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Amit K. Paul, Niclas A. West (iD), Joshua D. Winner, Rodney D. W. Bowersox (iD), Simon W. North, and William L. Hase (iD)

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Non-statistical intermolecular energy transfer from vibrationally excited benzene in a mixed nitrogen-benzene bath

Amit K. Paul,[1,2] Niclas A. West,[3] Joshua D. Winner,[3] Rodney D. W. Bowersox,[3] Simon W. North,[3] and William L. Hase[1,a)]

[1]*Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, USA*
[2]*Department of Chemistry, National Institute of Technology Meghalaya, Shillong 793003, India*
[3]*Department of Chemistry, Texas A&M University, College Station, Texas 77842, USA*

A chemical dynamics simulation was performed to model experiments [N. A. West *et al.*, J. Chem. Phys. **145**, 014308 (2016)] in which benzene molecules are vibrationally excited to 148.1 kcal/mol within a N_2-benzene bath. A significant fraction of the benzene molecules are excited, resulting in heating of the bath, which is accurately represented by the simulation. The interesting finding from the simulations is the non-statistical collisional energy transfer from the vibrationally excited benzene $C_6H_6{}^*$ molecules to the bath. The simulations find that at $\sim 10^{-7}$ s and 1 atm pressure there are four different final temperatures for $C_6H_6{}^*$ and the bath. N_2 vibration is not excited and remains at the original bath temperature of 300 K. Rotation and translation degrees of freedom of both N_2 and C_6H_6 in the bath are excited to a final temperature of ~ 340 K. Energy transfer from the excited $C_6H_6{}^*$ molecules is more efficient to vibration of the C_6H_6 bath than its rotation and translation degrees of freedom, and the final vibrational temperature of the C_6H_6 bath is ~ 453 K, if the average energy of each C_6H_6 vibration mode is assumed to be RT. There is no vibrational equilibration between $C_6H_6{}^*$ and the C_6H_6 bath molecules. When the simulations are terminated, the vibrational temperatures of the $C_6H_6{}^*$ and C_6H_6 bath molecules are ~ 537 K and ~ 453 K, respectively. An important question is the time scale for complete energy equilibration of the $C_6H_6{}^*$ and N_2 and C_6H_6 bath system. At 1 atm and 300 K, the experimental V-T (vibration-translation) relaxation time for N_2 is $\sim 10^{-4}$ s. The simulation time was too short for equilibrium to be attained, and the time for complete equilibration of $C_6H_6{}^*$ vibration with translation, rotation, and vibration of the bath was not determined. *Published by AIP Publishing.* https://doi.org/10.1063/1.5043139

I. INTRODUCTION

Understanding intermolecular energy transfer is important for numerous chemical processes, including atmospheric and combustion chemistry and chemical reactions in solution.[1–4] These dynamics are widely investigated by studying the efficiency of energy transfer from a vibrationally excited molecule to a much colder atomic or molecular bath. The parameter often determined is the average energy transfer $\langle \Delta E_c \rangle$ per collision of the excited molecule to the bath molecules.[5] Also of interest, e.g., for understanding turbulence,[6,7] is the relative importance of energy transfer to particular translational, rotational, and vibrational degrees of freedom of the bath. Time scales for energy transfer are important for understanding turbulence. The time scale for energy transfer to molecular vibrational modes may determine whether molecular energy transfer is able to couple with acoustic modes that cause turbulence to occur in hypersonic boundary layers.[7–9] There have been several experimental studies of such dynamics, in which pathways for transfer of energy to bath molecules CO_2,[10,11] H_2O,[12–16] HOD,[17–19] and DCl[20] were investigated.

The statistical model for energy transfer to the bath is that all the degrees of freedom have equivalent probabilities for receiving energy, given angular momentum and center of mass translation constraints. This is also known as the phase space theory (PST) model[21,22] for product energy partitioning in chemical reactions. Different statistical models have been proposed for intermolecular energy transfer, each with specific assumptions regarding the degrees of freedom involved.[23,24] It is often assumed that an intermediate needs to be formed between the excited and bath molecules, for a statistical model to be appropriate. However, simulations of energy transfer in collisions with organic surfaces have shown that statistical-like intermolecular energy transfer may occur with direct collisions and without formation of a collision intermediate.[25,26]

In recent work, a unified protocol for simulating liquid and gas phase intermolecular energy transfer was developed[27] and applied to both vibrationally excited C_6F_6 and azulene in a N_2 bath,[27–29] vibrationally excited propyl benzene cation in a helium bath,[30] and cold C_6F_6 in a warmer N_2 bath.[31] Here, this simulation method is used to model intermolecular energy from vibrationally excited benzene to compare with experiments in which a fraction of benzene molecules are excited within a N_2-benzene bath.

a)Author to whom correspondence should be addressed: bill.hase@ttu.edu

II. EXPERIMENTS AND SIMULATION METHOD

The experimental procedure for the experiments modeled here has been described in detail previously.[32] Laser excitation at 193 nm, i.e., 148.1 kcal/mol, is used to excite benzene molecules in the bath by a $S_0 \rightarrow S_2$ transition. S_2 then undergoes rapid internal conversion to form the vibrationally excited ground state $S_0{}^*$, with small amounts of intersystem crossing (5%) and fluorescence (2%).[33] Benzene formed in the S_2 state, by this laser excitation, has a lifetime of ~40 fs for internal conversion to $S_1{}^*$ and $S_0{}^*$. Internal conversion of the resulting vibrationally excited $S_1{}^*$ states to $S_0{}^*$ occurred within 5-10 ps.[33]

Temperature changes for the N_2-benzene bath depend on the fraction of C_6H_6 molecules excited by the laser excitation and the percentage of C_6H_6 molecules in the bath. The N_2 rotational temperature is probed by adding a small fraction of NO to the bath and using laser induced fluorescence to determine the NO rotational energy level populations. Energy transfer probabilities from $C_6H_6{}^*$ to N_2 and NO rotation are expected to be very similar so that the NO rotational temperature represents that for N_2. Here $C_6H_6{}^*$ is a laser excited benzene molecule with 148.1 kcal/mol of vibration energy and 300 K translation and rotation energies.

N_2/N_2, C_6H_6/C_6H_6, and N_2/C_6H_6 intermolecular potentials are required for the simulations. The potentials are written as sums of 2-body potentials. The N_2/N_2 potential used for the simulations was described previously.[27] The C_6H_6/C_6H_6 intermolecular potential is represented by the Optimized Potentials for Liquid Simulations (OPLS) model.[34] The OPLS global minimum for the benzene dimer has a T-shaped geometry with a binding energy of 2.32 kcal/mol,[35] whereas a recent CCSD(T)/CBS calculation predicts a similar geometry and a binding energy of 2.84 kcal/mol.[36] An experimental study gives ~2.9 kcal/mol.[37] The OPLS potential gives an overall good description of the benzene-benzene interaction. The N_2/C_6H_6 2-body potentials are written as

$$V(r) = A \, \exp(-Br) + C/r^n + D/r^m. \qquad (1)$$

The values of the parameters A, B, C, D, n, and m for the N_2/C_6H_6 C–N and H–N interactions were assumed to be the same as those for the azulene + N_2 SCS-MP2 potential[29] and are, respectively, 21 476.80 kcal/mol, 3.229 249 Å^{-1}, −1411.447 kcal Å^n/mol, 13 298.14 kcal Å^m/mol, 7, and 10 for the C–N interactions and 18 694.06 kcal/mol, 3.705 687 Å^{-1}, −2591.526 kcal Å^n/mol, 4584.946 kcal Å^m/mol, 8, and 11 for the H–N interactions.

The simulation reported here was performed to model experiments in which C_6H_6 constitutes 5% of the bath and 10% of the C_6H_6 molecules are excited. Since C_6H_6 is an appreciable component of the bath and a significant fraction of C_6H_6 is excited, there is appreciable heating of the bath in the experiments. To represent these experiments, a simulation model was used in which the bath consists of 190 N_2 and 10 C_6H_6 molecules, with 1 C_6H_6 molecule vibrationally excited. To achieve the binary/single collision limit for comparison with experiments, the bath density was chosen as 40 kg/m^3 or 32.5 atm which was found to be the binary/single collision limiting density for C_6F_6 + N_2 simulations.[27,28] For the smaller C_6H_6 molecule as compared to C_6F_6 and a very small percentage of C_6H_6 in the bath, the binary/single collision limiting density is expected to be achieved at 40 kg/m^3 or higher density. Performing the simulations in the binary/single collision limit allows extrapolation of the simulation results to lower densities/pressures.

The simulations were performed with the same methodology as described for previous intermolecular energy transfer bath simulations.[27–31] A vibrational energy of 148.1 kcal/mol was first added to the one excited $C_6H_6{}^*$ molecule to model the experimental 193 nm laser excitation. This energy was added randomly with classical microcanonical normal mode sampling,[38,39] as implemented in a modified version[27] of the general chemical dynamics computer code VENUS.[40] Translational and rotational energies for 300 K were then added to vibrationally excited $C_6H_6{}^*$. With initial conditions for $C_6H_6{}^*$ chosen, the next step was to equilibrate the bath around $C_6H_6{}^*$ by placing it at the center of the simulation box with its coordinates and momenta fixed. A MD simulation was then performed to thermally equilibrate the 190 N_2 molecules and remaining 9 C_6H_6 molecules of the bath at 300 K, using periodic boundary conditions and nearest neighbor updating to enhance the simulation. At the end of this equilibration, the desired initial 300 K temperature for the vibration, rotation, and center-of-mass translation degrees of freedom of the N_2 and C_6H_6 bath molecules was verified. Initially, the average center-of-mass translation energy for each N_2 and C_6H_6 molecule is $3RT/2 = 0.89$ kcal/mol, the average rotational energy of each N_2 and C_6H_6 molecule is $RT = 0.60$ kcal/mol and $3RT/2 = 0.89$ kcal/mol, respectively, and the average vibration energy of N_2 and each mode of C_6H_6 is $RT = 0.60$ kcal/mol. These are the proper equilibrium average energies, which match the equipartition model. With these random initial conditions for $C_6H_6{}^*$ and the N_2/C_6H_6 bath, a trajectory was then calculated for 2400 ps to study intermolecular energy transfer from $C_6H_6{}^*$ to the bath. To obtain results which could be compared with experiments, averaging was performed by calculating an ensemble of 48 trajectories, with random initial conditions. In a previous similar simulation for N_2 + C_6F_6 intermolecular energy transfer,[27] 48 trajectories gave statistically the same result as found for 96 trajectories. A simulation with only 24 trajectories gave semi-quantitative results.

An important quantity for the system investigated here is its temperature after complete equilibration between its translation, rotation, and vibration degrees of freedom. This may be determined from the system average total energy; in the following, $T = 300$ K. The average initial energies are as follows: $C_6H_6{}^*$, $E_{vib} = 148.1$ kcal/mol and $E_{rot} + E_{trans} = 3RT = 1.8$ kcal/mol; 90 N_2 bath molecules, $E_{vib} = 90RT = 53.6$ kcal/mol and $E_{rot} + E_{trans} = 90 \times 2.5RT = 134.1$ kcal/mol; and 9 C_6H_6 bath molecules, $E_{vib} = 9 \times 30RT = 160.9$ kcal/mol and $E_{rot} + E_{trans} = 9 \times 3RT = 16.1$ kcal/mol. With these initial energies and the total number of degrees of freedom, the temperature for the completely equilibrated system is 402 K. If N_2 vibration remains un-equilibrated at 300 K, but translation and rotation of N_2 and translation, rotation, and vibration of all 10 benzene molecules are equilibrated, their equilibrated temperature is 418 K.

III. SIMULATION RESULTS

The properties determined from the simulation are as follows: (1) the center-of-mass translation and rotational energies of the N_2 and C_6H_6 bath molecules, and the vibrational energies of the C_6H_6 bath molecules and (2) the energy of $C_6H_6^*$ versus time. Plotted versus time in Fig. 1 are the average center-of-mass translation and rotational energies of a N_2 and C_6H_6 molecule and the average energy of N_2 vibration and the average energy of a C_6H_6 vibration mode. Each of the 30 C_6H_6 vibration modes may have a specific average energy, dependent on its frequency and symmetry. However, this was not analyzed for the current simulation, but considered in Sec. IV. Consistent with previous simulations,[27–29] there is negligible energy transfer to N_2 vibration. The center-of-mass translation and rotation energies of the N_2 molecules increase with time, via V → R/T (vibration to rotation and translation) energy transfer. When the trajectories are terminated at 2400 ps, the average center-of-mass translational and rotation energies of N_2 have increased by ∼0.1 and ∼0.07 kcal/mol, respectively. The initial ratio between the N_2 translation and rotation energies is ∼1.5, and with the above increases in these energies, this ratio remained at ∼1.5. Thus, energy transfer to N_2 translation and rotation follows the equipartition principle. At the conclusion of the trajectories, the average N_2 translation-rotation temperature is ∼340 K.

Rotational and translational energy transfer to the C_6H_6 bath molecules is in accord with the above energy transfer to the N_2 bath. Shown in Fig. 1 are the average center-of-mass translation, rotation, and vibration mode energies of a C_6H_6 bath molecule versus time. At the conclusion of the trajectories, the average translation and rotation energies of the molecule are statistically the same as the average N_2 translation energy, with an average C_6H_6 translation-rotation temperature of ∼340 K. However, unlike N_2, there is V → V (vibration to vibration) energy transfer to C_6H_6, which is more important than V → R/T. The energy of each C_6H_6 vibration mode was not determined in the simulation (see

Sec. IV), and if each C_6H_6 vibration mode is assumed to have the same energy, the energy of each C_6H_6 vibration mode increased from an average RT value of ∼0.60 kcal/mol to ∼0.9 kcal/mol for the 9 bath molecules and 48 trajectories. The final energy of the vibration modes corresponds to a temperature of ∼453 K.

The average energy of vibrationally excited $C_6H_6^*$ versus time $\langle E(t) \rangle$ is given in Fig. 2. As found for previous simulations[27–30] and as shown in Fig. 2, $\langle E(t) \rangle$ is well fit by the bi-exponential

$$\langle E(t) \rangle = [E(0) - E(\infty)][f_1 \exp(-k_1 t) + f_2 \exp(-k_2 t)] + E(\infty),$$

(2)

where $f_1 + f_2 = 1$, $E(0)$ and $E(\infty)$ are the initial and final energies of $C_6H_6^*$, and k_1 and k_2 are the rate constants. The values for these fitting parameters are $E(0) = 149.9$ kcal/mol, $E(\infty) = 23.4$ kcal/mol, $f_1 = 0.901$, $f_2 = 0.089$, $k_1 = 0.00133$ ps^{-1}, and $k_2 = 0.000799$ ps^{-1}. At the end of the simulation, the final average energy of the $C_6H_6^*$ molecule is ∼34 kcal/mol. Of this energy, both translation and rotation are ∼1 kcal/mol, corresponding to a temperature of ∼340 K, which is the same as the final translation-rotation temperature of the N_2 and C_6H_6 bath molecules. As discussed above, the temperature is 402 K for fully equilibrated $C_6H_6^*$ with the N_2–C_6H_6 bath. The 402 K total energy of $C_6H_6^*$ is 26.4 kcal/mol and significantly smaller than the final simulation total energy of ∼34 kcal/mol. The final $C_6H_6^*$ vibrational energy of ∼32 kcal/mol corresponds to a temperature of ∼537 K, in contrast to the vibrational temperature of ∼453 K for the C_6H_6 bath. The average total energies of $C_6H_6^*$ and a single C_6H_6 bath molecule versus time are compared in Fig. 3. Given in the supplementary material are the average translation, rotation, and per mode vibration energies of a $C_6H_6^*$ molecule versus time and the average translation and rotation energies of a C_6H_6 bath molecule versus time. There is a short time increase in the rotational energy of the $C_6H_6^*$ molecule, as seen for a previous simulation of $C_6F_6^*$ vibrational relaxation in a N_2 bath.[27]

The average energy transfer per collision $\langle \Delta E_c \rangle$ from $C_6H_6^*$ is found from $\langle E(t) \rangle$ and given by
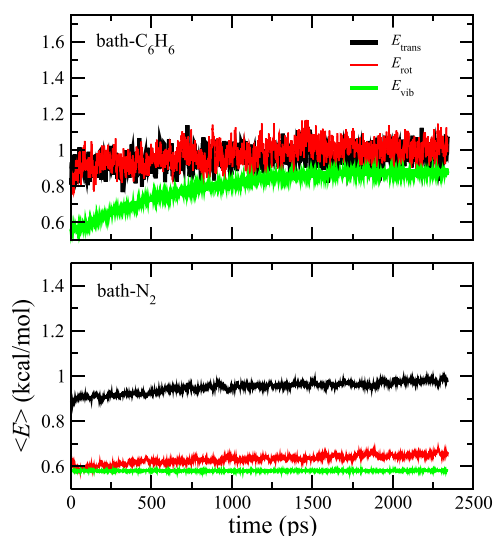

FIG. 1. Plotted versus time are the average center-of-mass translation and rotational energies of a N_2 and C_6H_6 molecule and the average energy of N_2 vibration and a C_6H_6 vibration mode, for the N_2/C_6H_6 bath molecules.
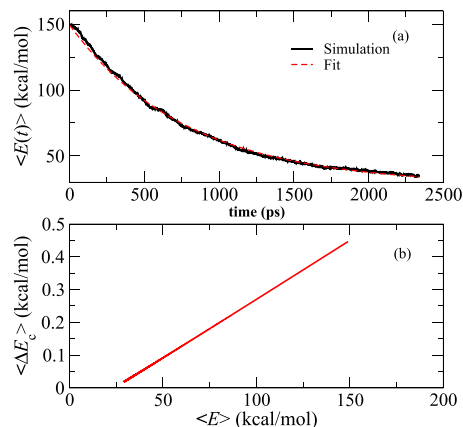

FIG. 2. (a) Average energy of the vibrationally excited $C_6H_6^*$ molecule versus time, $\langle E(t) \rangle$. The fit is with Eq. (2). (b) Average energy transfer from $C_6H_6^*$ per collision with the bath, $\langle \Delta E_c \rangle$ from Eq. (3), versus the average energy of $C_6H_6^*$, $\langle E \rangle$.
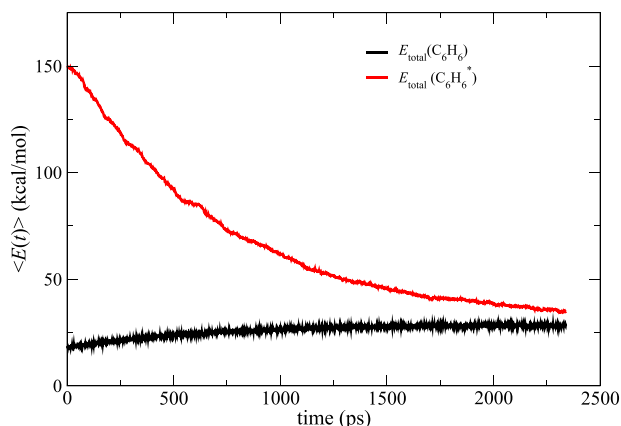
FIG. 3. Average total energies versus time of a vibrationally excited $C_6H_6^*$ molecule and a C_6H_6 bath molecule.

$$\langle \Delta E_c \rangle = [d\langle E(t)\rangle/dt]/\omega, \qquad (3)$$

where $d\langle E(t)\rangle/dt$ is the energy transfer per unit time and ω is the collision frequency in s^{-1}. $\langle \Delta E_c \rangle$ includes all collisions, both those that transfer energy from and to $C_6H_6^*$. The collision frequency is a sum of the collision frequencies for $C_6H_6^*$ colliding with the N_2 and C_6H_6 bath molecules and is

$$\omega = \omega(C_6H_6^* - N_2) + \omega(C_6H_6^* - C_6H_6). \qquad (4)$$

The collision frequency for each bath component may be expressed as $\omega = \omega_P \times P$, where P is the pressure of the bath gas, i.e., 31.0 atm and 1.5 atm for N_2 and C_6H_6, respectively. With parameters used to interpret experiments,[32] ω_P is 1.14×10^{11} and 1.74×10^{11} atm^{-1} s^{-1} for N_2 and C_6H_6, respectively. The resulting value of ω is 3.79×10^{12} s^{-1} for the simulations reported here.

From Eq. (3), $\langle \Delta E_c \rangle$ is plotted versus the average energy of $C_6H_6^*$, $\langle E \rangle$, in Fig. 2. At the initiation of the trajectory simulation, with $\langle E \rangle = 149.9$ kcal/mol, $\langle \Delta E_c \rangle$ has its largest value of 0.45 kcal/mol. When the simulation was terminated at 2400 ps, $\langle \Delta E_c \rangle = 0.02$ kcal/mol. Once $C_6H_6^*$ attains equilibrium with the bath $\langle \Delta E_c \rangle$ equals zero, since energy transfer from and to the initially excited benzene molecule becomes equivalent.

The simulation results may be compared with those determined experimentally.[32] The experiments contain a small percentage of NO in the bath. N_2 and NO are expected to have the same rotational temperature, and the rotational temperature of NO is determined by monitoring its rotational level populations. The N_2 rotational temperature is determined directly from the simulations. Although the experiments and simulations are performed at different bath pressures (i.e., the experimental and simulation pressures are 0.024 and 32.5 atm, respectively), the time dependencies of their N_2 rotational temperatures may be compared by plotting the N_2 rotational temperature versus the number of $C_6H_6^*$ collisions with the bath. This plot is given in Fig. 4, for which the bath conditions are different for the experiments and simulations. The experiments have a bath that is <7% C_6H_6, <1% NO, and ~92%–99% N_2, while the simulations have a bath that contains 5% C_6H_6 and 95% N_2. For the simulations,
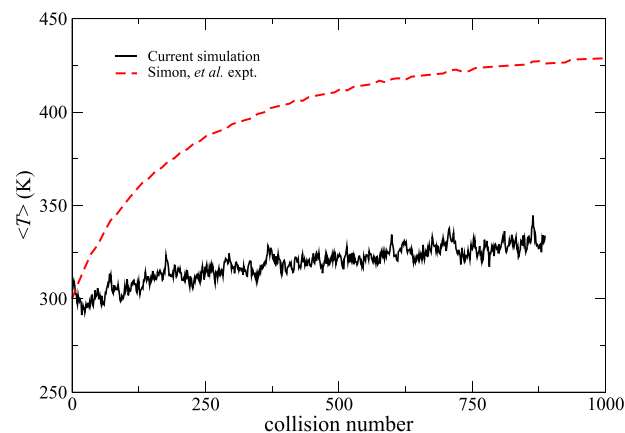

FIG. 4. Temperature of the bath versus collision number for the current simulation with 190 N_2 and 10 C_6H_6 molecules and one of the C_6H_6 molecules vibrationally excited. Results averaged over 48 trajectories. Comparison is made with the bath temperature obtained from experiments;[32] fractions of N_2 and C_6H_6 in the bath and excitation of C_6H_6 are described in the text.

10% of C_6H_6 is vibrationally excited, but the experimental percentage is 10%–30%. The N_2 rotational temperature increase is ~130 K in the experiments and ~32 K in the simulation. Apparently, more C_6H_6 molecules are vibrationally excited in the experiments than the percentage used for the simulation.

Given in Fig. 5 are the plots of $\langle \Delta E_c \rangle$ versus $\langle E \rangle$ obtained from experiment,[32] which may be compared with the simulation. A fit to experimental results is given for $\Delta T = 130$ K, where the initial and final bath temperatures were 300 and 430 K, respectively. Temperature dependent parameters for fits to ΔT of 130–310 K data sets were used to extrapolate the curve parameters to obtain a $\Delta T = 0$ K curve for an initial bath temperature of 300 K, which is also shown in Fig. 5. It is seen that the curve obtained from the classical microcanonical sampling of $C_6H_6^*$ and 190 N_2 + 9 C_6H_6 molecules in the bath, for which $\Delta T \sim 32$ K, is in good agreement with experiments and remains between the experimental curves for ΔT of 0 and 130 K. For the experimental curves, $\langle \Delta E_c \rangle$ is larger for
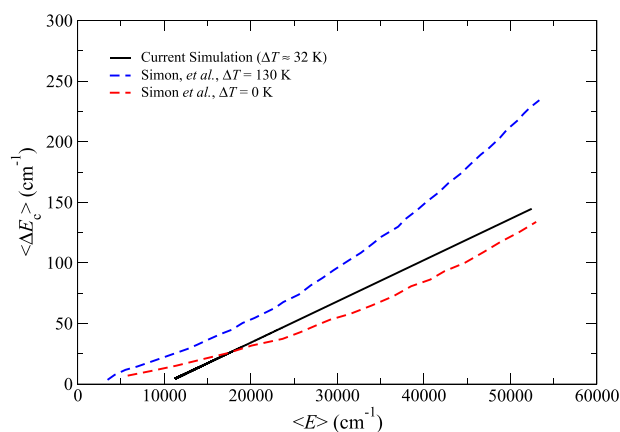

FIG. 5. Average energy transfer per collision, $\langle \Delta E_c \rangle$, versus the average energy of vibrationally excited $C_6H_6^*$. Comparison is made between the current simulation and experiment. Experimental results are given for significant heating of the bath, $\Delta T = 130$ K, with a significant number of C_6H_6 molecules excited, and results for negligible heating of the bath, $\Delta T = 0$ K, with few C_6H_6 molecules excited. For the simulation, $\Delta T \sim 32$ K.

ΔT = 130 K than for ΔT = 0 K. The simulation $\langle \Delta E_c \rangle$, for $\Delta T \sim 32$ K, falls between the ΔT = 0 and 130 K experimental $\langle \Delta E_c \rangle$ curves.

IV. CONCLUSION

The simulation reported here model experiments[32] in which a fraction of C_6H_6 molecules in a mixed N_2–C_6H_6 bath, initially at 300 K, are vibrationally excited by S_2 laser excitation and then undergo $S_2 \rightarrow S_0$ internal conversion, followed by intermolecular energy transfer and heating of the bath. The vibrationally excited C_6H_6 molecules are identified as $C_6H_6^*$. The simulation is performed for 2.4×10^{-9} s at a pressure of 32.5 atm, which is in the binary single collision limit, and corresponds to a simulation time of $\sim 10^{-7}$ s for the same number of collisions at 1 atm pressure. The experiments determine the N_2 rotational temperature of the bath versus time, and the simulations and experiments may be compared by considering the time dependencies of their N_2 rotational temperatures versus the number of $C_6H_6^*$ collisions with the bath. For the simulations, 10% of C_6H_6 is vibrationally excited, but the experimental percentage is unknown and approximately 10%–30%. The N_2 rotational temperature increase is ~ 130 K in the experiments and ~ 32 K in the simulation. This result is consistent with more C_6H_6 molecules vibrationally excited in the experiments than the percentage used for the simulation.

An important finding from the simulation is the hierarchy of energy transfer probabilities for $C_6H_6^*$ and the N_2 and C_6H_6 bath. With complete equilibration of the vibrationally excited $C_6H_6^*$ molecules and the N_2 and C_6H_6 bath, the elevated temperature of the system becomes 402 K. By contrast, at the end of the simulation, there are four temperatures for $C_6H_6^*$ and the bath. Consistent with experimental studies,[41] there is negligible energy transfer to N_2 vibration and the final N_2 vibration temperature remains at the initial bath temperature of ~ 300 K. The translation and rotation temperature of the N_2 and C_6H_6 bath molecules and the vibrationally excited $C_6H_6^*$ molecules is the same and is ~ 340 K. Energy transfer from $C_6H_6^*$ vibration to C_6H_6 vibration is more probable than to rotation/translation of the C_6H_6 bath molecules, and the final vibrational temperature of the C_6H_6 bath molecules is ~ 453 K. Vibrational energy is not equilibrated between $C_6H_6^*$ and the C_6H_6 bath, and the final $C_6H_6^*$ vibration temperature is ~ 537 K. Thus, for conditions corresponding to 1 atm pressure and $\sim 10^{-7}$ s, the simulations find four temperatures for the system studied here: ~ 300 K for vibration of the N_2 bath molecules; ~ 340 K for translation-rotation of the N_2–C_6H_6 bath molecules and the initially vibrationally excited $C_6H_6^*$ molecules; ~ 453 K for vibration of the C_6H_6 bath molecules; and ~ 537 K for vibration of the initially vibrationally excited $C_6H_6^*$ molecules.

The time scale for complete equilibration of the system studied here to a constant temperature is uncertain. Vibrational energy transfer for N_2 is quite slow and at 1 atm pressure V-T relaxation for N_2 occurs on a 10^{-4} s time scale.[41] For the current simulation of $C_6H_6^* + C_6H_6$ collisions, the finding of more probable energy transfer to C_6H_6 vibration, than to C_6H_6 rotation/translation in $C_6H_6^* + C_6H_6$ collisions,

agrees with a previous chemical dynamics simulation of $C_6H_6^* + C_6H_6$ collisions.[42] Resonant V $\rightarrow$ V energy transfer may be important for this efficient vibrational energy transfer. In future simulations, it would be of interest to use a normal mode Hamiltonian model[26,43] to investigate which vibrational modes of excited $C_6H_6^*$ most efficiently transfer energy to vibration of unexcited C_6H_6. Energy transfer dynamics for the current simulation extend to a time of $\sim 10^{-7}$ s for 1 atm pressure and it may be possible to extend the simulation to longer times, to investigate the time scale for complete energy equilibration. Energy transfer from the vibrationally excited $C_6H_6^*$ molecules is multi-exponential, which makes kinetic analyses of the time scale for energy equilibration complex.

SUPPLEMENTARY MATERIAL

See supplementary material for average translation, rotation, and per mode vibration energies of a $C_6H_6^*$ molecule versus time and the average translation and rotation energies of a C_6H_6 bath molecule versus time.

ACKNOWLEDGMENTS

[1] D. C. Tardy and B. S. Rabinovitch, Chem. Rev. **77**, 369 (1977).
[2] I. Oref and D. C. Tardy, Chem. Rev. **90**, 1407 (1990).
[3] J. R. Barker and B. M. Toselli, Int. Rev. Phys. Chem. **12**, 305 (1993).
[4] C. G. Elles and F. F. Crim, Annu. Rev. Phys. Chem. **57**, 273 (2006).
[5] H. Hippler, J. Troe, and H. J. Wendelken, J. Chem. Phys. **78**, 6718 (1983).
[6] R. Wagnild, P. K. Subbareddy, and H. B. Johnson, "Vibrational relaxation effects on acoustic disturbances in a hypersonic boundary layer over a cone," in *50th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition* (AIAA, Nashville, Tennessee, 2012), p. 922.
[7] B. E. Schmidt and J. Shepherd, "Measurements of instability in supersonic flow with injection by time-resolved flow visualization," in *54th AIAA Aerospace Sciences Meeting* (AIAA, San Diego, California, 2016), p. 0599.
[8] G. V. Candler, Prog. Aerosp. Sci. **72**, 37 (2015).
[9] T. J. Fuller, A. G. Hsu, R. Sanchez-Gonzalez, J. C. Dean, S. W. North, and R. D. W. Bowersox, J. Fluid Mech. **748**, 663 (2014).
[10] C. A. Michaels, A. S. Mullin, J. Park, J. Z. Chou, and G. W. Flynn, J. Chem. Phys. **102**, 6682 (1995).
[11] C. A. Michaels, A. S. Mullin, J. Park, J. Z. Chou, and G. W. Flynn, J. Chem. Phys. **108**, 2744 (1998).
[12] M. Fraelich, M. S. Elioff, and A. S. Mullin, J. Phys. Chem. A **102**, 9761 (1998).
[13] M. Fraelich, M. S. Elioff, R. L. Sansom, and A. S. Mullin, J. Chem. Phys. **111**, 3517 (1999).
[14] M. S. Elioff, R. Sansom, and A. S. Mullin, J. Phys. Chem. A **104**, 10304 (2000).

[15] M. S. Elioff, M. Fang, and A. S. Mullin, J. Chem. Phys. **115**, 6990 (2001); Erratum, **117**, 6880 (2002).

[16] Q. Liu, D. K. Havey, and A. S. Mullin, J. Phys. Chem. A **112**, 9509 (2008).

[17] D. K. Havey, Q. Liu, Z. Li, M. Elioff, M. Fang, J. Neudel, and A. S. Mullin, J. Phys. Chem. A **111**, 2458 (2007).

[18] D. K. Havey, Q. Liu, Z. Li, M. Elioff, and A. S. Mullin, J. Phys. Chem. A **111**, 13321 (2007).

[19] Q. Liu, D. K. Havey, Z. Li, and A. S. Mullin, J. Phys. Chem. A **113**, 4387 (2009).

[20] J. Du, L. Yuan, S. Hsieh, F. Lin, and A. S. Mullin, J. Phys. Chem. A **112**, 9396 (2008).

[21] J. C. Light, Discuss. Faraday Soc. **44**, 14 (1967).

[22] C. E. Klots, J. Phys. Chem. **75**, 1526 (1971).

[23] Y. N. Lin and B. S. Rabinovitch, J. Phys. Chem. **74**, 3151 (1970).

[24] D. Nilsson and S. Nordholm, J. Chem. Phys. **119**, 11212 (2003).

[25] T. Yan and W. L. Hase, Phys. Chem. Chem. Phys. **2**, 901 (2000).

[26] T. Yan, N. Isa, K. D. Gibson, S. J. Sibener, and W. L. Hase, J. Phys. Chem. A **107**, 10600 (2003).

[27] A. K. Paul, S. C. Kohale, S. Pratihar, R. Sun, S. W. North, and W. L. Hase, J. Chem. Phys. **140**, 194103 (2014).

[28] A. K. Paul, S. C. Kohale, and W. L. Hase, J. Phys. Chem. C **119**, 14683 (2015).

[29] H. Kim, A. K. Paul, and W. L. Hase, J. Phys. Chem. A **120**, 5187 (2016).

[30] H. Kim, B. Saha, S. Pratihar, M. Majumder, and W. L. Hase, J. Phys. Chem. A **121**, 7494 (2017).

[31] A. K. Paul, D. Donzis, and W. L. Hase, J. Phys. Chem. A **121**, 4049 (2017).

[32] N. A. West, J. D. Winner, R. D. Bowersox, and S. W. North, J. Chem. Phys. **145**, 014308 (2016).

[33] S. T. Tsai, C.-K. Lin, Y. T. Lee, and C.-K. Ni, J. Chem. Phys. **113**, 67 (2000).

[34] W. L. Jorgensen and D. L. Severance, J. Am. Chem. Soc. **112**, 4768 (1990).

[35] X. Ma, A. K. Paul, and W. L. Hase, J. Phys. Chem. A **119**, 6631 (2015).

[36] E. C. Lee, D. Kim, P. Jurečka, P. Tarakeshwar, P. Hobza, and K. S. Kim, J. Phys. Chem. A **111**, 3446 (2007).

[37] S. Hamon, S. D. Le Picard, A. Canosa, B. R. Rowe, and I. W. M. Smith, J. Chem. Phys. **112**, 4506 (2000).

[38] W. L. Hase and D. G. Buckowski, Chem. Phys. Lett. **74**, 284 (1980).

[39] G. H. Peslherbe, H. Wang, and W. L. Hase, Adv. Chem. Phys. **105**, 171 (1999).

[40] X. Hu, W. L. Hase, and T. Pirraglia, J. Comput. Chem. **12**, 1014 (1991).

[41] G. V. Candler, J. D. Kelley, S. O. Macheret, M. N. Shneider, and I. V. Adamovich, AIAA J. **40**, 1803 (2002).

[42] V. Bernshtein and I. Oref, J. Phys. Chem. B **109**, 8310 (2005).

[43] T.-Y. Yan and W. L. Hase, J. Phys. Chem. A **105**, 2617 (2001).