

Supplementary Information

A Bath Model to Simulate Association Followed by Ensuing Dissociation Dynamics of Benzene + Benzene System: A Comparative Study of Gas and Condensed Phase Results

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Discussion on Potential Energy

The total potential energy function for $C_6H_6 - C_6H_6 + N_2$ system as discussed in the manuscript can simply be expressed as

$$V = V_{C_6H_6} + V_{N_2} + V_{C_6H_6 - C_6H_6} + V_{N_2 - C_6H_6} + V_{N_2 - N_2} \quad (S1)$$

1. $C_6H_6 - C_6H_6$ Potential

The potential energy of $C_6H_6 - C_6H_6$ is taken from OPLS-AA model in which the two-body potential is represented as

$$V_{ij} = \sum_i \sum_j \frac{q_i q_j e^2}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^6} \quad (S2)$$

Where $A_{ii} = 4\varepsilon_i\sigma_i^{12}$ and $C_{ii} = 4\varepsilon_i\sigma_i^6$. ε and σ are the Lennard-Jones parameters. The combination rules are utilized for the inter-particle parameters, i.e., $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$. The OPLS-AA values for C_6H_6 are $\varepsilon_C = 0.07$ kcal/mol, $\sigma_C = 3.55$ Å, $q_C = -0.115$, $\varepsilon_H = 0.03$ kcal/mol, $\sigma_H = 2.42$ Å, $q_H = +0.115$.

2. N₂-C₆H₆ Potential

The two-body potential energy for N₂-C₆H₆ system is expressed by a modified Buckingham function as

$$V(r) = A \exp(-Br) + \frac{C}{r^n} + \frac{D}{r^m} \quad (S3)$$

The parameters A , B , C , n , D , and m for the C–N interactions are 21476.80 kcal/mol, 3.229249 Å⁻¹, -1411.447 kcal Åⁿ/mol, 7, 13298.14 kcal Å^m/mol, and 10, respectively, whereas, for H–N interactions, they are 18694.06 kcal/mol, 3.705687 Å⁻¹, -2591.526 kcal Åⁿ/mol, 8, 4584.946 kcal Å^m/mol, and 11, respectively.

3. N₂-N₂ Potential

The intermolecular two-body interaction between N₂-N₂ is expressed by modified Buckingham equation with some shifted term added as follows.

$$V(r) = A \exp(-B(r+b)) + \frac{C}{(r+c)^n} + \frac{D}{(r+d)^m} \quad (S4)$$

The values of the parameters A , B , b , C , c , n , D , d , and m are 13454.28 kcal/mol, 4.514701 Å⁻¹, 0.02306411 Å, -214.8792 kcal Åⁿ/mol, -0.5683582 Å, 6, 11305.30 kcal Å^m/mol, -0.2905575 Å, and 9, respectively.

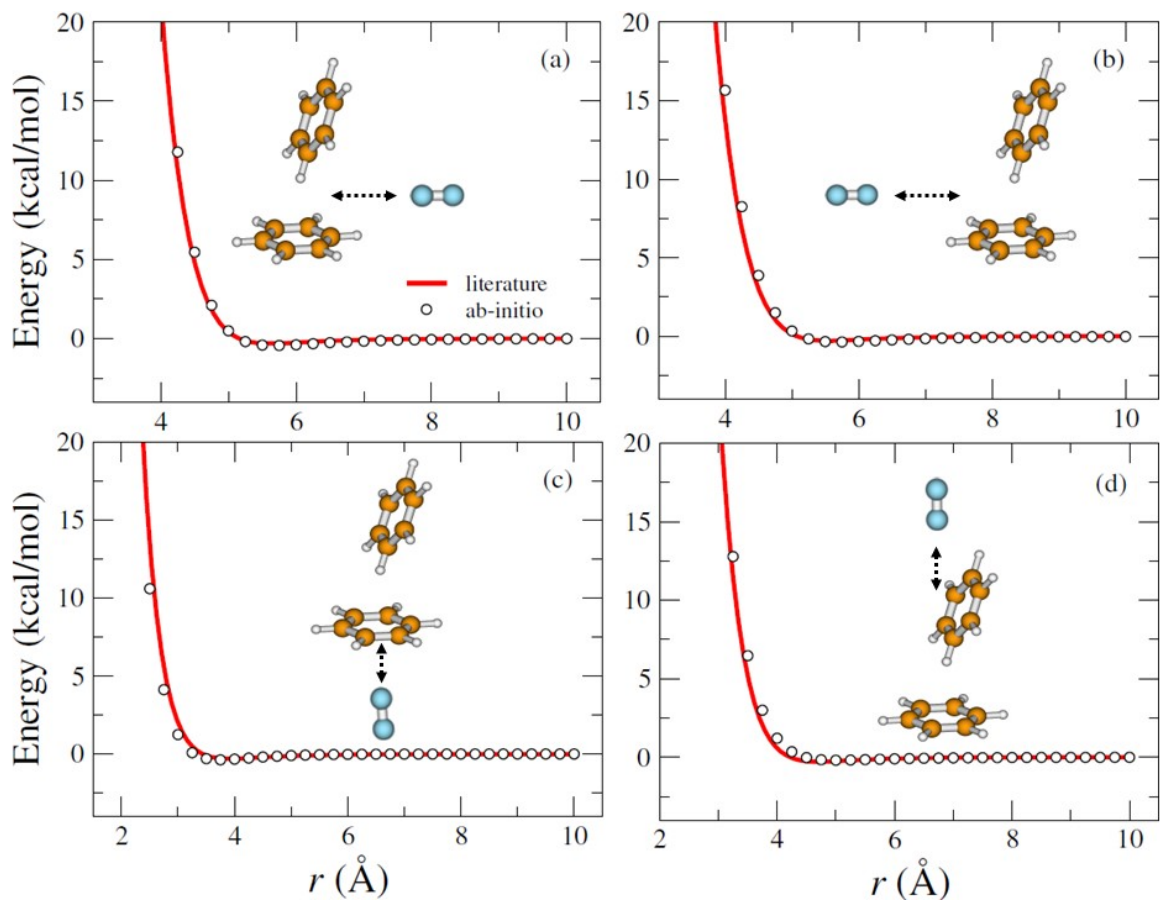


Fig. S1 Intermolecular potential energies of $N_2/(C_6H_6)_2$ for four different orientations. The ab-initio points are calculated by MP2/6-311++G** level of theory. The solid red lines are obtained from the C-N and H-N parameters used in the present simulation.

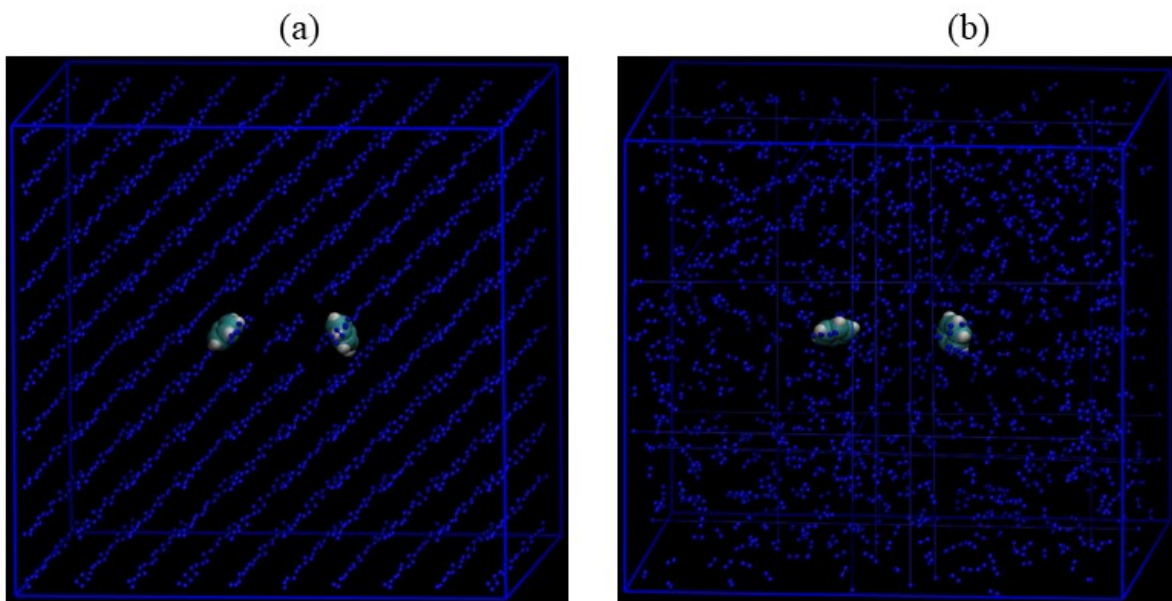


Fig. S2. Bath model of $C_6H_6 + C_6H_6 + 1000 N_2$ is shown right after preparation (a), and after equilibration (b).

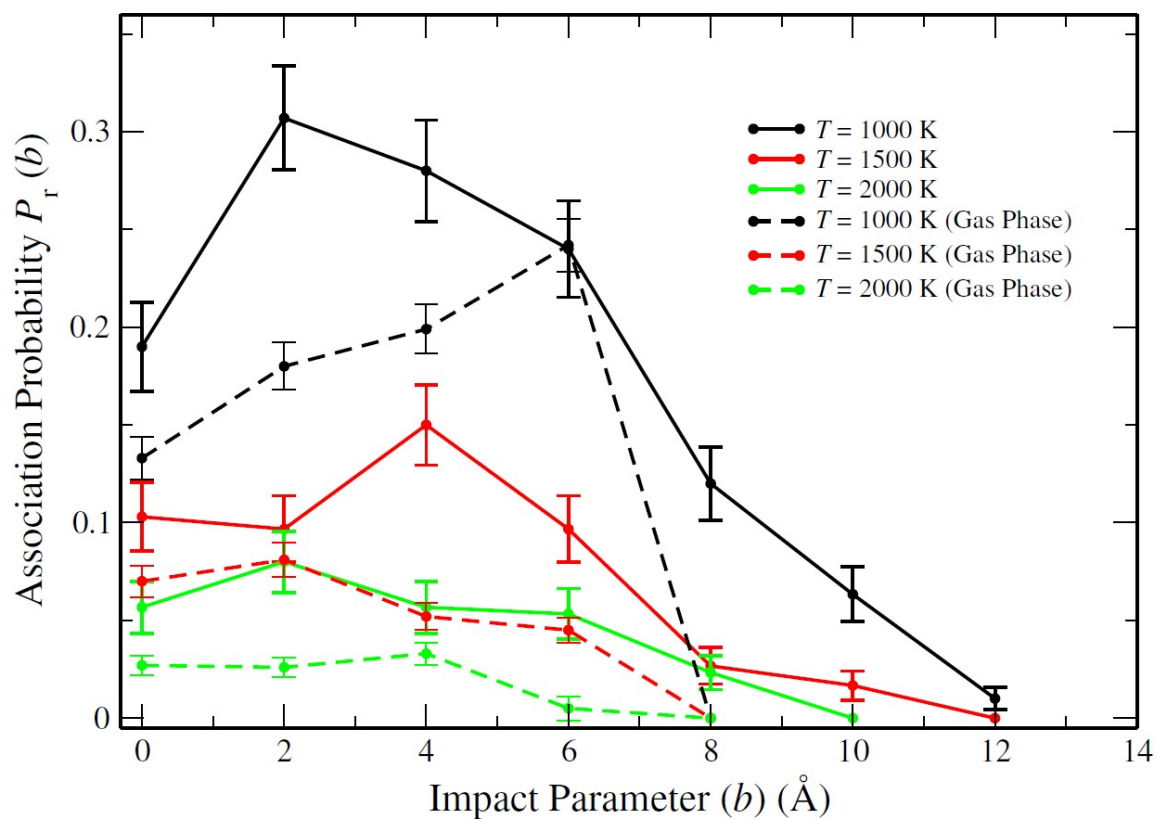


Fig. S3 A comparison between the gas phase and condensed phase association probability versus impact parameter.

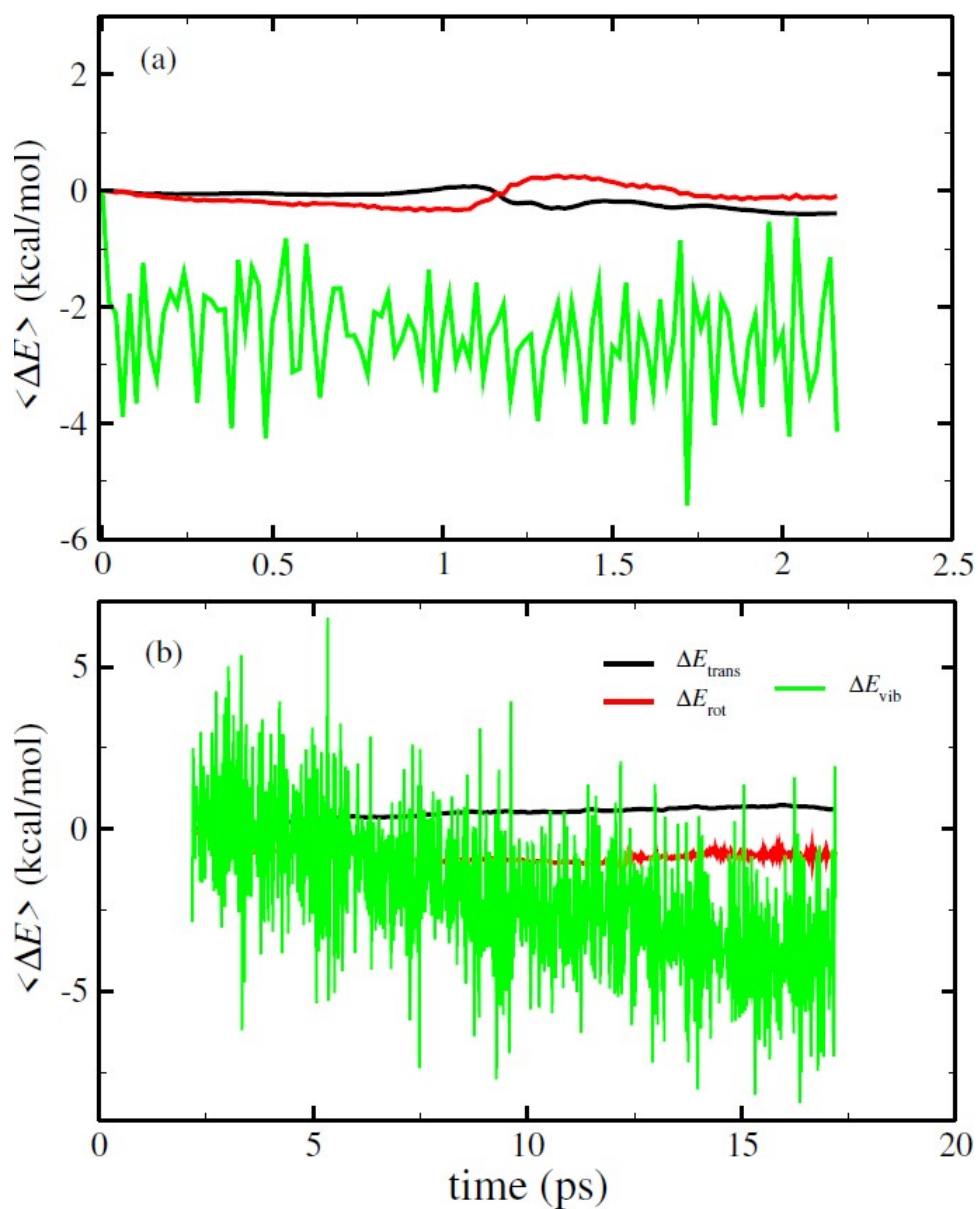


Fig. S4 The change in averaged centre-of-mass translational, rotational and vibrational energies of a benzene molecule with respect to the initial values versus time is presented. In panel (a), the change in energy is presented from the initial time till before the formation of the complex, whereas, in panel (b), the calculation is performed from the time of formation of the complex till when the complex last. The result is at 1500 K and $b = 4 \text{ \AA}$.

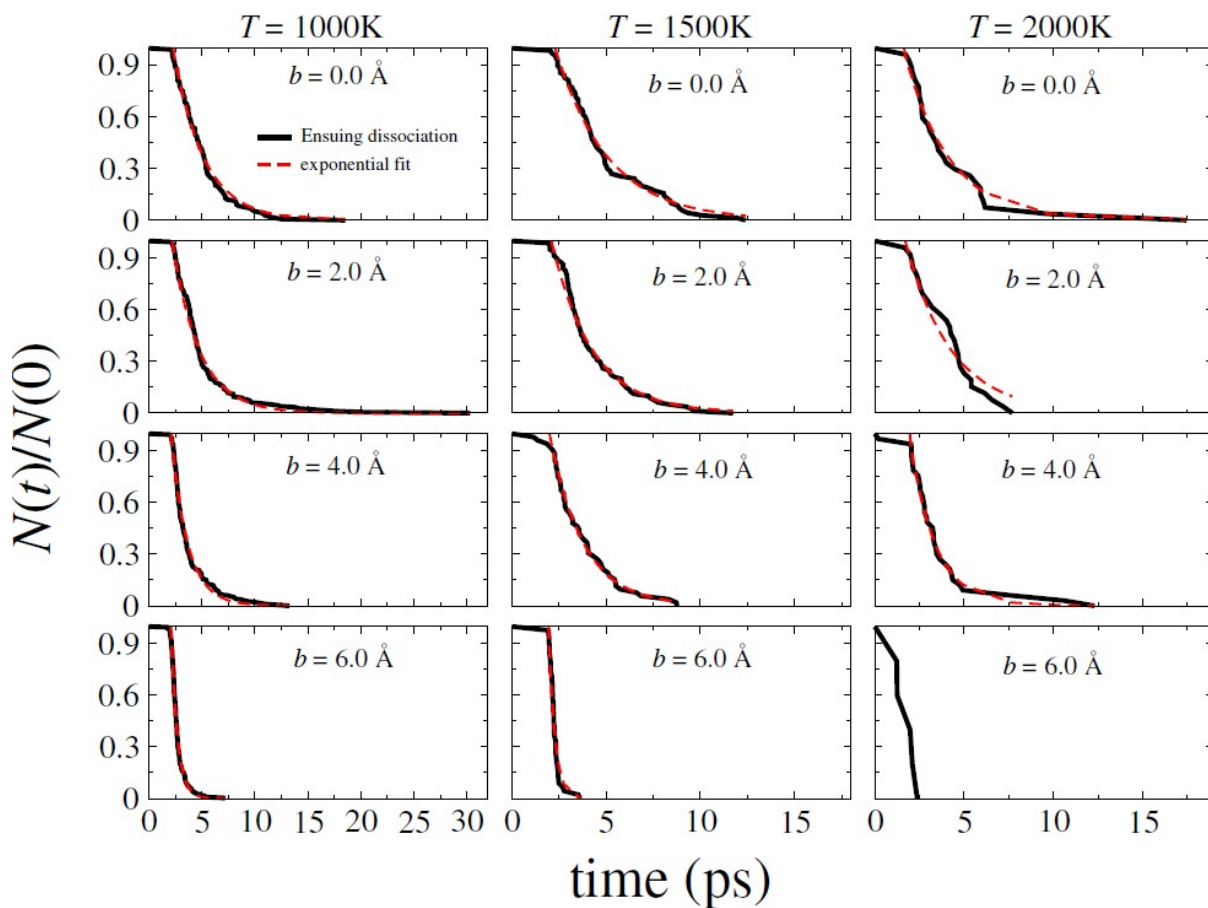


Fig. S5 Plot of $N(t)/N(0)$ versus time for the ensuing dissociation and a fit to the Eq. (5) for $b = 0, 2, 4, 6\text{ \AA}$ at 1000, 1500, and 2000 K in gas phase.

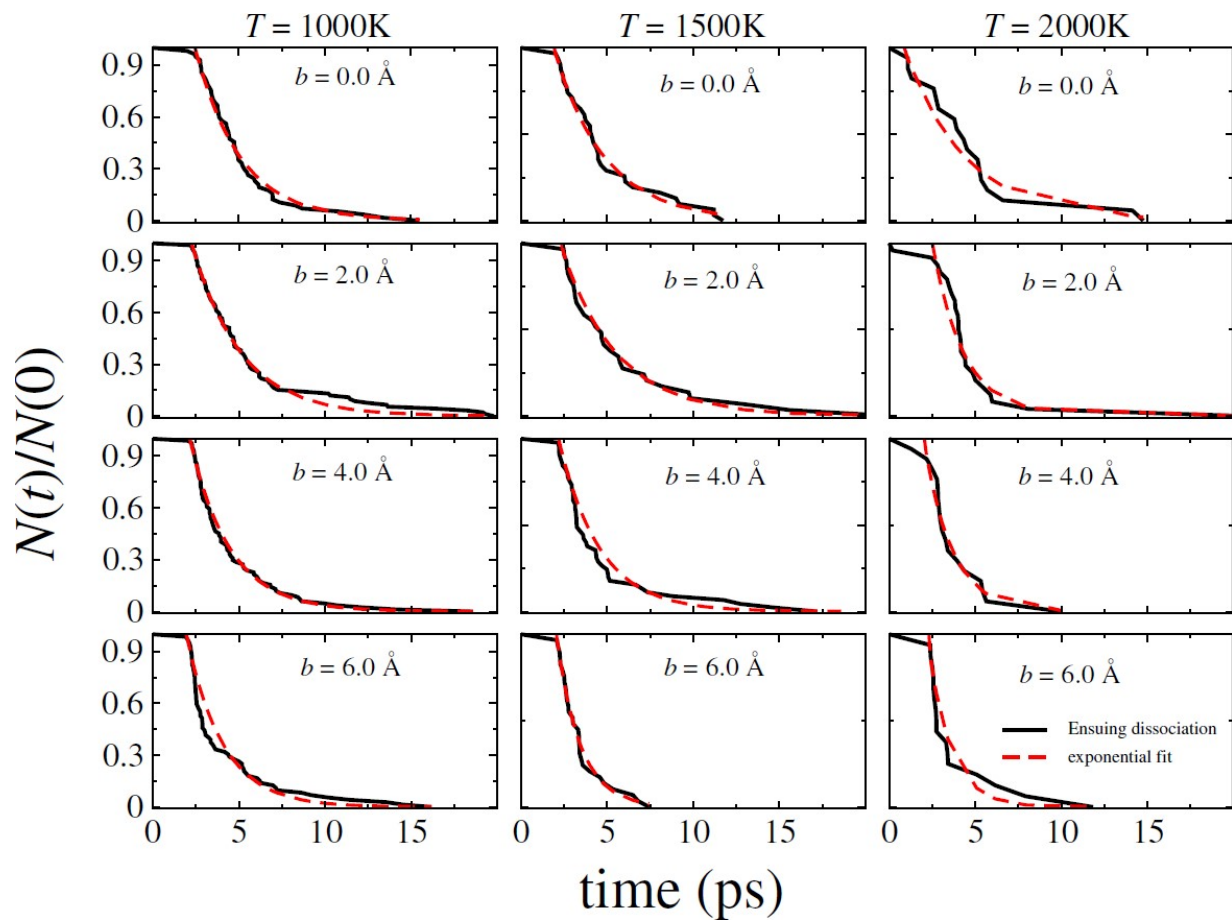


Fig. S6 Plot of $N(t)/N(0)$ versus time for the ensuing dissociation and a fit to the Eq. (5) for $b = 0, 2, 4, 6 \text{ \AA}$ at 1000, 1500, and 2000 K in 20 kg/m^3 bath density.

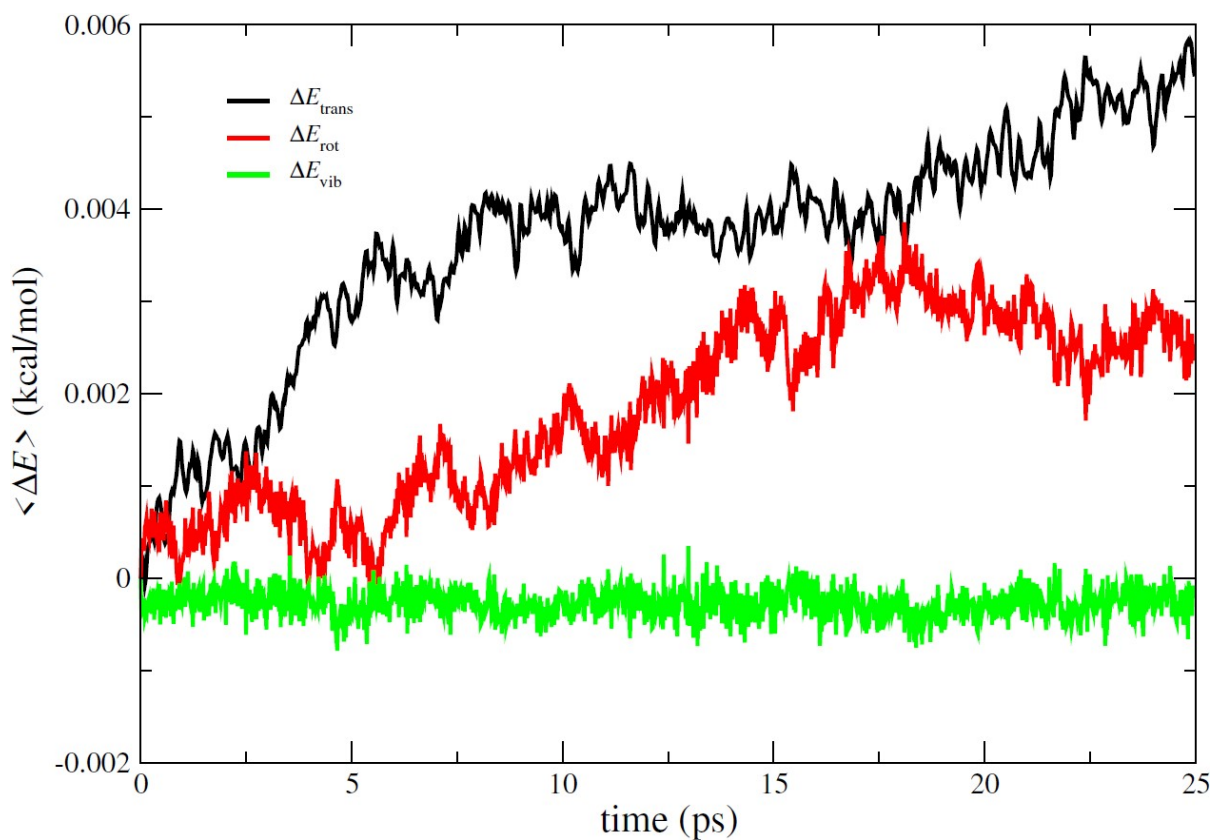


Fig. S7 The change in average centre-of-mass translational, rotational, and vibrational energy of N_2 with time. The calculation is done at 1500 K and with $b = 4 \text{ \AA}$.

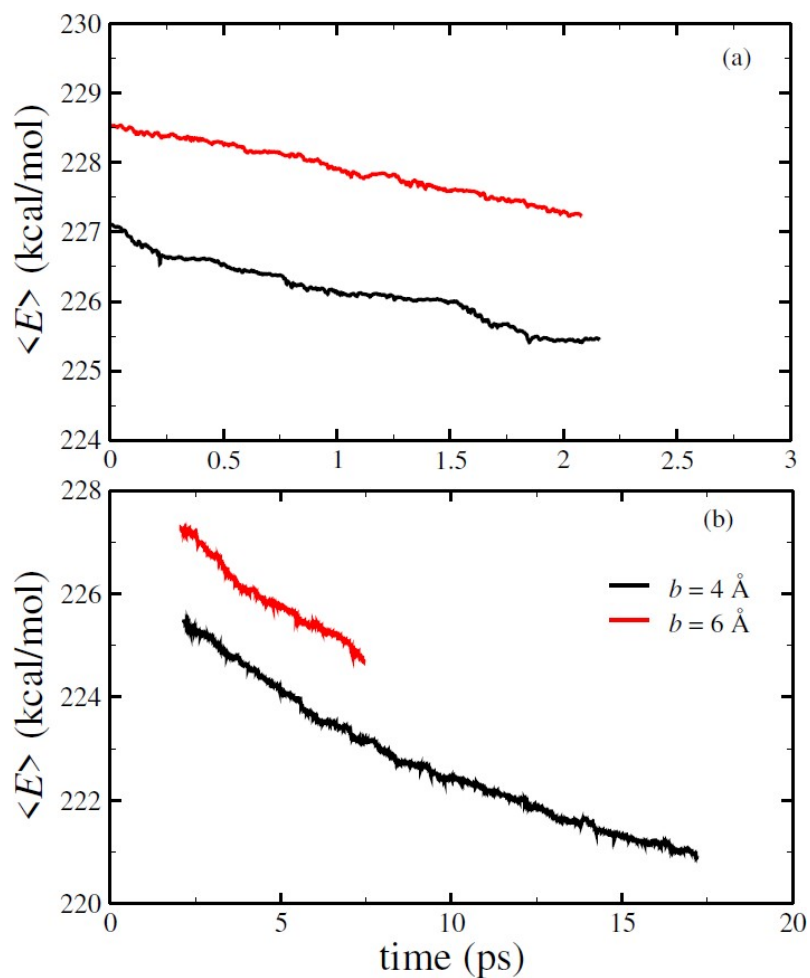


Fig. S8 Average total energy of the benzene molecules before complex formation (panel a) and during complex is presented at $b = 4$ and 6 \AA . Both the results are from 1500 K temperature and 20 kg/m^3 bath density.

Fitting Uncertainties

Table S1 The uncertainties for both the gas and condensed phase ensuing dissociation rate constant.^a

Impact Parameter \AA	Gas Phase			Condensed Phase		
	1000 K	1500 K	2000 K	1000 K	1500 K	2000 K
0	0.030	0.035	0.039	0.032	0.034	0.079
2	0.037	0.047	0.063	0.022	0.038	0.091
4	0.032	0.070	0.032	0.031	0.049	0.056
6	0.079	0.057	--	0.088	0.032	0.108

a. The unit of rate constant is in ps^{-1} .