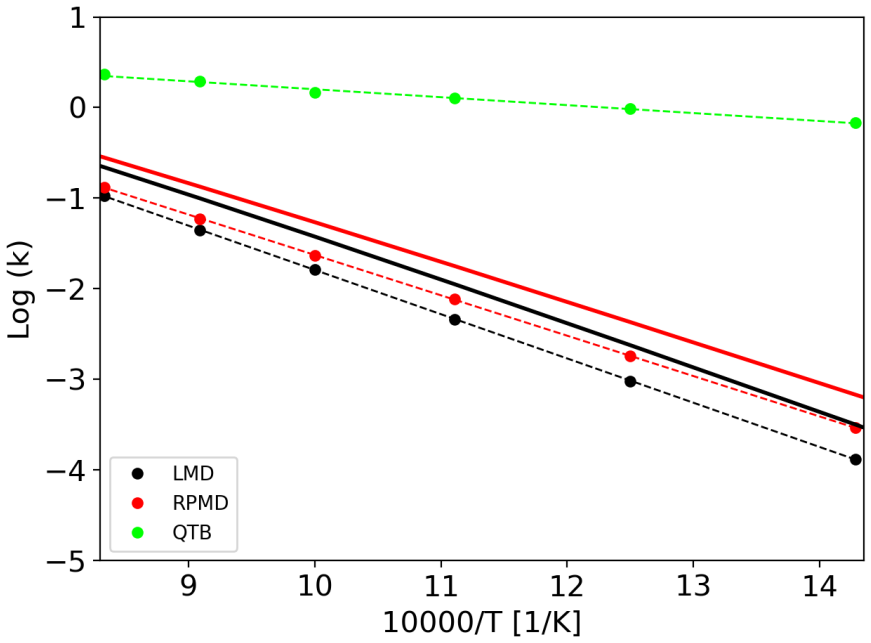

Figure S2: Quantum and classical rate constants as a function of temperature for 1-D Morse. In full lines we report values obtained from sum-of-state approach (both classical and quantum), while results from simulations (with $\gamma = 0.045$ fs^{-1}) are reported as dots: LMD (black), RPMD (red) and QTB (green).

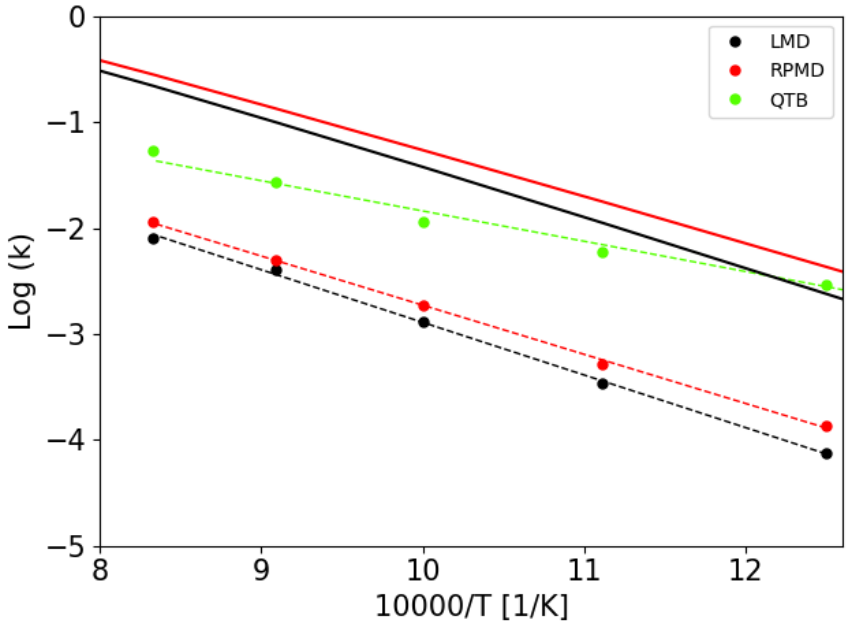

Figure S3: Quantum and classical rate constants as a function of temperature for 1-D Morse. In full lines we report values obtained from sum-of-state approach (both classical and quantum), while results from simulations (with $\gamma = 0.3$ fs^{-1}) are reported as dots: LMD (black), RPMD (red) and QTB (green).

S3.2 Molecular model

Table S3: Lifetimes in ps for the potential A at different temperatures (in K)

Temperature	LMD	RPMD	QTB
3000K	844±20	771±18	278±12
3500K	93±2	83±3	46±2
4000K	18.2±0.4	17.2±0.5	12.6±0.6
4500K	5.7±0.1	5.6±0.2	4.3±0.2
5000K	2.49±0.07	2.38±0.07	2.1±0.1

Table S4: Rate constants in ps^{-1} for the potential A as a function of temperature (in K)

Temperature	LMD	RPMD	QTB
3000K	0.00118	0.00129	0.00359
3500K	0.0107	0.0120	0.0215
4000K	0.0549	0.0581	0.0792
4500K	0.175	0.178	0.233
5000K	0.402	0.420	0.471

Table S5: Lifetimes in ps for the potential B at different temperatures (in K)

Temperature	LMD	RPMD	QTB
1350K	3460±176	2019±94	64±3
1500K	646±41	392±21	-
1700K	116±6	79±4	13.9±0.7
2000K	16.7±0.8	14.4±0.7	5.9±0.3
2500K	2.5±0.1	2.1±0.1	0.89±0.04

Table S6: Rate constants in ps^{-1} for the potential B as a function of temperature.

Temperature	LMD	RPMD	QTB
1350 K	0.000289	0.000495	0.0157
1500 K	0.00155	0.00255	-
1700 K	0.00859	0.0127	0.0721
2000 K	0.0600	0.0696	0.171
2500 K	0.397	0.472	0.748

Table S7: Lifetime in ps for the potential C at different temperatures (in K)

Temperature	LMD	RPMD	QTB
800K	7983±554	2267±116	8.9 ± 0.4
1000K	287±15	116±6	4.7±0.2
1200K	30±1	17.7±0.9	2.7±0.1
1500K	3.7±0.2	2.8±0.1	1.01±0.05
1800K	1.14±0.06	0.83±0.04	0.56±0.02
2000K	0.63±0.03	0.53±0.03	-

Table S8: Rate constants in ps^{-1} for the potential C at different temperatures (in K)

Temperature	LMD	RPMD	QTB
800K	0.000125	0.000441	0.112
1000K	0.00348	0.0086	0.212
1200K	0.0336	0.0571	0.370
1500K	0.271	0.351	0.986
1800K	0.875	1.197	1.780
2000K	1.595	1.901	-

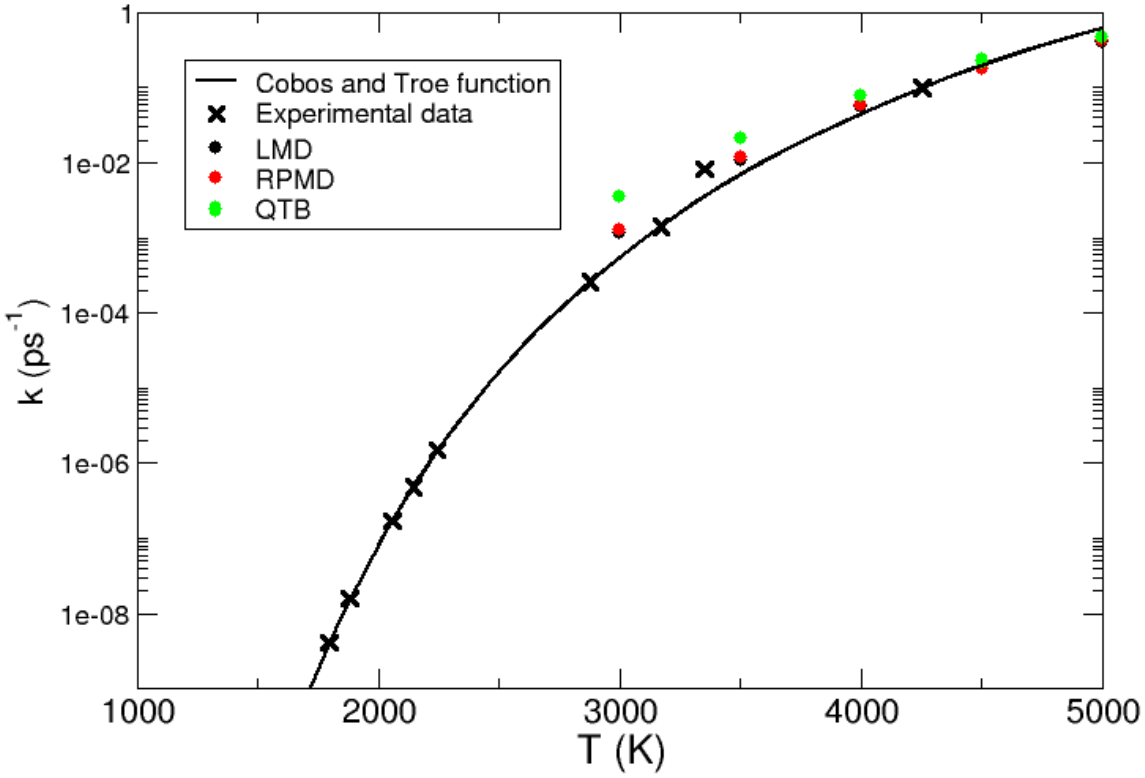

Figure S4: Rate constants for CH_4 fragmentation as obtained from RPMD, QTB and LMD simulations compared with experimental data and fitted functions as reported by Cobos and Troe.[2,3]

References

(1) Ceriotti, M.; Parrinello, M.; Markland, T. E.; Manolopoulos, D. E. Efficient stochastic thermostatting of path integral molecular dynamics. *J. Chem. Phys.* **2010**, *133*, 124104.

(2) Cobos, C. J.; Troe, J. The Dissociation-Recombination System CH4 + M → CH3 + H + M: Reevaluated Experiments from 300 to 3000 K. *Z. Phys. Chem. (N. F.)* **1990**, *167*, 129–149.

(3) Cobos, C. J.; Troe, J. The Dissociation-Recombination System CH4+ M → CH3 + H + M: II. Evaluation of Experiments up to 5000 K and Temperature Dependence of ¡E¿. *Z. Phys. Chem. (N. F.)* **1992**, *176*, 161–171.