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Supporting Information

Comparison of Intermolecular Energy Transfer from Vibrationally Excited Benzene in Mixed Nitrogen-Benzene Baths at 140 and 300 K

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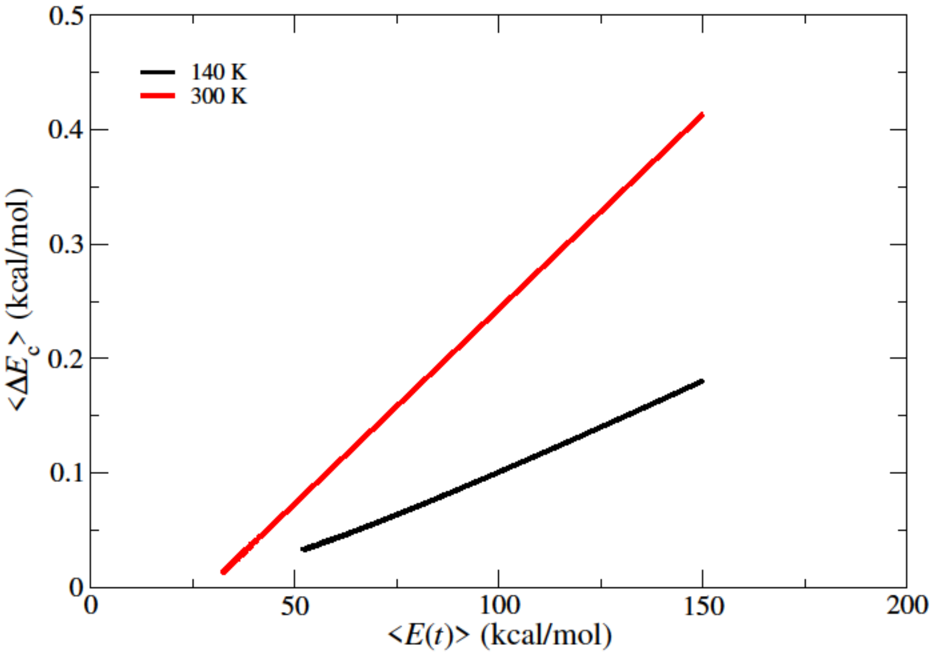

FIG. S1: Average energy transfer per collision for the bath with 396 N_2 and 3 Bz (red) at 140 K, and for 190 N_2 + 9 Bz (black) at 300 K. The latter curve is obtained from ref. 6

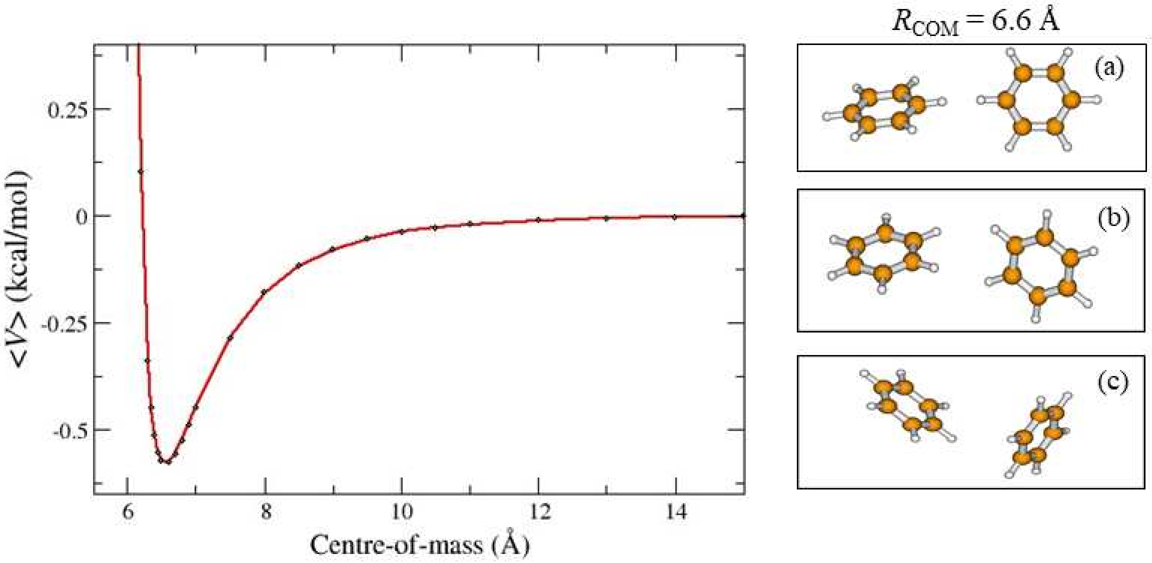

FIG. S2: Orientation averaged benzene−benzene (Bz−Bz) intermolecular potential versus the Bz−Bz center-of-mass separation. Panels a, b, and c are three orientations at the center-of-mass distance (R_{COM}) of 6.6 Å for which the potential energy values are 6.51, -1.04, and -0.302 kcal/mol, respectively.

Discussion:

The panel (a), (b), and (c) represents the Bz-Bz interactions with high, low, and intermediate potential energy and their corresponding energies are 6.51, -1.04, and -0.302 kcal/mol, respectively. In (a) one of the hydrogens from both Bz comes very close (1.71 Å) to each other and faces significant repulsive forces resulting this high potential value. In (b), such very close head to head approach of hydrogen is missing and the plane of one benzene is oriented towards the middle of the C-C bond of other perpendicularly placed Bz. Such an orientation makes the repulsive forces very less in one hand and also, there is some electrostatic attraction which makes the interaction attractive in nature. Finally, in (c), the benzene dimer is slightly tilted T shaped structure which is the most favorable interaction of benzene dimer at 4.93 Å distance. The distance here is 6.60 Å and the interaction potential energy is not so attractive.

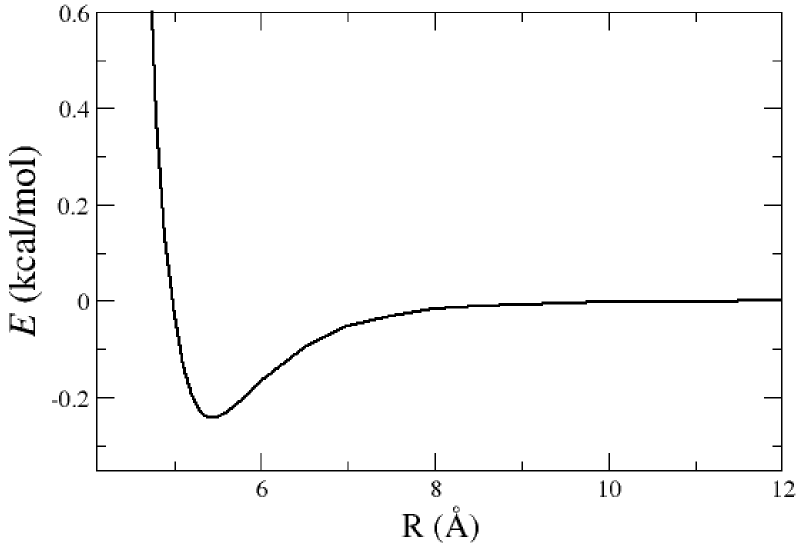

FIG. S3. Orientation averaged benzene−nitrogen (Bz−N_2) intermolecular potential versus the Bz−N_2 center-of-mass separation.

Additional Discussion of Potential Reasons for Differences Between Experiment and Simulations at 140 K

While the 140 K simulation shows the same qualitative increase in Bz* IET at low temperature as observed in 300 K and 140 K experiments, there are a number of other experimental potential sources of error which may help to explain why a more quantitative agreement was not achieved and why initial values of $<\Delta E_c>_{Bz*}$ differ by a factor of ~14 between experiments and simulations at 140 K. One possible source of error is the [Bz] which was achieved in low temperature experiments. If a larger vapor pressure of Bz was achieved than was calculated in the experiments, then this could account for the more efficient IET as well as the approximately four times larger temperature rise of the experimental bath N_2 rotational temperature than was obtained from simulations. However, IET efficiency in 300 K experiments and simulations were in agreement, so it is unlikely that the method of producing reliable [Bz] in experiments was the cause of the difference between 140 K experiments and simulations. Another experimental factor that could have affected the IET is an error in [Bz*]. Since it was not possible to know how much of the 193 nm laser light was absorbed in the vacuum chamber around the low temperature flow before the laser light reached the measurement location, only an estimate of the 193 nm light intensity was used to estimate the fraction of Bz* generated. Additionally, the 300 K absorption cross section was used to estimate the absorption of 193 nm light to generate Bz* and the absorption cross section is likely to be somewhat different at 140 K than at 300 K, possibly leading to error in the estimated [Bz*] in 140 K experiments. If there was actually a higher [Bz*] than anticipated then this could help to explain the increased final temperature observed in experiments, but if there was a lower [Bz*] then there would be a larger [Bz] and consequently more efficient overall IET through increased Bz*-Bz IET. For example, if the absorption cross section of Bz at 193 nm was three times larger at 140 K relative to 300 K, then the fractional absorption of Bz would almost three times larger as well leading to ~3 times the [Bz*] and somewhat less [Bz]. This could account for the difference in the final rotational temperatures of the experimental and simulated N_2 bath molecules, but would also lead to less efficient overall IET due to less Bz*-Bz IET. Another experimental factor to consider is if there were any multi-photon effects, then either reactions or even more highly vibrationally excited benzene, Bz**, could have yielded much higher IET. However, the low intensity of 193 nm light utilized and the additional absorption of the 193 nm light in the vacuum chamber around the cold flow make it unlikely that the 193 nm light had a large enough intensity to cause multi-photon effects. A final possible source of error is if collisionally stabilized Bz dimers absorbed 193 nm light significantly differently than the Bz monomers. However, the estimated negligible concentration of collisionally stabilized dimers makes it unlikely that there were a significant number of these collisionally stabilized dimers to absorb a significant amount of the light.

One assumption in the experimental work that may need to be examined more closely in the future is whether NO behaves sufficiently like the bath N_2 molecules at low temperatures such that NO can still act as a proxy for determining N_2 IET properties. If Bz*-NO IET at 140 K was more than about a factor of 100 more efficient than Bz*-N_2 IET, then the 1% NO could have caused Bz*-NO to compete with Bz*-N_2 and Bz*-Bz IET much more than anticipated. This would have resulted in both the more efficient overall Bz* IET as well as more IET to the NO/N_2 bath rotation than to the bath Bz vibration. It is possible that Bz*-NO interactions at low temperature (such as dipole-quadrupole or dipole-induced-dipole interactions) could be significantly larger than Bz*-N_2 interactions, and could have produced this increase in Bz*-NO IET efficiency at 140 K. Previously the IET from a similar collision pair, pyrazine*-NO, was found to have a $<\Delta E_\mathrm{d}>$ ~1.8 times that of pyrazine*-N_2 collisions at 300 K.[1] However, if Bz*-NO IET is similar to the above systems and if the Bz*-NO IET becomes even more efficient that Bz*-N_2 IET at low temperatures, then this could help to explain why our simulations and experiments are in quantitative agreement at 300 K and only qualitative agreement at 140 K. Another assumption that may need to be re-examined is if it is possible that quenching of electronically excited benzene states by NO occurs much more rapidly at low temperatures leading to significant changes in overall IET efficiency.[2] Increased quenching of electronically excited Bz by NO would have allowed for more efficient IET to NO and could help to bring the simulations and experiments into closer agreement.

Overall, one of the limitations of the experiments here is that they only examined one mode of the bath over the limited time scale of the possible cold flow achieved from the Laval instrument. Therefore, if there were any IET energy sinks or longer time scale processes, then they would not have been revealed by these experiments. Furthermore, the initial assumption that all of the energy of Bz* has re-equilibrated on the time scale of the experiments may be incorrect. As the simulations have now revealed, even Bz-Bz* IET was larger at 140 K than initial estimates utilized from simulations at 200 K, implying that the bath Bz vibration is out of equilibrium with the bath N_2 rotation and translation at the end of the simulations and would likely lead to a smaller long-time scale re-equilibration tail in experiments.

Along with possible experimental sources of error, it is worth examining if any sources of error in the simulations can resolve quantitative differences between experiments and simulation at 140 K. The possible sources of error in the simulation could be from intermolecular potential energy parameters and trajectory initial conditions. It was shown previously that the IET dynamics in the bath model used here is not too sensitive for the fine change in the potential energy parameters.[3,4] As mentioned in Section II, there are three intermolecular potential energies used in the simulation. N_2/N_2 and N_2/C_6H_6 potential energy parameters were developed and described in detail previously.[3,5] The ab initio energy points for N_2/N_2 interactions were calculated with MP2/aug-cc-pVTZ level. The calculated energy points were comparable with the same in complete basis set (CBS) limit.[3] N_2/C_6H_6 potential energy parameters were obtained based on SCS-MP2/6-311++G** level of calculations.[5] Hence, both the potential energies are accurate enough such that difference in the IET parameters derived from these simulations and those of the experiments could not be explained by the relatively small error in the potentials. Moreover, C_6H_6/C_6H_6 OPLS-AA potential energy parameters provide Bz-Bz equilibrium geometry and energy in excellent agreement with the CCSD(T)/CBS level of calculation.[6,7] Therefore, the error associated with the potential energy parameters is likely negligible. On the other hand, instead of classical sampling, quasiclassical microcanonical sampling, which is expected to be more accurate, could have been used to choose the initial condition of Bz*. However, based on previous studies, one can predict that the curve of $<\Delta E_c>$ values would be of a similar magnitude, but of a slightly different shape.[4] Therefore, the classical simulations performed here were sufficient for comparison of the overall number of collisions required for rethermalization processes between simulation and experiment. Therefore, based on the above discussions and the comparability of the current results with the previous Bz*-Bz IET dynamics,[8] there may not be much error in the simulation results other than the statistical uncertainties. However, as one can see from Fig. 8, the $<\Delta E_c>$ versus $<E(t)>$ curve from simulation is almost linear and different from the one from experiment. If a multi-exponential or stretched exponential function was required to fit $<E(t)>$, the resulted $<\Delta E_c>$ versus $<E(t)>$ would not have been linear. Such a requirement has not been seen in the current simulations.

It may also be interesting to know how much the value of $<\Delta E_c>_{Bz*}$ would have been increased if the percentage of Bz-Bz complexes was increased or the lifetime of those complexes were longer. Out of the total 39 trajectories, two smaller ensembles were formed with a larger and smaller percentage of complexes, respectively. For the ensemble with more complex forming trajectories, there were 15 trajectories and 28% of the time complexes were formed in those trajectories. For the other ensemble with 24 trajectories, this was only 15%.

The $<\Delta E_c>_{Bz^*}$ was 1.2 times larger at $<E(t)>_{Bz^*}$ of 150 kcal/mol for the ensemble with more complex formation than the one obtained from the overall ensemble of 39 trajectories. A separate but similar analysis was also performed where two smaller ensembles were formed with trajectories having longer and shorter lifetime of the complexes, respectively. There were 20 trajectories in the ensemble where the lifetime of any of the Bz-Bz complexes was 50 ps (100 times the 0.5 ps dimer vibrational period) or more. The other 19 trajectories formed the second ensemble. In this analysis the $<\Delta E_c>_{Bz^*}$ was seen 1.4 times larger at $<E(t)>_{Bz^*}$ of 150 kcal/mol for the ensemble with longer complex lifetimes than that from the overall ensemble. Thus, while both the percentage and lifetime of the Bz-Bz complexes have a direct influence on IET, the latter resulted in more efficient IET than the former. Interestingly, for all these smaller ensembles in both the analyses, the averaged N_2 rotational temperature versus time remains almost same as that of the total ensemble of 39 trajectories. In Fig. S4, the profiles of $<E(t)>_{Bz^*}$ versus t are shown for both the analysis mentioned above along with the same curve obtained from overall ensemble of 39 trajectories (i.e., the curve presented in Fig. 3 of the manuscript) for comparison. Fig. S5 presents $<\Delta E_c>_{Bz^*}$ versus $<E(t)>_{Bz^*}$ for all the corresponding curves given in Fig. S4.

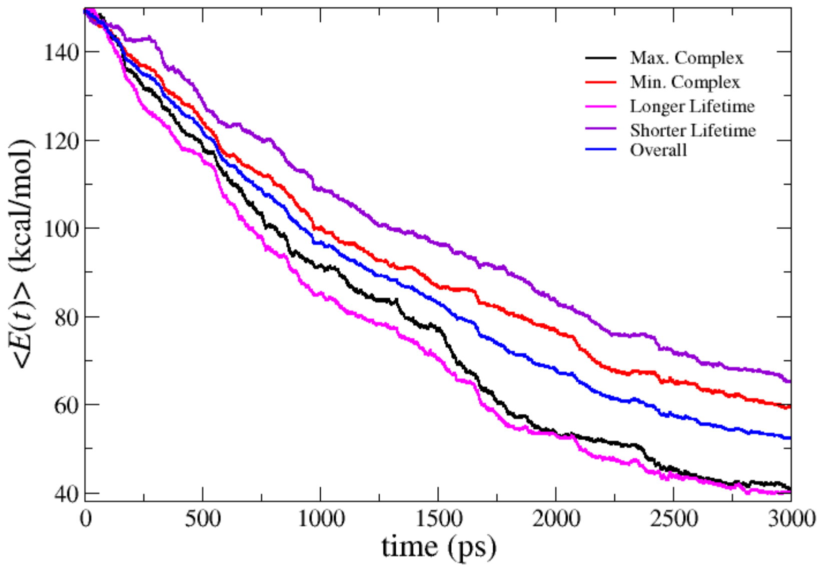

FIG. S4. Average total energy of Bz* <$E(t)$>$_{\mathrm{Bz}^*}$ versus time for the ensembles with, 1. maximum time complex formation (black), 2. minimum time complex formation (red), 3. Any of the Bz-Bz complexes having lifetime 50 ps or more, 4. Complexes having lifetime less than 50 ps, and 5. all 39 trajectories.

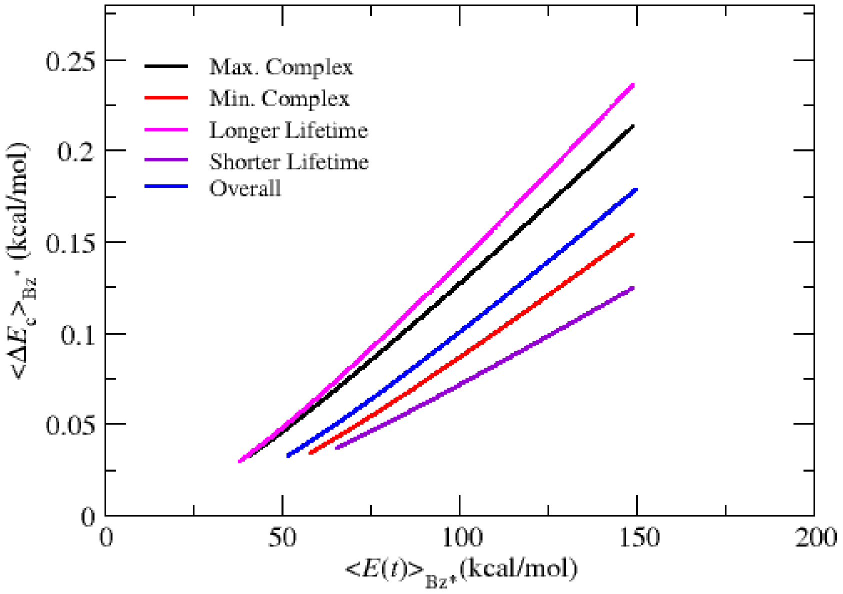

FIG. S5. <ΔE_c>$_{\mathrm{Bz}^*}$ versus <$E(t)$>$_{\mathrm{Bz}^*}$ for all the ensembles presented in Fig. S3.

It is important to note here that the intramolecular vibrational energy redistribution (IVR) for Bz dimer is restricted due to weak coupling between the intramolecular (monomer) and intermolecular (formed by the association of Bz + Bz) vibrational modes.[7] Even with high total vibrational energy, some of the Bz dimers can have sufficient lifetime, which could have some effect on the overall IET in the simulation.

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