Collision-Induced Intramolecular Energy Flow in Highly Excited Toluene

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The collision-induced relaxation of vibrationally excited molecules has been the subject of continuing interest for the past several decades.[1-14] In recent years, furthermore, collisions involving large molecules have been studied actively, revealing valuable information on the rates and the mechanisms of vibrational energy processes. In particular, molecules vibrationally excited to near their dissociation threshold can undergo bond dissociation and vibrational relaxation, processes that play an important role in reaction dynamics. Recent studies[3,5-11] show that when the excited molecule is a large organic molecule, the average amount of energy transfer per collision is not very large. The average energy transfer per collision between the highly vibrationally excited benzene and a noble gas atom is known to be about 30 cm^{-1}, which is much smaller than benzene derivatives such as hexafluorobenzene or other hydrocarbons such as toluene and azulene.[5,12-14] For example, for hexafluorobenzene + Ar, the measured value of the mean energy transfer per collision by the ultraviolet absorption method is −330 cm^{-1},[13] whereas the calculated value using quasiclassical trajectory methods at 300 K is −150 cm^{-1}.[5] For toluene + Ar, the amount of energy transfer is about −200 cm^{-1}.[14] These magnitudes are much larger in comparison to results for benzene colliding with argon. Among such large molecules, toluene is a particularly attractive molecule for studying collision-induced intramolecular energy flow and bond dissociation because of the presence of both methyl and ring CH bonds.

In this paper, as an extension of th previous work in ref. 11, we study the collision-induced dynamics of highly vibrationally excited toluene interacting with argon using quasiclassical trajectory calculations. We now consider the collision system in which one CH (either CH_{methyl} or CH_{ring}) vibration is in a highly excited state and the other in a ground state, while in Ref. 11 we considered both of CH_{methyl} and CH_{ring} bonds are in highly excited states. In the latter, it was not clear which CH bond is more effective for collision-induced inter- and intra-molecular energy transfer in collision with Ar. Thus, we now elucidate which CH bond is more effective for collision-induced inter- and intra-molecular energy transfer, as considering and comparing the results of inter- and intra-molecular energy transfer dynamics when

either CH_{methyl} or CH_{ring} is in highly excited states. Using the results obtained in the calculations, we discuss the relaxation of the excited CH vibration, and the time evolution of collision-induced intramolecular energy flow from the highly excited CH vibration. Thus, we elucidate the nature and mechanism of competition between methyl CH mode and ring CH mode in transferring energy to the incident atom. We set the initial vibrational energy of the methyl CH bond or the ring CH bond equal to the state just 0.10 eV below the dissociation threshold at 300 K.

Interaction Model

The present work follows the interaction model and numerical procedure, which have already been reported in ref. 11. Briefly, we recapitulate the essential aspects of the
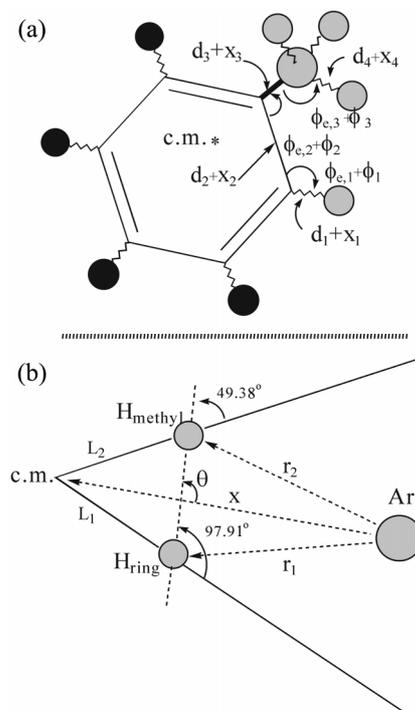

Figure 1. Collision model. (a) The stretching and bending coordinates of vibrations included in the model. The star denotes the center-of-mass (cm) of toluene. (b) The relative coordinate between Ar and the cm of toluene (x), the Ar-to-H_{ring} distance (r_1) and the Ar-to-H_{methyl} distance (r_2) are shown.

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interaction of Ar with toluene in this section, reproducing the collision model in Figure 1 for easy reference. In Figure 1a, we define all pertinent vibrational modes in the region of toluene in interaction with the incident atom Ar. From the methyl CH bond to the ring CH bond, included in the interaction region are the CH_{methyl}, $C-CH_3$, $(CC)_{ring}$ and CH_{ring} stretches, and the CCH_{methyl}, CCC and CCH_{ring} bends, where $(CC)_{ring}$ is the ring's CC bond linking the methyl group and the H_{ring} atom. We consider the interaction of Ar with a non-rotating toluene, the collision partners lying in the same plane. The overall interaction energy is the sum of the Morse-type intermolecular part, Morse-type intramolecular stretches and the harmonic bends. The first part includes Ar to CH_{methyl} and Ar to CH_{ring} interactions. All potential and spectroscopic constants needed in the calculation are listed in ref. 11. From the plot of energy contour around CH_{methyl} and CH_{ring}, we found that the intermolecular interaction energy surface exhibits a potential well along Ar approaching the center-of-mass of toluene at the angle $\theta = 77°$. The angle θ is measured from the line connecting the hydrogen atoms H_{methyl} and H_{ring} to the line connecting Ar and center of mass of toluene as shown in Figure 1. In all collision systems considered here, the incident atom approaches the center of mass of toluene in the $\theta = 77°$ direction.

We solve the equations of motion for the relative motion, four stretches and three bends using the DIVPAG double-precision routine of the IMSL library[15-18] to describe the time evolution of bond distances, angles, and vibrational energies, as well as the relative coordinate for the model system. We sample 10000 trajectories for each run at 300 K, where the sampling includes determining collision energies chosen from the Maxwell distribution. The initial vibrational phases and displacements are chosen from microcanonical ensembles with the total vibrational energy constant. The initial separation between the center of mass of toluene and Ar is set as 13 Å, and trajectories are terminated when the separation reaches 15 Å after they passed through the closest distance of approach. The integration step is set as 0.169 fs, which is one-tenth the period of the largest frequency, the ring CH vibration, and is small enough to conserve the total energy. The initial vibrational energy of the excited CH bond is set to 0.10 eV below its dissociation threshold, which is 3.9717 eV for the CH_{methyl} bond and 4.9569 eV for the CH_{ring} bond. Thus, for the highly excited CH_{methyl}, the initial vibrational energy is $D_{CHmethyl} - 0.1000$ eV $= 3.8717$ eV or 31230 cm^{-1} above the bottom of the potential well. For the highly excited CH_{ring} bond, the initial vibrational energy $D_{CHring} - 0.1000$ eV $= 39170$ cm^{-1}. In calculating energy transfer from the molecule to Ar, *i.e.*, the deexcitation of CH_{methyl} (or CH_{ring}), we measure the initial vibrational energy in excess of the zero point, in which case, the energy values for CH_{methyl} and CH_{ring} are 29700 and 37600 cm^{-1}, respectively, which can be identified as the initial total energy content of toluene E_T. In each collision system we set either CH_{methyl} or CH_{ring} to this high-energy state, while all other vibrational modes are in their ground states.

Results and Discussion

We first consider the collision system in which the CH_{methyl} vibration is highly excited (*i.e.*, E_T is 29700 cm^{-1}), while the ring CH and all other modes are in their ground states; we shall refer to this as system (i). Then, we consider the case in which the ring CH vibration is highly excited (*i.e.*, E_T is 37600 cm^{-1}), while the methyl CH and all other modes are in their ground states, and we shall refer it as system (ii). It should be noted that we now consider the collision system in which one CH (CH_{methyl} or CH_{ring}) vibration is in a highly excited state and the other in a ground state, while in ref. 11 we considered both CH_{methyl} and CH_{ring} bonds are in highly excited states.

For systems (i) and (ii), the amounts of ensemble-averaged energy transfer for all nondissociative trajectories are $<\Delta E>$ $= -298$ cm^{-1} and -25.5 cm^{-1}, respectively. Here, a negative number represents the molecule losing energy to Ar *via* V $\rightarrow$ T pathway. These values are only 1.0 and 0.068% of E_T. When both CH_{methyl} and CH_{ring} bonds are in highly excited states, that is, 0.1 eV below their respective dissociation thresholds (namely, 29700 cm^{-1} for $C-H_{methyl}$ and 37600 cm^{-1} for $C-H_{ring}$), the amount of ensemble-averaged energy transfer for all nondissociative trajectories is -694 cm^{-1} and energy loss for this highly excited toluene was also only about 1% of E_T.[11]

The amount of energy lost by CH_{methyl} is more than ten times that lost by CH_{ring}. Thus, the highly excited CH_{methyl} shows a much greater tendency of transferring its vibrational energy to translation than the highly excited CH_{ring} does. If we approximate the Ar-CH_{ring} interaction in toluene as a representation of the Ar-CH interaction in benzene, the nearly 10 to 1 ratio of energy transfer efficiency of CH_{methyl} to CH_{ring} found in the present study is in general agreement with energy transfer experiments for toluene and benzene.[5,12,13,19] However, it is important to note that the above comparison between the ensemble-averaged energy transfer for all nondissociative trajectories for Ar-CH_{methyl} and for Ar-CH_{ring}, *i.e.*, $<\Delta E>$ $= -298$ cm^{-1} versus -25.5 cm^{-1}, is made for their CH bonds initially having their vibrational energies below the dissociation threshold by 0.10 eV. Thus, the CH bonds have unequal amounts of E_T, namely, 29700 cm^{-1} versus 37600 cm^{-1}.

To expand this discussion of the collisional deexcitation of toluene, we now repeat the above calculations for CH_{methyl} and CH_{ring} with the same initial energy content. For this purpose, we take $E_T = 24000$ cm^{-1} that has been considered in previous studies.[5,14] For this initial energy content, we obtain the ensemble-averaged energy transfer $<\Delta E>$ $= -80.1$ and -34.7 cm^{-1} for CH_{methyl} and CH_{ring}, respectively. These results indicate that when E_T is lowered to 24000 cm^{-1}, the energy lost by the excited ring CH increases somewhat but that by the excited methyl CH decreases significantly. However, the magnitude of $<\Delta E>$ for CH_{methyl} is still much larger than that for CH_{ring} even at this low E_T. The calculated value of $<\Delta E>$ for CH_{methyl} is smaller than those reported in earlier papers, *e.g.*, $<\Delta E>$ $= -125$ cm^{-1} at $E_T = 20000$ cm^{-1} [10]

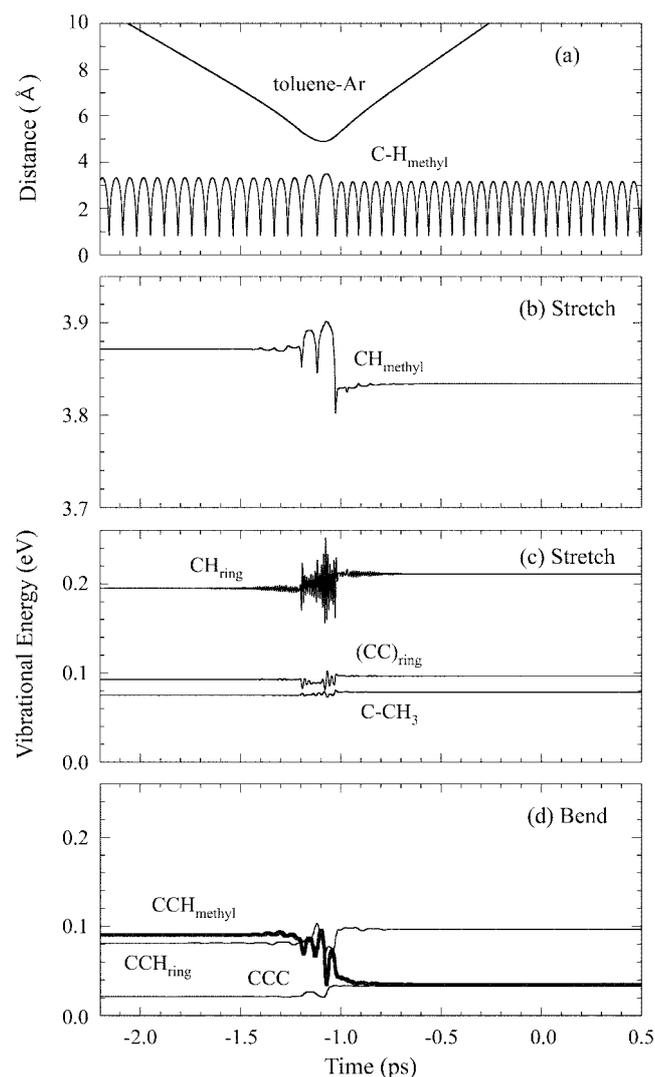**Figure 2**. Time evolution of the trajectory representing nondissociative events with the highly excited CH_{methyl}, system (i). (a) Collision and CH_{methyl} bond trajectories. (b) The vibrational energy of highly excited CH_{methyl} stretch. (c) The vibrational energies of ground state CH_{ring}, (CC) ring and C-CH_3 stretches. (d) The vibrational energies of ground state CCH_{methyl}, CCH_{ring} and CCC bends. The CCH_{methyl} curve is shown in a heavy line for convenience.

and -120 cm^{-1} at $E_T = 24000$ cm^{-1}.[14] On the other hand, $<\Delta E>$ for CH_{ring} is very close to the value of -33 cm^{-1} for benzene CH at $E_T = 24000$ cm^{-1} reported by earlier researchers.[5]

Now, we discuss the dynamics of relaxation processes by calculating time evolution of the trajectories.[11,17,18] In Figure 2a, we show the toluene-Ar distance (*i.e.*, the collision trajectory) and the C-H_{methyl} bond distance (*i.e.*, bond trajectory) for the highly excited methyl CH system, system (i). This representative trajectory is for the collision with energy 0.0367 eV, which is fairly close to 3/2 $kT = 0.0388$ eV. The initially highly excited CH_{methyl} bond vibrates at the frequency 484 cm^{-1} and then blue-shifts to 558 cm^{-1} after collision. The closest distance that Ar can reach toward the center of mass of toluene is 5 Å occurring near $t = -1.1$ ps. Closest distances for all trajectories in the toluene-Ar collision in the present study lie between 4 and 8 Å, the

lower limit being close to the average minimal distance of 3.08 Å by Bernshtein and Oref.[20] Since the slope of the collision trajectory changes only slightly it is difficult to identify the time at which the collision begins and that at which it ends. However, the variation of the time evolution of vibrational energies, especially the CH_{methyl} energy shown in Figure 2b, clearly shows when the collision begins and ends. From the variation of the energy curve in Figure 2b, we find that the collision begins at -1.45 ps and completes at -0.75 ps, so the duration of collision is 0.70 ps, which is close to 0.6 ps reported by Bernshtein and Oref in their trajectory calculations.[21] However, a sharp decrease in the vibrational energy over a short period, where the vibrational energy varies with two large amplitudes, indicates that the essential part of relaxation of the highly excited CH_{methyl} is over within 0.2 ps, which is much shorter than the duration of collision. When both CH_{methyl} and CH_{ring} bonds are in highly excited states, the ensemble-averaged time scale for the relaxation of C-H_{methyl} is 0.23 ps,[11] which is almost the same as the present case, that is, only the CH_{methyl} vibration is highly excited, while the ring CH and all other modes are in their ground states. Comparing the CH_{methyl} curve in Figure 2b with the collision trajectory in Figure 2a, we note that this short time scale for energy relaxation takes place when a significant amount of acceleration of the collision trajectory occurs before and after turning the corner of closest approach.[22]

In Figure 2b we note that the initial vibrational energy 3.8717 eV levels off to the final value of 3.8338 eV, a relaxation step with $\Delta E = -0.0379$ eV or -305 cm^{-1}. The time evolution for three other stretches is shown in Figure 2c. The CH_{ring} stretching mode gains some energy, while both (CC)$_{ring}$ and C-CH_3 stretches gain only a very small amount of energy. As shown in Figure 2d, while the CCH_{ring} and CCC bends gain energy, the CCH_{methyl}, which is directly coupled to the CH_{methyl} stretch, loses energy. The net energy loss is then carried away by Ar. On the other hand, when both CH_{methyl} and CH_{ring} bonds are in highly excited states, most of the energy lost by C-H_{methyl} deposits in the CCH_{ring} bend, followed by the CH_{ring} stretch and CCH_{methyl} bend, and a small amount is removed by the incident atom.[11] Thus, the characteristic of the energy transfer for the present case is very different from the former case.

The time evolution of the collision event representing system (ii) is considered in Figure 3. Here the collision energy is 0.0362 eV. In Figure 3a, the period of the C-H_{ring} vibration varies only slightly on collision, showing that the vibrational frequency of CH_{ring} changes from 430 cm^{-1} to 459 cm^{-1}. The ensemble-averaged energy loss per collision is only -30.6 cm^{-1} as shown in Figure 3b, representing an inefficient relaxation process for the highly excited ring CH. An important difference between systems (i) and (ii) is the duration of collision shown in Figures 2b and 3b. From the time evolution of the CH_{ring} vibrational energy shown in Figure 3b, we find the collision beginning at $t = -2.20$ ps. The Ar-CH_{ring} interaction continues for 1.25 ps undergoing sharp oscillations before the CH_{ring} vibrational energy levels
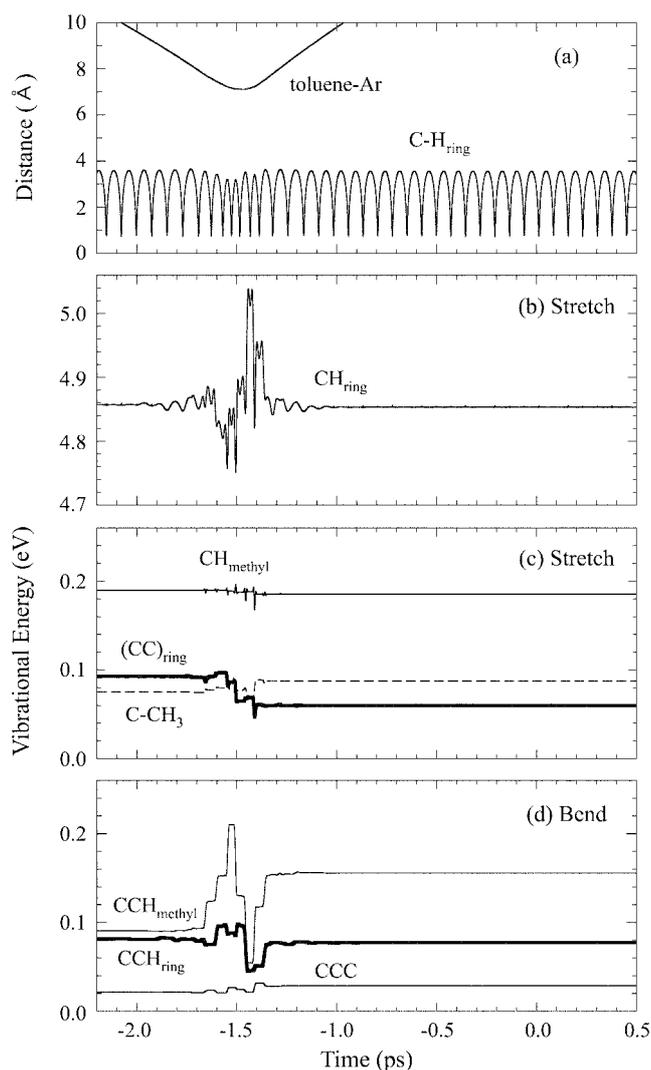
Figure 3. Time evolution of the trajectory representing nondissociative events with the highly excited CH_{ring}, system (ii). (a) Collision and CH_{ring} bond trajectories. (b) The vibrational energy of highly excited CH_{ring} stretch. (c) The vibrational energies of ground state CH_{methyl}, $(CC)_{ring}$ and $C-CH_3$ stretches. (d) The vibrational energies of ground state CCH_{methyl}, CCH_{ring} and CCC bends. The CCH_{ring} curve is shown in a heavy line for convenience.

off to its limiting value. That is, after many energy give-and-take steps, each involving a large amount of energy, the CH_{ring} bond finally comes out when the collision is over with its vibrational energy nearly unchanged. This situation is markedly different from the CH_{methyl} case where fewer energy give-and-take steps (two steps in the representative trajectory shown in Figure 2b) lead to a larger energy transfer. Such energy give-and-take steps are particularly prominent in the heavy-light-heavy mass distribution in the impulsive limit.[23] Although the collision energy is low, such steps appear to manifest in the present systems, especially in system (ii). In sysem (i), the methyl ring is bound to a ring carbon thus making the $C-C-H_{methyl}$ region more flexible compared to $C-H_{ring}$, where H_{ring} is directly bound to a ring carbon. The rigidity in the latter system contributes to the appearance of a larger number of steps, each representing

the $C-H\cdots Ar$ impact, even though the collision energy is not very high. The mass distribution of 12-1-40 leads to five impacts in the impulsive limit.[23]

As shown in Figure 3c, both $(CC)_{ring}$ and CH_{methyl} stretches lose some energy, while the $C-CH_3$ stretch gains energy. An interesting situation is that the CCH_{methyl} bend which is farther away from the highly excited CH_{ring} site now gains energy, while it loses energy in the previous system where the nearby CH_{methyl} is highly excited (see Figure 3d). That is, the CCH_{ring} bend directly coupled to the highly excited CH_{ring} loses energy as CCH_{methyl} coupled to the highly excited CH_{methyl} does in the previous system. We note that the closest distance of approach for this representative trajectory is nearly 7 Å, which is significantly larger than that shown in Figure 2a.

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