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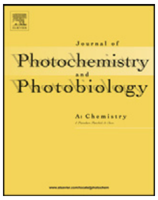

Formation of *p*-xylylene from *p*-xylene by a two-photon process and hexamethyl Dewar benzene from hexamethylbenzene by a one-photon process at 193 nm

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ABSTRACT

While studying a series of methyl-substituted benzenes, $C_6H_{6-n}(CH_3)_n$ with $n = 2, 3, 4, 6$, and perfluorobenzene in the gas phase using 193-nm laser flash photolysis, we observed the formation of *p*-xylylene (benzoquinodimethane) due to the elimination of two hydrogen atoms as a result of a two-photon process. The results were explained in terms of an intermediate hot molecule formed by internal conversion which finally led to the ground electronic state. Quadratical dependencies on the photoproducts were observed for toluene, xylene, mesitylene, and perfluorobenzene in the presence of a foreign gas, while linear dependencies were observed for durene and hexamethylbenzene. Dewar-type benzene was detected from photolysis of hexamethylbenzene.

1. Introduction

Vacuum ultraviolet (VUV) and ultraviolet laser chemistry, in which molecules are excited to high electronic states but at energy levels below the ionization potential, have been extensively studied. In the VUV (193 nm) laser chemistry of benzene, a hot molecule, a highly vibrationally excited state in the ground electronic state, denoted S_0^{**}, is a key intermediate. The products of benzene can be explained in terms of passing through S_0^{**} [1–6].

Products (1.1) are the result of a one-photon process at 184.9 nm: fulvene [1], 1-3-hexadiene-5-yne [2], and phenyl radical (C–H dissociation) [3,4]. Products (1.2) are the results of two-photon processes through S_0^{**}: C_2–C_4 fragments [5], two hydrogen-eliminated molecules [3], 1-3-hexadiene-5-yne, and others [6]. The hot benzene, S_0^{**}, at 193 nm was detected in transient spectra in 1983 by one of the authors [7].

Scheme 1 has been thought to apply to alkyl-substituted benzenes. A benzyl radical produced by toluene C–H dissociation was observed in 1985 as a product (1.1) [8]. Hot molecules can be an intermediate for reactions following the second and/or third photon absorption. A benzyl radical formed [9] by two-photon absorption was also found as a product (1.2) of Scheme 1. Detailed analysis of Scheme 1 [10–12], several reviews [13–15], and comprehensive studies [16] based on a new experimental technique, multimass ion imaging, are now available. In addition, target molecules of Scheme 1 have been extended to bio-related molecules, including tryptophan at 193-nm nanosecond pulses [17] and adenine in the femtosecond time domain [18].

These photochemical mechanisms at 193-nm laser irradiation in Scheme 1 have been shown to work for single-substituted alkylbenzenes [10–16,19,20]. Doubly and triply substituted benzenes, xylenes and mesitylene, have been photolyzed, and a major part of the dissociation was explained in terms of Scheme 1 based on nanosecond laser photolysis and mass spectrometry [10,21–25]. Benzocycloalkenes and cyclophanes can be regarded as dialkyl-substituted benzenes and dissociate into the corresponding radicals and molecules via Scheme 1 [26–28]. Isomerizations of toluene [19] and *m*-xylene [24] have been found by multimass ion imaging techniques to compete with direct C–C and C–H dissociations.

A series of methyl-substituted benzenes, $C_6H_{6-n}(CH_3)_n$ with $n = 2, 3, 4, 6$, and perfluorobenzene were studied by conventional ArF laser flash photolysis. As expected, two-photon processes in the transient spectra occurred for toluene, xylene, and mesitylene in the presence of a foreign gas. One of the findings in the photolysis was *p*-xylylene formation due to the elimination of two hydrogen atoms as a result of a two-photon process, as shown in Scheme 1. Based on the cyclophane laser chemistry [27], and the elimination of two hydrogen atoms from benzene by two-photon absorption [3], xylylene formation from *p*-xylene is predictable and realized. The second finding is that hexamethyl Dewar benzene (HMDB) was produced as a final product from photolysis of hexamethylbenzene

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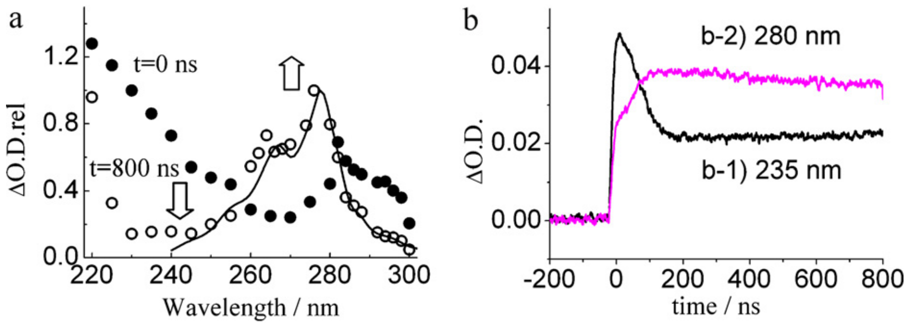
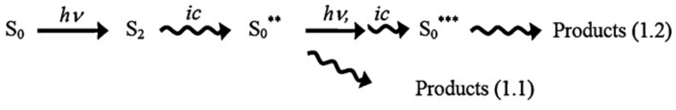


Fig. 1. (a) Transient absorption spectra of *p*-xylene at 1.3 kPa in the presence of 27 kPa of nitrogen at a laser fluence of 10 mJ/cm^2. Full circles (●) are at 0 ns, and open circles (○) at 800 ns. The normalized spectrum of *p*-xylylene (—) is formed by the photolysis of cyclophanes [27]. (b) Typical time profiles of transient signals are shown at 235 nm (b-1) and 280 nm (b-2). The initial decay component in (b-1) and the initial rise component in (b-2) are due to the collisional relaxation of hot species by nitrogen. The remaining components with almost constant absorbances for (b-1) and (b-2) after 200 ns are attributed to photoproducts (*p*-xylylene).



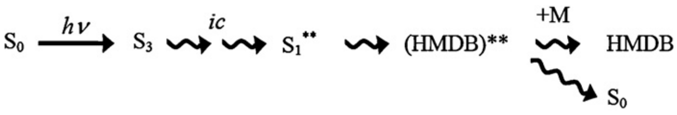
Scheme 1.

(HMB). The laser-intensity dependencies of the product formation showed a one-photon process. The theoretical study of benzene photoisomerization to Dewar benzene has predicted that this reaction occurs through an S_1 to S_0 conical intersection leading to Dewar benzene [29]. The crossing is suggested to occur in a high energy state in S_1. This concept can be applied to the present experimental results; some part of hot HMDB is collisionally relaxed to HMDB, as shown in Scheme 2, in the presence of a foreign gas M.

A foreign gas is effective in obtaining unstable photoproducts; otherwise they might decompose under collision-free conditions. In fact, 1-3-hexadiene-5-yne formation from benzene was identified in the presence of foreign gases [6]. Similar one-photon dependency has been observed for 1,2,4,5-tetramethylbenzene (durene), suggesting that isomerization is effective for multi-substituted benzenes. Multi-substituted benzenes have been shown to form Dewar-type benzenes since the 1960s. Dewar benzene (DB) was derived from benzene itself, when the latter was photolyzed in the liquid phase [30]. Perfluorobenzene [31], 1,2,4,5-*tert*-butylbenzene [32], and hexakis(trifluoromethyl)benzene [33] are photochemically converted to the corresponding DBs. The observation of a one-photon process for durene and HBM indicates that multi-substituted benzenes can be easily converted to DBs.

2. Experimental

A conventional method of nanosecond laser photolysis was applied to gaseous benzenes in a quartz cell irradiated by an ArF excimer laser (Lambda Physik COMPex102: 193.3 nm, fwhm 14 ns, and maximum energy 200 mJ/pulse). The method was primarily the same as that previously described [6]. Time $t = 0$ ns was defined as the time at the peak absorbance in the transient signals, when a spiky signal was observed, as seen in Fig. 1b. The excitation wavelength of 193 nm pumps the S_3 state corresponding to the $^1E_{1u}$ state of benzene for the methyl-substituted benzenes $C_6H_{6-n}(CH_3)_n$ with $n = 2, 3, 4, 6$ [34].



Scheme 2.

The HMB and durene to be photolyzed were dissolved in cyclohexane, and a 100 μL drop of 8.3×10^{-3} M solution was deposited onto the bottom of the sample tube. The solvent was then pumped carefully away until the background pressure was less than 0.7 Pa, and 27 kPa of nitrogen gas was added. HMB and durene were sealed in a quartz tube and kept at 423 K for over 20 min before irradiation. The corresponding pressure of HMB was calculated to be 0.5 kPa at 423 K. The temperature was controlled by a chromel–alumel thermocouple and a heater combination. Other methylbenzenes and hexafluorobenzene were photolyzed at room temperature. The typical irradiation energy reached 40 mJ/pulse for product analysis and less than 35 mJ/pulse for flash photolysis.

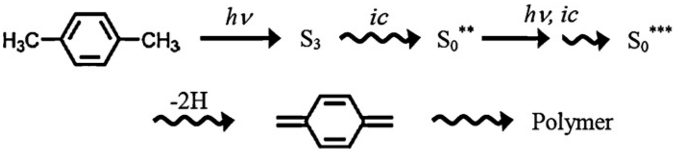
Benzene was purchased from Aldrich Chemical Co. (Milwaukee, WI) with a stated purity of 99.9%. Toluene and *p*-xylene were from Merck Japan (Tokyo, Japan) with stated purities of 99.5%. Mesitylene and durene were from Nacalai Tesque (Kyoto, Japan) with stated purities of 98%. Hexamethylbenzene (TCI, Tokyo, Japan; >99%), hexafluorobenzene (Aldrich Chemical Co.; >99%), and hexamethyl Dewar benzene (Aldrich Chemical Co.; >97%) were used as received. Nitrogen gas was purchased from Osaka Sanso (Osaka, Japan) with a stated purity of 99.999%.

3. Results and discussion

3.1. Formation of p-xylylene by a two-photon process of p-xylene

The results of the laser photolysis of *p*-xylene can be summarized as Scheme 3. Formation of hot *p*-xylene S_0^{**} by rapid internal conversion (ic) was probably complete in less than 1 ps, as benzene ic from S_2 occurs in 40 fs [35]. The second photon of 193-nm laser light pumps the S_0^{**} state to the S_3^{**} state, followed by internal conversion leading to S_0^{***}; subsequently, S_0^{***} loses 2H to form *p*-xylylene. These two-photon processes are considered to proceed in an excitation laser pulse of 20 ns. S_0^{***} is defined as hot *p*-xylene with an internal energy of $2h\nu$. The mechanism can be regarded as an extension of Scheme 1, which has been established for benzene, toluene, and some alkylbenzenes.

White smoke was seen immediately after laser irradiation, probably due to polymerization of *p*-xylylene. *p*-Xylene has been studied by laser flash photolysis, and the product of C–H disso-



Scheme 3.

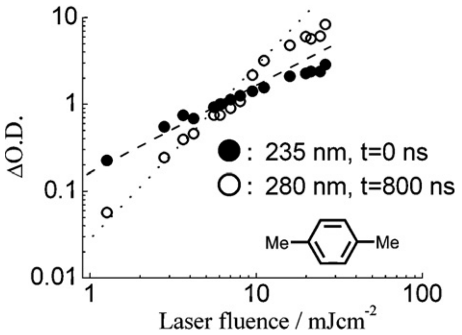


Fig. 2. The correlation between laser fluence and transient absorption of *p*-xylene at 0 ns (●) for 1.3 kPa in the presence of 27 kPa of nitrogen observed at 235 nm (S_0^{**}); the dotted line (...) has a slope of 1.0, indicating a one-photon process. The correlation between laser fluence and transient absorption of *p*-xylene at 800 ns (○) and 280 nm (*p*-xylylene) with the dashed line (----) has a slope of 2.0, indicating a two-photon process.

ciation to methyl benzyl radical has been recognized [10,21–24]. Furthermore, the rate constant has been well-explained in terms of a statistical model [10]. One-photon processes are completely quenched in the presence of foreign gases, as observed and discussed for the two-photon process of toluene [9].

The transient spectra, time profiles, and laser fluence dependencies in Figs. 1 and 2 support Scheme 3. The transient spectrum at 800 ns after irradiation corresponded to *p*-xylylene formation. The transients denoted by circles (○) (Fig. 1a) with a peak around 275 nm at a delay of 800 ns almost reproduce the spectrum (solid line in Fig. 1a) of *p*-xylylene, which was previously obtained by the photolysis of *p*-cyclophane [27].

The $t = 0$ ns spectrum in Fig. 1a in the wavelength region shorter than 260 nm can be assigned to hot *p*-xylene (S_0^{**}) formed by internal conversion from the pumped state of the S_3, as we previously observed for benzene and toluene [7,9]. The monotonical spectrum shape between 220 and 260 nm is similar to that of hot benzene molecules and is collisionally cooled to the spectrum at 800 ns in the presence of 27 kPa of nitrogen. The species with weak absorption in the wavelength region below 230 nm can be explained in terms of the shifted ground state absorption due to the temperature increase of the sample. The absorption spectrum to the S_2 state of the ground state *p*-xylene starts around 225 nm and has a peak at 210 nm. The absorbed energy is converted to vibrationally excited states and is collisionally averaged in the sample down to a red-shifted absorption.

The hump around 280–300 nm can be assigned to hot *p*-xylylene at the $t = 0$ ns spectrum in Fig. 1a. The xylyl (*p*-methylbenzyl) radical has a peak at 265 nm [10], and the spectrum of *p*-xylylene with a peak at 275 nm was previously obtained from the photolysis of *p*-cyclophane [27]; therefore, the transient spectrum at 800 ns can be assigned to *p*-xylylene. The xylyl radical by a one-photon process would not be included in the transient spectra. Xylyl radical formation due to the C–H bond dissociation from S_0^{**} by a one-photon process has been observed under collision-free conditions with the formation rate constant of $2.7 \times 10^5\ s^{-1}$ at 193-nm excitation [10]. This slow process can be completely quenched by addition of nitrogen as a foreign gas. The survival of multiphoton processes via S_0^{**} after quenching the slow process has been thoroughly discussed for the case of toluene [9] and has also been applied to the case of benzene photolysis [6]. The xylyl radical by a two-photon process was not clearly observed, but *p*-xylylene was detected in the transient spectra. The activation energy of xylyl radical formation is 381 kJ/mol, but the xylyl radical decomposes to *p*-xylylene with an activation energy of 295 kJ/mol [36]. This low activation energy was probably the reason why *p*-xylylene was easily detected. As a result, the dissociation rates of the two hydrogen atoms from the hot *p*-xylene S_0^{***} were faster than the collisional relaxation rate by the added gas.

The time profiles in Fig. 1b also support Scheme 3; the profile (b-1) at a short wavelength of 235 nm shows collisional cooling of the hot species of S_0^{**}, and the profile (b-2) around the peak of *p*-xylylene at 280 nm shows collisional relaxation – in other words, collisional spectral narrowing.

The laser fluence dependencies in Fig. 2 support Scheme 3. The transient absorption of *p*-xylene at 0 ns (●) and 235 nm is assignable to S_0^{**}, which is produced by one-photon absorption. In fact, the species at 0 ns (●) and 235 nm can be plotted on a line with a slope of 1.0, indicating a one-photon process. The photoproduct *p*-xylylene at 800 ns and 280 nm (○) can be plotted on a line with a slope of 2.0, indicating that *p*-xylylene forms by a two-photon process. This behavior is similar to that observed for the case of benzene irradiated by 193-nm laser pulses [6]. Scheme 3 well explains that the primary species is hot *p*-xylene (S_0^{**} and that the formation of *p*-xylylene requires the second photon).

3.2. One-photon process for formation of hexamethyl Dewar benzene

The results for mesitylene are consistent with Scheme 1, i.e., the laser fluence dependencies showed that the transient species at $t = 0$ (expected to be S_0^{**}) have a slope of 1.0 and at $t = 800$ ns (products) a slope of 2.0 (Fig. 3). Mesitylyl radical due to H elimination from photo-excited S_0^{**} (S_0^{***}) is the most probable candidate for the product according to Scheme 1. In contrast, HMB and durene showed a slope of 1.0 for both transients ($t = 0$ and 800 ns), indicating that a different mechanism is at work for $C_6H_{6-n}(CH_3)_n$ with $n = 4$, 6. The one-photon process for HMB is tentatively explained in Scheme 2. In fact, HMDB was detected by gas chromatography and gas chromatography–mass spectrometry (GC–MS) after HMB was irradiated with 193-nm laser light. Only one-shot irradiation of HMB afforded the GC-MS signal of HMDB. Products from hexafluorobenzene have not been identified by 193-nm excitation, but hexafluoro Dewar benzene (HFDB) may be a candidate, as HFDB has been reported to be a product by 253.7-nm excitation [31].

Transient spectra and time profiles can be explained in terms of Scheme 2—i.e., after rapid internal conversion through a conical intersection, hot HMDB should be included in the spectrum at $t = 0$ ns in Fig. 4a and is collisionally cooled to a relaxed HMDB, which corresponds to the spectrum at $t = 400$ ns in Fig. 4a. During the course of the collisional relaxation, some of the hot HMDB would be relaxed to the ground state HMB. HMDB has an absorption peak close to but shorter than 200 nm, as shown in Fig. 4c, and its tail is extended to a long wavelength region; therefore, the absorption of hot HMDB is expected in a wavelength region longer than 200 nm. The spectrum at $t = 0$ in Fig. 4a and time profiles in Fig. 4b are consistent with this explanation; the hot HMDB is collisionally relaxed in the presence of 27 kPa of nitrogen, while almost flat signals are observed in the absence of foreign gas. The observed relaxed signals HMDB in Fig. 4a can be plotted on the spectrum of HMDB in Fig. 4c. The sharp decrease in the wavelength region shorter than 235 nm in the transient spectra in Fig. 4a can be attributed to the ground-state depletion of HMB. The open circles were plotted without data correction and the open squares were plotted after correcting for HMB depletion under the assumption that 55% of the excited HMB is converted to HMDB and the remaining 45% returns to HMB. The spectra showed some absorptions around the 250–300 nm region, which were not identified.

Since DB was photochemically generated in the liquid phase [30], some substituted benzenes were successfully converted to the corresponding DBs [31–33]. Palmer et al. have predicted that the isomerization occurs at a conical intersection from a high-energy region of an S_1/S_0 crossing surface [29]. Just after crossing,

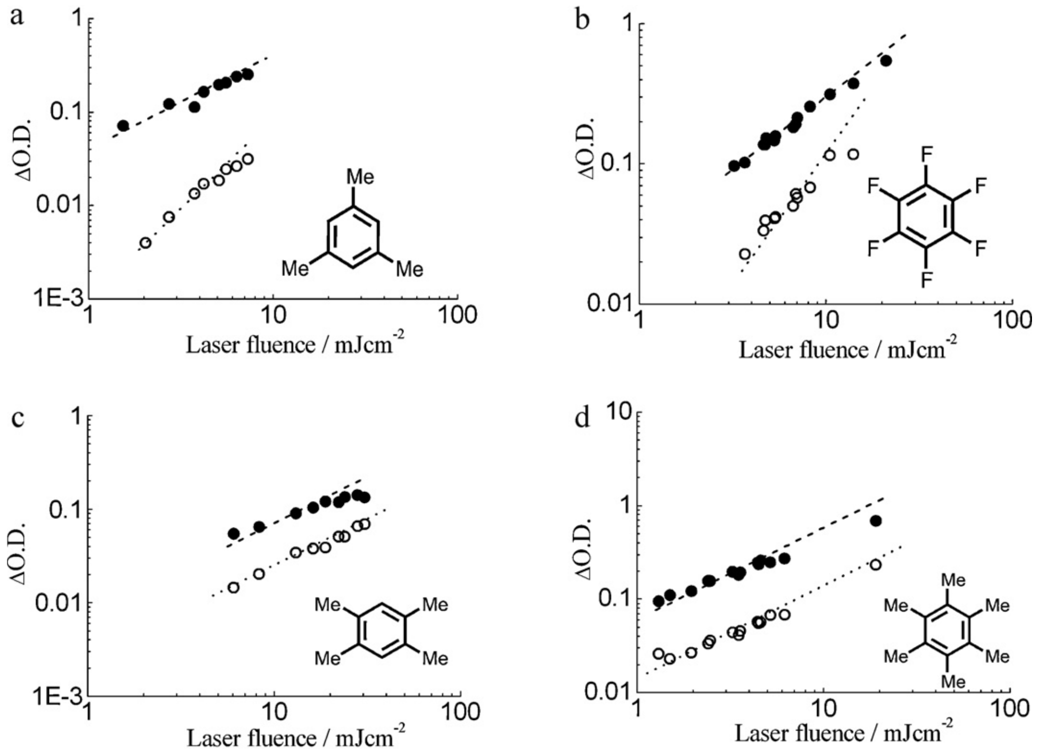


Fig. 3. The correlation between laser fluence and transient absorption at 0 ns (●) for 0.5 kPa in the presence of 27 kPa of nitrogen observed at 235 nm (expected to be S$_0^{**}$) and at 275 nm at 800 ns; the generated products are (a) mesitylene, (b) hexafluorobenzene, (c) durene, and (d) hexamethylbenzene. The products at 800 ns (○) appear to have been formed by two-photon processes for mesitylene and hexafluorobenzene, and by one-photon processes for durene and hexamethylbenzene. The dotted lines (. . .) have a slope of 1.0 for all four cases. The dashed lines (- - - -) have a slope of 2.0 in panels (a) and (b), and 1.0 in (c) and (d).

there is an excess of energy; therefore, the hot DB requires rapid cooling to reach a state with a low internal energy, and will otherwise yield a wider distribution of products, including some that return to the S$_0$ state. Efficient isomerization has been observed for substituted benzenes. The following two observations are notable with regard to the isomerization. The low-energy difference between HMB and HMDB has been estimated to be 234–251 kJ/mol, versus a difference of 331 kJ/mol between benzene and Dewar benzene [37]. Another point is the effective cooling provided by the added gases. The larger the size of the molecule,

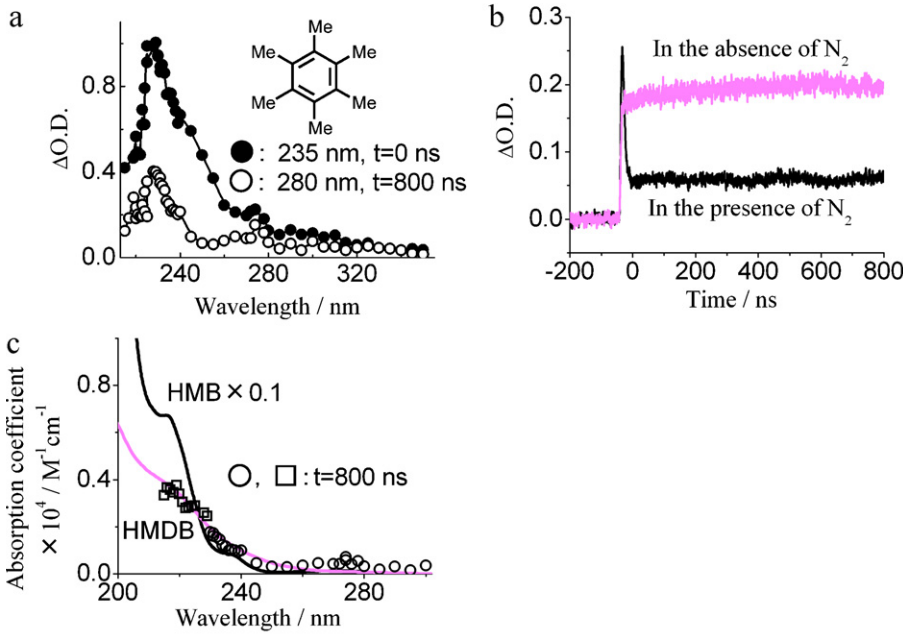


Fig. 4. (a) Transient spectra at $t = 0$ (●) and $t = 400$ ns (○) of hexamethylbenzene in the presence of 27 kPa of nitrogen, with a laser fluence of 10 mJ/cm^2. (b) A typical time profile at 235 nm for 0.5 kPa of hexamethylbenzene in the absence (upper trace) and presence (lower trace with a spike around $t = 0$) of 27 kPa of nitrogen. (c) Absorption spectra of hexamethylbenzene (gray line) and hexamethyl Dewar benzene (black line). Open circles are the points of the spectrum at $t = 800$ ns from Fig. 4a. Open squares (□) are plotted after correction for hexamethylbenzene depletion with a conversion efficiency of 0.55 to hexamethyl Dewar benzene.

the higher the energy of collisional energy transfer. Energy-transfer quantities from self-collisions of *p*-xylene are 1.7 times those of benzene [38].

3.3. Two-photon process versus one-photon process

If the molar extinction coefficient of the intermediate of a two-photon process is high enough at the irradiation wavelength, the two-photon process will be dominantly observed, while a low molar extinction coefficient of the intermediate will lead to a one-photon process. In the case of benzene, the two-photon intermediate S_0^{**} is predicted to have a molar extinction coefficient of 8300 M^{-1} cm^{-1} at a laser wavelength of 193 nm, while the ground state benzene has a coefficient of 4650 M^{-1} cm^{-1} [6]. The molar extinction coefficients at a high temperature can be evaluated using a modified Sulzer–Wieland model. The Sulzer–Wieland model was originally developed for explaining the absorption spectra of diatomic molecules at a high temperature, and a modified version of the model has been useful for polyatomic molecules, including benzene [7]. These predictions indicate that the benzene system sometimes displays a significant increase in the molar extinction coefficient during excitation. It is quite reasonable, then, that a two-photon process occurs. On the other hand, a dominant one-photon process has been found to occur in the cases of C–H and C–C dissociations of tetramethylethylene (TME) and C7 olefins [39]. The photochemistry can be explained in terms of dissociation via S_0^{**} produced by internal conversion. TME has a maximum coefficient of 14,400 M^{-1} cm^{-1} at 187 nm and 9250 M^{-1} cm^{-1} at 193 nm. In the case of the TME S_0^{**} the coefficient would be greatly reduced based on the modified Sulzer–Wieland model for an absorption spectrum at high temperature, and as a result, a one-photon process would be dominant. Prediction of the change in the molar extinction coefficients is an indispensable requirement when judging whether two-photon or one-photon processes occur.

On the basis of the above requirement, a two-photon process would occur in the laser photolysis for systems of toluene and hexafluorobenzene, while a one-photon process would be expected for HMB and durene based on the VUV spectra [34,40]. The molar extinction coefficient of toluene is 4900 M^{-1} cm^{-1} at 193 nm, while that of the hot toluene S_0^{**} produced after internal conversion is predicted to be 20,000 M^{-1} cm^{-1}; in fact, two-photon benzyl radical formation has been observed for the toluene system [9]. For HFB, an increase in the molar extinction coefficient at 193 nm and a two-photon process are expected from the results of the laser photolysis of HFB [41]. The molar extinction coefficient of HMB is 60,000 M^{-1} cm^{-1} at 193 nm for the $^1E_{1u}$ transition [34], while that of the HMB** (= S_0^{**}) is predicted to be considerably lower on the basis of the Sulzer–Wieland model. If the hot species is hot HMDB (HMDB**), according to Scheme 2, the original $V \leftarrow N$ transition should be lower in the hot state at 193 nm. The absorption peak of HMDB is not clear, but would be shorter than 201 nm, and the molar extinction coefficient is only 2800 M^{-1} cm^{-1} at room temperature at this wavelength [42]. The absorption spectrum will be broadened and the molar extinction coefficient of HMDB** will be well lowered. Neither S_0^{**} nor HMDB** would have molar extinction coefficients substantially lower than that of 60,000 M^{-1} cm^{-1} for HMB. The one-photon process of HMB at 193 nm is acceptable. It is not easy to predict whether the one- or two-photon process is dominant for *p*-xylene; the results showed the two-photon process, and the one-photon process is a likely mechanism for mesitylene; however, the two-photon process was seen at a particular wavelength of 235 nm in the laser intensity dependence.

4. Conclusions

A series of methyl-substituted benzenes and perfluorobenzenes were irradiated in the gas phase by an ArF excimer laser. One of the findings was the formation of xylylene or the elimination of two hydrogen atoms as a result of a two-photon process of *p*-xylene, and the other was the generation of Dewar-type benzene from HMB as an example of a one-photon process. The isomerization would occur via a conical intersection, and the hot species would be collisionally relaxed to HMDB and in part to HMB. The two-photon process, as shown in Scheme 1, can be enhanced under the condition that the intermediate S_0^{**} has a reasonably high molar extinction coefficient at the laser wavelength; otherwise, a one-photon process will be dominant. The one-photon process for HMB indicates that the plausible intermediate HMDB** has an extinction coefficient too low to effectively absorb the second photon of the laser pulse within the excitation pulse duration.

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