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Methylation effects on the collisional quenching of vibrationally excited benzene derivatives by unexcited parent molecules

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Abstract

The collisional quenching of vibrationally excited methyl substituted benzenes and deuterated isomers, produced from Nd–YAG 266 nm absorption, by unexcited parent molecules was studied by measuring the time-resolved C–H (or C–D) infrared fluorescence at $\sim 3.3\ \mu\text{m}$ (or $\sim 4.4\ \mu\text{m}$). The collisional quenching efficiency is enhanced almost linearly as the number of methyl groups increases. The deuterium effect of methyl substituted benzene series is not much significant compared to that of azabenzenes and benzene having no methyl group. The results provide a detailed energy transfer mechanism that the vibration–rotation/translation energy transfer channel via low frequency vibrational modes such as methyl internal rotation plays an important role in the quenching process of vibrationally excited methyl substituted benzenes by parent bath molecules. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The importance of the collisional energy quenching in the atmospheric and combustion chemistries is well recognized [1]. Although the collisional relaxation dynamics of highly vibrationally excited large molecules have been extensively investigated over past many years [2–5], a detailed mechanism of energy flow between molecules is still not completely understood due to the high density of states resulting from many vibrational modes of molecule.

A number of experimental results demonstrated that the collisional quenching efficiency could de-

pend on the properties of the vibrationally excited energy donor molecule. Troe and coworkers observed that the average energy loss per collision of vibrationally excited ethyl- and isopropyl-cycloheptatrienes increases slightly with the size of the excited molecule, for a given bath gas [6]. Barker's group reported the average energy loss per collision of vibrationally excited various molecules, such as pyrazine, benzene, toluene, and azulene (C_{10}H_8), showing an increase with the number of atoms in a molecule, especially for the quenching with parent unexcited molecules [7–10]. They also observed that, when benzene and toluene are deuterated, the average quenching energy loss for the collisions with the unexcited parent molecule is reduced [7,8]. Wu and Weisman recently reported that deuteration causes very little change in the efficient vibrational energy loss behavior of the

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triplet pyrazine (T_1), but the methylation increases the average energy loss per collision significantly [11].

The transient IR diode absorption technique has provided the quantum state resolved information of energy accepting molecule such as CO_2 [12–18]. Sadlacek et al. probed the vibrational energy gain of bath CO_2 molecules for the collisional quenching of vibrationally excited C_6H_6 , C_6F_6 , and C_6D_6 , showing that the average energy gains per collision in the CO_2 (00^01) vibrational state are in the order of $\text{C}_6\text{H}_6 > \text{C}_6\text{F}_6 > \text{C}_6\text{D}_6$ [12]. For the excitation of CO_2 (00^00), Flynn and co-workers observed that C_6F_6 is a more efficient vibrational energy donor molecule than pyrazine [13–17]. Wall et al. reported that the energy transfer of vibrationally excited pyridine to CO_2 (00^01) is more efficient than that of pyrazine [18].

Our recent experiments [19] have provided quantitative information for the collisional quenching efficiency of vibrationally excited methyl substituted azabenzenes. For the collisional quenching by the parent bath molecule, the average energy loss per collision increases with the number of methyl groups. The deuteration of pyrazine and pyridine leads to a significant decrease in the quenching efficiency, indicating the dominant vibration–vibration (V–V) energy transfer channel, as expected from the fact that there is an exact energy matching of vibrational modes. However, it is likely that the methyl group opens a pathway for the vibration–rotation/translation (V–R/T) energy transfer. To clarify the source of this behavior, we study the collisional quenching of the vibrationally hot methyl substituted benzene derivatives with focus on the role played by the methyl group.

In the present paper, we report the averaged quenching rate and the average energy loss per collision for the collisional quenching of vibrationally excited methyl substituted benzene series and their deuterated isomers by unexcited parent molecules. The experiment using the time resolved IRF technique has been performed for toluene, xylene, mesitylene, and their deuterated isomers. For comparison with pyridine, 2-picoline- d_7 and 4-picoline- d_3 were chosen for study. Unlike benzene, pyridine has a permanent dipole moment,

2,2 D [20]. The vibrationally excited molecules are prepared by Nd–YAG 266 nm absorption. From the photophysics of toluene it is well known that at 266 nm, the molecule can be excited to the S_1 state, and subsequently undergoes radiationless transition to form a highly vibrationally excited molecule in the ground electronic state within 70 ns [21]. 2-Picoline is excited to the S_2 state and then undergoes a fast internal conversion in less than 2 ps [22]. Other methyl substituted benzenes were also found to form the vibrationally excited states following a fast internal conversion [23]. As the vibrationally excited molecules are collisionally deactivated by unexcited parent molecules, the time resolved IRF from the C–H (or C–D) stretching vibration modes at $\sim 3.3 \mu\text{m}$ (or $\sim 4.4 \mu\text{m}$) is monitored.

2. Experimental

The collisional relaxation was monitored with the time-resolved IRF technique. The gas phase molecules in a 25 cm long and 2.5 cm diameter Pyrex cell were irradiated by the pulse of a Nd–YAG 266 nm laser (Continuum Surelite II). The C–H (or C–D) stretching IRF at $\sim 3.3 \mu\text{m}$ (or $\sim 4.4 \mu\text{m}$) was passed through a broad-band pass filter (Optical Coating Laboratory) at $3 \mu\text{m}$ (or $4.5 \mu\text{m}$), and focused by a 5-cm focal length CaF_2 lens onto a liquid nitrogen cooled InSb photovoltaic detector (Graseby), which was matched with a preamplifier (EG&G). The detector/preamplifier, showing a rise time of approximately $3 \mu\text{s}$, was shielded by a copper cage to prevent electrical interference. The signals were averaged with a Tektronix TDS 400 MHz digital oscilloscope for ~ 3000 pulses in order to achieve a moderate signal/noise ratio in each measurement.

The average of the laser intensity used for exciting the benzene derivatives was $30\text{--}40 \text{ mJ cm}^{-2}$ pulse at a repetition rate of 10 Hz. For picolines, the average of the laser intensity was $1\text{--}2 \text{ mJ cm}^{-2}$ pulse at 10 Hz. To eliminate the multiphoton process, we measured the IRF decay profile as a function of the laser intensity, and chose the laser intensity range that the decay profile is not changed when the laser intensity increases twice. The

pressure of the sample was in the range of 20–40 mTorr. The diffusion was checked as follows. The decay profile for 20 mTorr of toluene was measured in the presence of 50 mTorr of helium gas and compared with that of 20 mTorr of toluene. We found that there is only less than 10% error due to the diffusion [19]. The pressure in the closed cell was monitored with a 1-Torr MKS Baratron capacitance manometer.

All measurements were made at room temperature (298 ± 1 K). Toluene (99.9%), toluene- d_8 (99+%), *o*- (98%), *p*-xylene (99+%), *o*-, *p*-xylene- d_{10} (99+%), *p*-xylene- $\alpha,\alpha,\alpha',\alpha',\alpha',\alpha'-d_6$ (99+%), mesitylene (98%), mesitylene- d_{12} (98%), 2-picoline- d_7 (97%), and 4-picoline-methyl- d_3 (98%), purchased from Aldrich, were degassed by several freeze (77 K)–pump–thaw cycles before the experiment.

3. Results and discussion

Fig. 1 shows the IRF decay profiles of 30 mTorr toluene, toluene- d_8 , *p*-xylene, *p*-xylene- d_{10} , and mesitylene at 3.3 μm (C–H stretching) or 4.4 μm (C–D stretching). The decay signals after 3 μs (detector rise time) can be fit by the exponential function, as shown in Fig. 1. In order to compare the quenching efficiency, we consider the time τ at

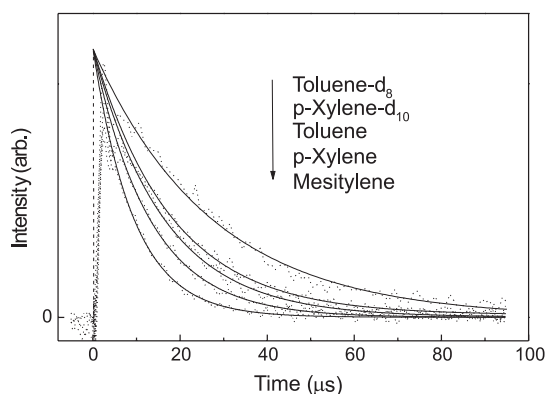


Fig. 1. Time-resolved IRF signals of C–H (or C–D) stretching vibration mode at 3.3 (or 4.4) μm range for 30 mTorr toluene, toluene- d_8 , xylene, xylene- d_{10} , and mesitylene. The decay profile after 3 μs is fitted by a single-exponential decay function, which is shown as the solid line.

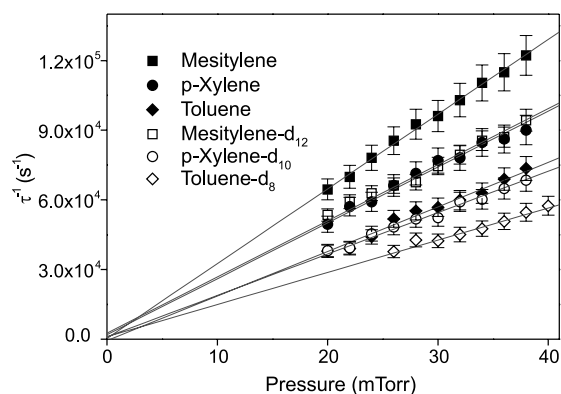


Fig. 2. The inverse of time constant (τ^{-1}) as a function of sample pressure, for toluene, toluene- d_8 , *p*-xylene, *p*-xylene- d_{10} , mesitylene, and mesitylene- d_{12} . The line is a linear fit for the data points, whose slope provides the averaged rate constant (k) of an excited molecule by an unexcited parent molecule.

which the IRF intensity drops to I_0/e . The plot of τ^{-1} vs. pressure produces a straight line with slope k , as illustrated in Fig. 2. Let us define k as an averaged rate constant for the overall quenching process. For toluene, $k = (1.9 \pm 0.1) \times 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ was obtained from the linear fit. In the case of deuterated benzene derivatives, the decay curve of C–D IRF was better fitted by the biexponential function, which has a 20 times slower component than the other. The slow decay component takes less than 10% of the total decay amplitude. This will be discussed later. The k value of deuterated molecules was obtained from the single-exponential fit, only at an early time range where the contribution of the slow rate decay component is negligible. The k values for all benzene derivatives (toluene, toluene- d_8 , *p*-xylene, *o*-xylene, *p*-xylene- d_{10} , *p*-xylene- d_6 , mesitylene, and mesitylene- d_{12}) and deuterated picolines (2-picoline- d_7 and 4-picoline- d_3) are as given in Table 1.

Using the k value, we define a quenching probability as k/k_{LJ} , where k_{LJ} is the Lennard-Jones bimolecular collision rate constant, $k_{\text{LJ}} = (8\pi kT/\mu)^{1/2} \sigma_{\text{LJ}}^2 \Omega$, where σ_{LJ} is the collision diameter and Ω is the collision integral. The value of Ω can be calculated from the following relation [24]: $\Omega = [0.636 + 0.567 \log(kT/\epsilon)]^{-1}$, where ϵ is the Lennard-Jones well depth. The Lennard-Jones collision parameters were estimated from the

Table 1

The averaged rate constant (k), quenching probability (P_{LJ}), and average energy loss per collision $-\langle\Delta E\rangle$ at 298 ± 1 K

Collider	k (10^6 Torr $^{-1}$ s $^{-1}$)	k_{LJ}^a (10^6 Torr $^{-1}$ s $^{-1}$)	P_{LJ} (10^{-2} k/k_{LJ})	$-\langle\Delta E\rangle$ (cm $^{-1}$) at 25 000 cm $^{-1}$
Toluene	1.9 ± 0.2	23.7	8.0 ± 0.8	880 ± 70
Toluene-d $_8$	1.3 ± 0.1	22.7	5.7 ± 0.5	770 ± 60
<i>o</i> -Xylene	2.4 ± 0.2	25.1	9.6 ± 0.9	1080 ± 80
<i>p</i> -Xylene	2.5 ± 0.2	25.5	9.8 ± 0.9	1080 ± 80
<i>p</i> -Xylene-d $_{10}$	1.8 ± 0.2	24.4	7.4 ± 0.7	940 ± 80
<i>p</i> -Xylene-d $_6$	2.5 ± 0.2 (C–H)	24.8	10.0 ± 0.9	1000 ± 80
	1.9 ± 0.2 (C–D)		7.7 ± 0.7	970 ± 80
Mesitylene	3.2 ± 0.2	26.7	12.0 ± 0.9	1240 ± 80
Mesitylene-d $_{12}$	2.5 ± 0.2	25.5	8.9 ± 0.8	1100 ± 80
2-Picoline-d $_7$	1.9 ± 0.1	22.2	8.6 ± 0.8	950 ± 90
2-Picoline ^b	2.6 ± 0.2	23.0	11.0 ± 0.9	1140 ± 80
4-Picoline-methyl-d $_3$	2.7 ± 0.2 (C–H)	23.3	12.0 ± 1.0	1050 ± 90
	2.1 ± 0.2 (C–D)		9.0 ± 0.9	1010 ± 90
4-Picoline ^b	2.7 ± 0.2	23.6	11.0 ± 1.0	1140 ± 80

^a Lennard-Jones collision rate constant, $k_{LJ} = (8\pi kT/\mu)^{1/2} \sigma^2 \Omega$, where σ and Ω are the diameter and integral, respectively.^b Ref. [19].

following semi-empirical relations with the critical temperature (T_c), and the critical pressure (P_c); $\sigma_{LJ} = (2.3454 + 0.2972\omega)(T_c/P_c)^{1/3}$ and $\varepsilon/k = (0.8082 - 0.4504\omega)T_c$. ω is estimated from $\omega + 1 = 3\theta/7(1 - \theta)\log P_c$, where $\theta = T_b/T_c$ (T_b is the boiling temperature). The k_{LJ} was calculated as 23.7×10^6 Torr $^{-1}$ s $^{-1}$ for toluene, 25.1×10^6 Torr $^{-1}$ s $^{-1}$ for *o*-xylene, 25.5×10^6 Torr $^{-1}$ s $^{-1}$ for *p*-xylene, and 26.7×10^6 Torr $^{-1}$ s $^{-1}$ for mesitylene from the known critical point constants [20]. For the deuterated isomers, the values of σ_{LJ} and ε are assumed to be the same as those of hydrogen compounds. The quenching probability $P_{LJ} = k/k_{LJ}$ is calculated for all compounds, as given in Table 1. For toluene and toluene-d $_8$, the quenching probability is calculated as $(8.0 \pm 0.8) \times 10^{-2}$ and $(5.7 \pm 0.5) \times 10^{-2}$, respectively. For the hydrogenated and deuterated benzene series, the quenching probability increases almost linearly with the number of methyl groups, by $\sim 1.5 \times 10^{-2}$ per methyl group. The quenching probability of toluene is less than that of 2-picoline or 4-picoline. The quenching probabilities of *o*- and *p*-xylenes are almost same, showing that the methyl group enhances the quenching efficiency without any significant hindrance from adjacent methyl group. Deuteration of toluene, *p*-xylene, and mesitylene reduces the quenching probability by 2.3×10^{-2} , 2.4×10^{-2} , and 3.1×10^{-2} , respec-

tively, corresponding to 2.9×10^{-3} , 2.4×10^{-3} , and 2.6×10^{-3} per deuterium. 2-Picoline-d $_7$ also shows a quenching probability lower than 2-picoline by 2.4×10^{-2} , corresponding to 3.4×10^{-3} per deuterium, which is higher than those of methyl substituted benzenes.

As described elsewhere, the average vibrational energy can be extracted approximately from the observed time-dependent IRF intensity. A relative intensity $I'(t)$ can be defined as the following equation [7]:

$$I'(E) = \frac{1}{\rho_s(E)} \sum_{i=1}^{\text{modes}} \sum_{v_i=1}^{v_{\max}} v_i \rho_{s-1}(E - v_i h\nu_i),$$

where $\rho_s(E)$ and $\rho_{s-1}(E - v_i h\nu_i)$ are, respectively, the density of states for all s oscillators at energy E , and that for $s - 1$ oscillators, omitting one mode and the energy contained in it. The summations are carried out for all vibrational modes that emit in the wavelength range we probe and for all vibrational levels of each mode permitted by conservation of energy. The density of states was evaluated using the vibrational frequency assignment [25,26] and the Whitten–Rabinovitch semi-empirical method [27]. The experimental IRF intensity decay curve was converted to the energy decay curve following the n th order polynomial fit, and subsequently differentiated with respect to the

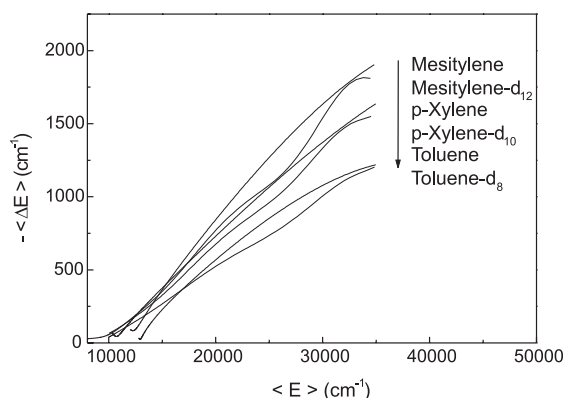


Fig. 3. The average vibrational energy loss per collision $-\langle\Delta E\rangle$ as a function of average vibrational energy $\langle E\rangle$, for toluene, toluene- d_8 , *p*-xylene, *p*-xylene- d_{10} , mesitylene, and mesitylene- d_{12} .

Lennard-Jones collision number to obtain the average energy loss per collision $\langle\Delta E\rangle$. The resulting curves of $-\langle\Delta E\rangle$ as a function of average vibrational energy $\langle E\rangle$ for the methyl substituted benzenes are shown in Fig. 3. The $-\langle\Delta E\rangle$ value increases with $\langle E\rangle$, which is consistent with those of aromatic molecules reported by other groups [6–11]. The $-\langle\Delta E\rangle$ values at $\langle E\rangle = 25\,000\text{ cm}^{-1}$ are given in Table 1.

The $-\langle\Delta E\rangle$ value of toluene, xylene, and mesitylene are 880 ± 80 , 1080 ± 90 , and $1240 \pm 90\text{ cm}^{-1}$, respectively, at $\langle E\rangle = 25\,000\text{ cm}^{-1}$. At $\langle E\rangle = 24\,000\text{ cm}^{-1}$, the $-\langle\Delta E\rangle$ value of toluene is 840 cm^{-1} , which is consistent with 847 cm^{-1} reported by Barker's group [8]. The $-\langle\Delta E\rangle$ value at $\langle E\rangle = 25\,000\text{ cm}^{-1}$ vs. the number of vibrational modes in molecule is plotted, as illustrated in Fig. 4. The $-\langle\Delta E\rangle$ values of the benzene series can be linearly correlated with the number of vibrational modes. The $-\langle\Delta E\rangle$ value of deuterated benzene is less than that of the corresponding hydrogenated benzene, but shows a linear increase with almost the same slope as that of the benzene series.

The results can be compared with those of pyridines having the same number of methyl groups [19], showing that the $-\langle\Delta E\rangle$ values of the benzene series are lower than those of the pyridine series. For example, the $-\langle\Delta E\rangle$ value of 2- and 4-picoline is 1140 cm^{-1} , while that of toluene is 880 cm^{-1} . The methyl substitution in toluene and

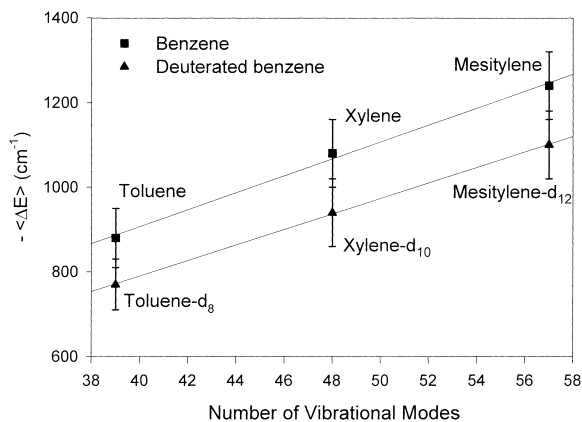


Fig. 4. The $-\langle\Delta E\rangle$ value at $\langle E\rangle = 25\,000\text{ cm}^{-1}$ of the benzene series as a function of the number of vibrational modes.

xylene enhances the $-\langle\Delta E\rangle$ value by 200 and 160 cm^{-1} , respectively, at $\langle E\rangle = 25\,000\text{ cm}^{-1}$. We reported that the methyl group in pyridine series increases the $-\langle\Delta E\rangle$ value by 200–400 cm^{-1} , depending on the position of methyl group [19]. These comparisons show that the contribution of methyl group in the $-\langle\Delta E\rangle$ value depends apparently on the presence of a dipole moment in a molecule.

For the collisional energy relaxation dynamics, two distinct pathways have been suggested from a number of experimental [13–17,28–30] and theoretical works [31–35]. The first type is the V–R/T energy exchange mediated through short-range repulsive wall of the donor/acceptor potential, which leads to a substantial gain in the energy content of the acceptor. The second type is the V–V energy exchange mediated by long-range attractive region of the donor/acceptor potential [31], which results in little rotational and translational excitation accompanying the vibrational excitation. A quasi-classical trajectory calculation study of energy transfer in benzene–benzene collisions suggests that the V–V energy transfer is a dominant quenching channel in the collisional relaxation [32].

Despite the number of vibrational modes being lesser than that of benzene, the pyridines show a higher collisional quenching efficiency. The dipole moment in the pyridine molecule would increase the attractive intermolecular interaction. As the

long-range attractive part of the intermolecular potential is known to mediate the V–V energy transfer, a higher quenching efficiency of pyridine molecules would result from the enhanced V–V energy transfer process. According to the transition dipole coupling model suggested by Dai's group [29,30], successful V–V energy transfer takes place to the infrared active vibrational modes of bath molecule. Pyridine has a greater number of infrared active vibrational modes compared to benzene [25,26].

For the deuterium substitution of toluene, the $-\langle\Delta E\rangle$ value decreases by 110 cm^{-1} at $\langle E\rangle = 25000\text{ cm}^{-1}$ (Table 1), which is consistent with 100 cm^{-1} at $\langle E\rangle = 24000\text{ cm}^{-1}$, reported by Barker's group [8]. This decrease corresponds to 14 cm^{-1} for one deuterium substitution. The deuterium substitution of *p*-xylene and mesitylene decreases the $-\langle\Delta E\rangle$ value by 140 and 190 cm^{-1} , respectively, which correspond to about 14 and 16 cm^{-1} per deuterium. The $-\langle\Delta E\rangle$ values of deuterated pyrazine and pyridine are 570 and 670 cm^{-1} , while those of hydrogenated molecules are 770 and 930 cm^{-1} , respectively [19]. One deuterium substitution reduces the $-\langle\Delta E\rangle$ value by 50 and 52 cm^{-1} for pyrazine and pyridine, respectively. For benzene, we estimated that the deuterium substitution reduces the $-\langle\Delta E\rangle$ value by 49 cm^{-1} per deuterium at $\langle E\rangle = 24000\text{ cm}^{-1}$ from the Barker group data [8] that the $\langle\Delta E\rangle$ values are 869 and 576 cm^{-1} for benzene and benzene- d_6 , respectively. Therefore, the deuterium effect of methyl substituted benzene is lesser than those of benzene, pyrazine, and pyridine having no methyl group. The deuterium substitution of 2-picoline decreases the $-\langle\Delta E\rangle$ value by 190 cm^{-1} , which corresponds to 27 cm^{-1} per deuterium, and thus, its deuterium effect is more significant than those of methyl substituted benzenes.

Deuteration affects only higher frequency vibrational modes significantly; the C–D stretching mode frequency is about 29% lesser than that of the C–H stretching, while the lower frequency modes are almost unaffected. A significant deuterium effect in the average energy loss can be expected from the V–V energy transfer channel. There is little deuterium effect in the V–R/T energy transfer that usually occurs via the lowest fre-

quency modes. Therefore, the low deuterium effect of methyl substituted benzenes than those of benzene, pyrazine, and pyridine, definitely indicates that the low frequency modes, such as methyl internal rotation, probably would open the gateway for V–R/T energy transfer. The increased deuterium effect of 2-picoline could have resulted from the contribution of a V–V energy transfer channel, as explained above.

In the quenching of *p*-xylene- d_6 , the quenching probability of C–H stretching is the same as that of *p*-xylene, while the C–D stretching is quenched by a slightly higher probability than that of *p*-xylene- d_{10} . The result indicates that the quenching probability is not much influenced by the number of high frequency C–H stretching modes, providing another evidence for the V–R/T energy transfer channel via low frequency vibrational modes. A similar behavior is observed from 4-picoline- d_3 . The $-\langle\Delta E\rangle$ value of *p*-xylene- d_6 is less than that of *p*-xylene by 80 cm^{-1} , which is about a half of that of *p*-xylene- d_{10} . For 4-picoline- d_3 , the $-\langle\Delta E\rangle$ value is less than that of 4-picoline by 90 cm^{-1} by substituting only three deuterium atoms, showing that its deuterium effect is more significant than that of *p*-xylene- d_6 . Therefore, the results of partially deuterated *p*-xylene- d_6 and 4-picoline- d_3 consistently show that the methyl group plays an important role in the quenching process of methyl substituted benzene and that there is an increase of the V–V energy transfer quenching channel in pyridines. The result that the same $-\langle\Delta E\rangle$ value was obtained from both C–H and C–D IRF decays confirms the fact that the vibrational energy redistribution is fast relative to the duration of a collision.

Barker's group observed the unusual energy dependence of $-\langle\Delta E\rangle$ for benzene- d_6 and toluene- d_8 , exhibiting a maximum and then decreases as $\langle E\rangle$ increases [8]. We also observed that the deuterated molecules show a somewhat different behavior of the $-\langle\Delta E\rangle$ curve from the hydrogenated molecules, as seen in Fig. 3. This seems to have resulted from the decay profile showing the long decay time component as explained above. However, for 2-picoline- d_7 and deuterated pyrazine and pyridine, the slow decay rate component is not observed and the $-\langle\Delta E\rangle$ curve shows a smooth

increase as $\langle E \rangle$ increases, as for other hydrogenated azabenzene and benzene derivatives. In benzene series, the UV laser intensity is about 20 times higher than those of picolines, so this slow decay rate component may be related to the UV excitation laser power. Barker's group suggests the contribution of a thermal effect in the low frequency range [36]. More studies are needed to discuss this further. Since the quenching probability and the $-\langle \Delta E \rangle$ value increase linearly with the number of methyl groups by almost the same slope as that of hydrogenated molecules, it is difficult to suggest a different quenching dynamic for the deuterated benzene molecules based only on the curve shape.

In summary, the collisional quenching of vibrationally excited methyl substituted benzene and deuterated series by unexcited parent molecules has been studied using the time-resolved IRF spectroscopic technique. The vibrationally excited benzene derivatives are produced by absorbing the Nd-YAG 266 nm laser pulse, and the time resolved IRF of C–H (or C–D) stretching modes at 3.3 μm (or 4.4 μm) was probed as a function of pressure. We estimated an averaged quenching rate constant and a quenching probability of the vibrationally excited molecule by parent bath molecule from an exponential fit to the IRF decay profile. The average vibrational energy loss per collision, $-\langle \Delta E \rangle$, is obtained by inverting the IRF intensity to the average vibrational energy. Both the quenching probability and the collisional average energy loss of methyl substituted benzenes increase linearly with the number of methyl groups. The collisional quenching efficiency of pyridine series is higher than that of the benzene series, indicating that the dipole moment in the pyridine molecule facilitates the V–V energy transfer. One deuterium substitution of methyl substituted benzene decreases the $-\langle \Delta E \rangle$ value by about 15 cm^{-1} , whereas it is $\sim 50 \text{ cm}^{-1}$ for azabenzene and benzene molecules having no methyl group, at the average vibrational energy of 25 000 cm^{-1} . These results provide a strong evidence that the low frequency modes, such as methyl internal rotation in methyl substituted benzene, increases the quenching efficiency mainly via the V–R/T energy transfer. This conclusion can be confirmed

by the results of the partially deuterated molecules, *p*-xylene- d_6 and 4-picoline- d_3 .

Acknowledgements

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