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The photodissociation of toluene studied by forward photofragment translational spectroscopy

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The translational energies of different fragments produced in laser induced unimolecular reactions are investigated in a molecular beam experiment. The time-of-flight of the photoproducts is measured in the forward direction with a mass spectrometer. By operating the ion source at low electron impact energies it is possible to nearly eliminate fragmentation and observe the nascent products at their parent mass. With this technique the primary and secondary reaction channels can be identified and branching ratios and product translational energy distribution down to small kinetic energies can be measured. The method is illustrated in a study of the photodissociation of toluene (methylbenzene) at three excitation energies (E_{ex} =51 590, 52 240, and 63 240 cm⁻¹). From the measured product time-of-flight spectra the branching ratio as well as the translational energy distributions of the product molecules benzyl+H and phenyl+CH₃ in the two reaction channels were determined. The measured product energy distributions are compared with RRK (Rice–Ramsperger–Kassel) and SACM (statistic adiabatic channel model) statistical theories. The experimental results agree very well with the SACM theory for the phenyl, but not for the benzyl products. This is attributed to a barrier in the exit channel for the latter product. © 1995 American Institute of Physics.

I. INTRODUCTION

Unimolecular reactions are important intermediates in complex reaction processes, for example, in atmospheric chemistry,^{1,2} in combustion processes,³ in plasma physics or in reactions in liquids.⁴ They also provide an ideal means for the study of molecular dynamics since the number of reaction parameters is reduced compared to bimolecular reactions.

For the study of laser-induced unimolecular reactions of polyatomic molecules in the gas phase under nearly collision free conditions, essentially two experimental techniques have been exploited.⁵ Several variations on time-resolved pumpprobe techniques⁶ involving for detection either absorption spectroscopy,^{7,8} laser-induced fluorescence $(LIF),^9$ resonance-enhanced multiphoton ionization (REMPI),¹⁰ and direct light emission¹¹ have been used. The other method is photofragment translational spectroscopy^{12,13} under molecular beam condition. The goal is to determine the primary products and their branching ratio, to measure the lifetime of the excited reactant molecule, and to determine the distribution of the excess energy on the internal quantum states and translational degrees of freedom.6,14

In the present work photofragment translational spectra in a molecular beam experiment have been measured after nanosecond laser pulse excitation of the reactant molecules. In contrast to conventional photofragment translational spectroscopy the product molecules are detected in the laboratory frame only in forward direction. Products with low kinetic energy can now be observed and no rotatable source or detector is needed. The interpretation of the measured data is straightforward if the product angular distribution is isotropic in the center-of-mass frame, as is the case for the molecular systems studied in this work. By varying the distance between laser excitation and detection zone, the time-of-flight resolution and the desired product signal (given by the detection solid angle) can be optimized as required. The detection of reaction products on the axis of the incident reactant beam is possible by the reduced ion fragmentation of the reactant molecules at low energy of the ionizing electrons.^{15,16} By choosing the electron energies just above the ionization potential of the product radical but below the appearance potential of the reactant molecule, only the product radicals are detected.^{16–19}

The advantages and implications of this technique are demonstrated in the present article for the laser-induced unimolecular bond fission of toluene (methylbenzene). After photoexciting the molecules at 193 nm to the electronically excited S_3 state, high vibrational states in the electronic ground state are populated via fast internal conversion ($\langle ps \rangle$).^{20,21} The excited complex lives a few hundred nanoseconds (cf. Table I) before it decays to products with small kinetic energies. The reaction has been investigated extensively in several groups with different methods and makes toluene an ideal system for demonstrating the new experimental technique. In previous experiments two reaction paths R_1 and R_2 were found



Thermal rate constants for the reaction channel R_1 at 300 K and in the temperature range from 1200 to 1500 K to-

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TABLE I. Survey of experimental studies of the specific rate constants of the photodissociation of toluene.

E_{ex} (cm ⁻¹)	Specific rate constants (s^{-1})	Method	Detected product	Beam/cell	Reference
46 020	$1.5 \pm 1 \times 10^{5}$	LIF	H atom	Cell	32
52 080	$1.9\pm0.2 imes10^{6}$	UV Absorption	Benzyl	Cell	25
52 080	$2.6\pm0.5\times10^{6}$	LIF	H atom	Cell	31
52 730	$2.01 \pm 0.04 \times 10^{6}$	UV Absorption	Benzyl	Cell	28
52 730	$1.9\pm0.2 imes10^{6}$	UV Absorption	Benzyl	Cell	8
52 730	$3.0\pm0.3\times10^{6}$	LIF	H atom	Cell	32
52 730	$2.2 \pm 1.0 \times 10^{6}$	(2+1)REMPI	Methyl	Cell	33
52 730	$2.5\pm0.2\times10^{6}$	(3+1)REMPI	Methyl	Beam	35
52 730	$2.3\pm0.2\times10^{6}$	(1+1)REMPI	H atom	Beam	35
64 450	$9.3\pm0.7\times10^{7}$	UV Absorption	Benzyl	Cell	30

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gether with the rate constants for the reverse reaction have been previously determined from extensive shock wave studies using time-resolved UV absorption.^{22–24} The same timeresolved UV absorption technique was used to measure *specific* rate constants of *laser*-induced unimolecular reactions of toluene and other alkyl benzenes.^{7,8,25,27–30} Instead of probing the benzyl radical via UV absorption, the reaction channel R_1 was also studied via Lyman- α laser-induced fluorescence (LIF) of the H atom reaction product.^{31,32} With this detection method specific rate constants from the temporal behavior (cf. Table I) as well as mean translational energies from the LIF Doppler profile (cf. Table III) were obtained.^{31,32}

The second reaction path R_2 to a phenyl radical and a methyl radical was investigated by Troe and co-workers using (2+1) resonance-enhanced multiphoton ionization (REMPI) of the methyl radical at 333.5 nm³³ and nonresonant vuv (121 nm) one photon ionization³⁴ in a gas phase cell experiment. From the temporal increase of the methyl ion signal the specific rate constant was determined (cf. Table I). The product yield directly provides the branching ratio of the reaction paths (cf. Table V). In a very recent molecular beam experiment (3+1) REMPI detection of the methyl radicals at 450.8 nm and (1+1) REMPI detection of the hydrogen molecule at 121.6 nm was used in order to measure the specific rate constants after exciting toluene at 193 nm.^{35,36}

Photofragment translational spectroscopy with a rotatable mass spectrometer detector has been used by Lee and co-workers to study both reaction channels. In these experiments cycloheptatriene was first excited at 248 and 266 nm. In a subsequent step the cycloheptatriene isomerizes to highly excited toluene.^{37,38} The high electron energies used for product ionization lead to an extensive ion fragmentation, so that ions from different neutral precursors can fragment on the same mass. To avoid a direct entrance of the reactant beam in the detection chamber measurements were carried out at laboratory angles larger than 5°, so that products with a small excess velocity which only arise at small laboratory angles could not be studied.

In the present work highly vibrationally excited toluene molecules were generated either directly by 193 nm laser excitation or via isomerization of cycloheptatriene following excitation at λ =248 nm or λ =193 nm. The difference in the

enthalpies of formation of $\approx 11\ 000\ \text{cm}^{-1}$ between the two isomers³⁹ provides for an additional energy to that of the photon energy. Accidentally, direct excitation of toluene at $\lambda = 193\ \text{nm}$ and via cycloheptatriene at $\lambda = 248\ \text{nm}$ leads to nearly the same internal energies of 51 740 cm⁻¹ and 51 090 cm⁻¹, respectively. Following photoexcitation, bond fission to either benzyl+H or to phenyl+methyl takes place. In Fig. 1 the reaction mechanisms are sketched.

II. EXPERIMENTAL SET-UP

Figure 2 shows a schematic diagram of the apparatus with important diameters and pressures. The molecular beam vacuum apparatus consists of four differentially pumped vacuum stages. The molecules are expanded through a nozzle (diameter 100 μ m) into the first chamber (pumped by a baffled 6000 ℓ /s diffusion pump). To prevent condensation and clustering of the molecules, the stainless steel nozzle chamber is resistively heated with a tantal wire between 300 and 500 K. Different expansion conditions were selected using helium and argon at different pressures as seed gases.



FIG. 1. The photodissociation of toluene is schematically described in an energy diagram displaying the energy levels of the different molecules involved in the reaction. To generate highly vibrationally excited toluene molecules either cycloheptatriene can be excited electronically at 193 or 248 nm followed by a rapid internal conversion (IC) to the vibrationally excited levels of the electronic ground state S_0^* and a subsequent isomerization to toluene or by direct excitation of toluene at 193 nm. Starting from the highly vibrationally excited S_0^* state toluene fragments to either benzyl+H or to phenyl+methyl.



FIG. 2. Schematic diagram of the molecular beam apparatus showing typical distances, aperture diameters, and total pressures with molecular beam on and off.

This leads to different final velocity distributions of the reactant molecules. After the nozzle expansion the molecules pass a 0.79 mm diameter skimmer, two differentially pumped stages (pumped by a 2000 ℓ /s diffusion pump and a 400 ℓ /s turbo molecular pump) before the beam enters the detection chamber (pumped by a 220 ℓ /s turbo molecular pump) where it is ionized by electron impact in a commercial quadrupole mass spectrometer (Extranuclear #279-9) with crossed beam electron impact ionizer (Extranuclear #041-2). A scheme of the vacuum apparatus together with important lengths, typical diameter of apertures and pressures is shown in Fig. 2.

The beam velocities depend sensitively on the source temperature, the total stagnation pressure as well as on the used seed gas and its relative portion. Therefore, in each measurement cycle the beam velocities were determined with a time-of-flight technique using the laser induced depletion of the reactant molecules (see also below). Typical velocities of about 550 and 900 m/s for Ar and He as seed gases were found. The internal energy of the molecules after the expansion is difficult to measure and depends on the expansion conditions as well. However, in the range of expansion conditions used here no dependence in the extracted product energy distributions could be detected. This reflects the fact, that the translational energy distributions are quite insensitive to small changes of the initial internal energy. A mean value for the thermal energy was estimated to be about 500 cm^{-1} . This is in accordance with measurements of the specific rate constant,³⁵ which are very sensitive to the internal energy.

A pulsed excimer laser (Lambda Physik LPX 110), operating at 248 or 193 nm, excites the molecules. The light of the laser is directed into the apparatus through a MgF₂ window and crosses the molecular beam perpendicularly at either one of two positions at \approx 280 mm from the nozzle close to the ionization volume for measurement of ionization potentials and at \approx 80 mm for measurement of translational energies. The energy of the laser pulse directly after crossing the molecular beam is measured with a pyroelectric detector (Gentec ED500). Together with the spot area (typical 2 mm²), the effective fluence at the excitation area was calculated. Typical operation conditions were repetition rates of 100 Hz at λ =248 nm and of 30 Hz at λ =193 nm with laser fluences of \approx 2 mJ/cm².



FIG. 3. Time-of-flight spectra recorded at the masses (a) 91 amu, (b) 90 amu, (c) 89 amu, (d) 77 amu, and (e) 65 amu after laser excitation of cycloheptatriene at 193 nm.

The laser radiation illuminates a photodiode which triggers a multichannel scaler. The signal pulses from the electron multiplier of the detector are counted and add timeresolved in the different channels of the scaler (dwell time 100 ns). The module is controlled by a personal computer via a Camac bus. The spectra are displayed on the computer monitor to control on-line the measurement.

III. RESULTS

A. Identification of reaction channels

Figure 3 shows a typical series of time-of-flight spectra recorded for different product masses after exciting cycloheptatriene at λ =193 nm. Each of the time-of-flight spectra shows a peak superimposed on a constant background of about the same intensity. This background signal results from reactant molecules that are not excited by the laser and fragment in the ionizer. The shape of the time-correlated contribution depends both on the velocity distribution of reactant and product molecules. The analysis of the product translational energy distributions, described in Sec. III C, identifies



FIG. 4. Time-of-flight spectra at the masses 91 and 65 amu after exciting toluene at 193 nm. The intensities are normalized to 1 at the maximum and 0 at the background level. The shape of the time-of-flight spectra is identical.

the neutral product on mass 91 amu [Fig. 3(a)] being the benzyl radical (C_7H_7) from the reaction channel R_1 and the product on mass 77 amu [Fig. 3(d)] being the phenyl radical (C_6H_5) of reaction channel R_2 in agreement with the results in the literature. The product on mass 90 amu (C_7H_6) appears only at high laser fluences of more than 10 mJ/cm². This fact together with its time-of-flight spectrum identifies it as a decay product of the benzyl radical after two photon absorption of cycloheptatriene at 193 nm.^{40,41}

In order to identify the spectrum measured at 65 amu we show in Fig. 4 a comparison of the time-of-flight spectra at masses 91 amu ($C_7H_7^+$) and 65 amu ($C_5H_5^+$), recorded under the same experimental conditions. To enable a direct comparison both spectra were normalized to a peak intensity of one. It is evident, that the spectra have the same shape, indicating that the ion signals on mass 65 and 91 amu originate from the same neutral precursor C_7H_7 . The same is found for the time-of-flight spectra at masses 90 amu ($C_7H_6^+$) and 89 amu ($C_7H_5^+$) which both stem from the same neutral radical C_7H_6 . These assignments are supported by measurements of the ionization potential, which are described in detail in Refs. 18 and 40.

B. Branching ratio

In an unimolecular reaction with more than one reaction path the branching ratio BR (i/j) of two reaction channels *i* and *j* is defined as the ratio of the product yields N_i and N_j

$$\mathsf{BR}(i/j) \equiv \frac{N_i}{N_j},\tag{1}$$

whereas the relative reaction efficiency Q_i of a reaction path is defined as the relative portion of this channel *i*

TABLE II. Measured branching ratios BR and relative reaction efficiencies for benzyl+H and phenyl+ CH_3 .

$E_{\rm ex}$ (cm ⁻¹)	Signal ratio I_1/I_2^{a}	BR ^b	$Q_2^{b,c}$ (10 ⁻²)
51 590	9.7±1.1	3.3 ± 0.4	23±3
52 240	10.3 ± 0.9	3.5 ± 0.3	22 ± 2.5
63 240	11.0 ± 1.0	3.7 ± 0.4	21±2.5

^a I_1 : benzyl signal; I_2 : phenyl signal.

^bOnly the statistical error.

 $^{c}Q_{2} = 1/(1 + BR).$

$$Q_i = \frac{N_i}{\sum_k N_k}.$$
(2)

The branching ratio can be expressed in terms of the relative efficiency by BR $(i/j) = Q_i/Q_j$. The major difficulty in the determination of Q_i and BR (i/j) is the conversion of the measured product signal to absolute particle numbers N_i , since the percentage of detected products has to be known and since in the most cases the detection probability is different for different product molecules. To overcome the former difficulty, in this experiment the laser was irradiated in front of the ionizer, so that product molecules were detected from the whole newton sphere. The area under the measured time-of-flight spectrum after correcting for the velocity dependent ionization cross section is then directly proportional to the product yield. The latter problem in the case of electron impact ionization detection is due to the fact that the ionization cross section and fragmentation probability depend sensitively on the molecule and the electron energy. In order to take these values from the literature, the measurements were carried out at higher electron impact energies. Relative ionization cross sections σ_r of 15.2×10^{-16} cm² and 12.3×10^{-16} cm² (calculated after Ref. 42) and fragmentation probabilities of 0.23 and 0.1³⁸ for benzyl and phenyl, respectively, were used.

The measurements to determine the branching ratio BR =BR(1/2) were carried out at mass 65 amu (signal I_1) for reaction channel R_1 and at mass 77 amu (signal I_2) for reaction channel R_2 at three different excitation energies. The results are summarized in Table II. The signal ratios I_1/I_2 are converted into the branching ratio BR as mentioned above. The given results are mean values of several measurements and are discussed in Sec. IV B.

C. Translational energy distributions

Benzyl time-of-flight spectra were measured at different expansion conditions achieved by different seed gases, stagnation pressures, and nozzle temperatures to avoid systematic errors after exciting toluene at λ =193 nm and cycloheptatriene at λ =248 nm and λ =193 nm. Two typical examples for benzyl time-of-flight spectra are shown on the left-hand side [Figs. 5(a) and 5(b)]. For comparison the calculated spectra are plotted, which base on product translational energy distributions [cf. Figs. 5(c) and 5(d)] calculated with the phase space limit SACM/PST of the statistical adiabatic channel model (SACM) theory⁴³ and using expressions based on the RRK (Rice–Ramsperger–Kassel) theory.^{44,45} In



FIG. 5. On the left hand time-of-flight spectra of the benzyl radical following excitation of (a) toluene and (b) cycloheptatriene at 193 nm are shown. Together with the experimental data calculated spectra are plotted. It is evident, that the distributions based on the SACM/PST theory results in a too narrow distribution, whereas the RRK calculations with q = 10 and q = 12, respectively, fits the data well. On the right hand calculated SACM/PST (--) and fitted RRK (-) translational energy distributions are shown, which were used to fit the experimental spectra for maximum translational energies of (c) 21160 cm⁻¹ and (d) 32160 cm⁻¹.

the calculations the velocity distribution of the parent molecules were taken into consideration in the convolution as described in Refs. 40, 46 and 47. A dissociation energy for toluene to benzyl+H of $E_0=31\ 0.80\ \mathrm{cm}^{-148}$ was used. The further molecular parameters for the SACM/PST calculation are taken from Ref. 26, which base on the values from Refs. 19–56. It is evident, that the SACM/PST calculation results in too narrow TOF distributions, i.e., the mean translational energy is too small. In contrast, the RRK-type expression is a phenomenological distribution which can be fitted to the data by using an adjustable parameter q

$$P_{E}(E_{T}) = \frac{q+1}{E_{T}^{\max q+1}} \cdot (E_{T}^{\max} - E_{T})^{q}.$$
(3)

 E_T^{max} is the maximum translational energy and q can be related to the number of degrees of freedom participating at the reaction, which determines the mean translational energy as well as the width of the distribution. Best agreement was achieved with q = 10 (for excitation of toluene at $\lambda = 193$ nm and cycloheptatriene at $\lambda = 248$ nm) and q = 12 (for excitation of cycloheptatriene at $\lambda = 193$ nm). For this q values the mean translational energy can be calculated via $\langle E_T \rangle = E_T^{\text{max}}/(q + 2)$ leading to $\langle E_T \rangle = (1760^{+250}_{-245})$ cm⁻¹ and $\langle E_T \rangle = (2300^{+380}_{-340})$ cm⁻¹, respectively. In comparison the mean translational energies of 970 and 1300 cm⁻¹ calculated with the SACM/PST theory for the two excitation energies are definitely lower (see also Table III). These results are discussed in Sec. IV.

Time-of-flight spectra of the phenyl radical (reaction channel R_2) were also measured at different expansion conditions following excitation of toluene at λ =193 nm and cycloheptatriene at λ =248 nm and λ =193 nm. Two examples are shown in Figs. 6(a) and 6(b). The measured spectra are compared with calculations based on the SACM/PST theory [Figs. 6(c) and 6(d)]. In these calculations the energy for dissociating toluene to phenyl+methyl was taken to be E_0 =36 000 cm^{-1.33} Here, the SACM/PST calculation fits the measured spectra well. Mean translational energies of $\langle E_T \rangle = (900^{+175}_{-90}) \text{ cm}^{-1}$ after exciting toluene at 193 nm and $\langle E_T \rangle = (1240^{+120}_{-150}) \text{ cm}^{-1}$ after exciting cycloheptatriene at 193 nm were obtained.

IV. DISCUSSION

A. Product translational energy distribution

For the reaction channel to benzyl+H mean translational energies of $\langle E_T \rangle = (1760^{+250}_{-245})$ cm⁻¹ and $\langle E_T \rangle$ $= (2300^{+380}_{-340})$ cm⁻¹ were determined for excitation energies of $E_{\rm ex}$ =52 240 cm⁻¹ and $E_{\rm ex}$ =63 240 cm⁻¹, respectively. The SACM/PST calculation yielded too small energies of 970 and 1300 cm⁻¹. Note the small percentage of $\langle E_T \rangle$ with respect to the maximum translational energy $E_T^{\rm max}$ of 8% and 7%, respectively, i.e., only a small amount of the excess energy is distributed in the translational degrees of freedom, and the shape of the distribution, which decreases monotonically. Both observations reflect the fact that the number den-

TABLE III. Comparison of measured mean product translational energies for toluene \rightarrow benzyl+H with calculations.

$\frac{E_T^{\max a}}{(\mathrm{cm}^{-1})}$	$\langle E_T \rangle$ (cm ⁻¹)	Used distribution	Method	Reference
21 160	(1760^{+250}_{-240})	RRK with $q = 10^{+2.0}_{-1.5}$	PTS of benzyl	This work
32 160	(2300^{+380}_{-350})	RRK with $q = 12^{+2.5}_{-2.0}$	PTS of benzyl	This work
20 355	(1564^{+130}_{-115})	RRK with $q = 11 \pm 1$	PTS of benzyl	38
21 650	2728 ± 175	Maxwellian: $T=2630\pm87$ K	LIF of H atoms	32
21 000	2343 ± 140	Maxwellian: $T=2280\pm140$ K	LIF of H atoms	31
32 000	3462 ± 245	Maxwellian: $T=3330\pm235$ K	LIF of H atoms	31
20 660	970	SACM/PST	Calculation	This work
31 660	1300	SACM/PST	Calculation	This work
14 900	1295	RRKM	Calculation	32
21 650	1610	RRKM	Calculation	32

^aMaximum translational energy $E_{\text{max}} = E_{\text{ex}} - E_0$.

sity of open channels and therefore the occupation of product internal states increases strongly with increasing energy above the dissociation threshold. Since internal and translational energy are directly related, $P_E(E_T)$ decreases with increasing E_T . The results of this work are compared with measured and calculated translational energies in Table III and Fig. 7.

Besides our measurements, experimental results from Bersohn's and Lee's group are available. In Lee's group, the translational energy distributions were also measured via photofragment translational spectroscopy in a molecular beam experiment.³⁸ In contrast to our measurements, they detected the reaction products with a rotatable mass spectrometer at laboratory scattering angles of more than 5°. After excitation of cycloheptatriene at 266 nm a mean translational energy of 1560 cm⁻¹ was determined for reaction pathway R_1 ,³⁸ which is in an excellent agreement with the results of this work.

The group of Bersohn measured the Doppler profile of the Lyman- α line of the H atom product. The translational temperatures were determined from a Maxwellian fit and mean translational energies of (2343 ± 140) cm⁻¹,³¹ (3462 ±245) cm⁻¹,³¹ and (2728\pm175) cm^{-131,32} were found after exciting cycloheptatriene at 248 and 193 nm and toluene at 193 nm, respectively. These mean translational energies are about 50% higher than the experimental results of Lee's



FIG. 6. On the left hand time-of-flight spectra of the phenyl radical following excitation of (a) toluene and (b) cycloheptatriene at 193 nm are shown. Together with the experimental data calculated spectra are plotted. The SACM/PST distribution fits the data well. On the right hand the calculated SACM/PST (—) translational energy distributions for the maximum translational energies of (c) 21 160 cm⁻¹ and (d) 32 160 cm⁻¹ are shown.



FIG. 7. Comparison of measured mean product translational energies of the reaction toluene \rightarrow benzyl+H with two calculations. Experimental results from Refs. 38 (\bigtriangledown), Refs. 31, 32 (\square) and from the present work (\bullet) are shown together with a RRKM calculation (\diamond) (Ref. 32) and a SACM/PST calculation (—without a barrier and --- with a barrier of about 500 cm⁻¹).

group and this work (cf. Table III and Fig. 7).

As mentioned above, the SACM/PST calculation yields mean translational energies which are about a factor of 2 smaller than the experimental results measured by Lee *et al.* and in this work and about a factor of 2.7 compared to Bersohn's results. In contrast, a RRKM calculation of the threedimensional density of states (Eq. 6 and Table IV in Ref. 32) yield a mean translational energy of 1610 cm⁻¹ at E_T^{max} = 21 650 cm⁻¹. Another RRKM calculation performed in Lee's group³⁸ yield a mean translational energy of 970 cm⁻¹ at E_T^{max} = 20 355 cm⁻¹.

To explain the reasons for these large discrepancies, we can exclude experimental errors in this work due to clustering or multiphoton processes since many different expansion conditions and low laser fluences were used (\ll 5 mJ/cm²) without observing significant changes. In addition, such systematic errors would also affect for the second reaction channel, where experiment and calculation agree satisfactorily (see below).

One noticeable point in the Doppler measurements^{31,32} is the significant discrepancy between the mean translational energies after excitation of toluene at λ =193 nm of (2728 ±175) cm⁻¹ and cycloheptatriene at λ =248 nm of (2343 ±140) cm^{-1.31} Since the excitation energies E_{ex} are nearly identical in both cases one would expect similar product translational energies. One possible reason for the greater mean translational energy after excitation at 193 nm could be multiphoton excitation, which is much more important at λ =193 nm compared to 248 nm. A difficulty in the LIF measurements presented in Refs. 31 and 32 comes from the H atom detection. H atoms can be produced in different processes. From the Doppler profile alone the origin of the H atoms cannot be unambiguously identified. For example, the benzyl radical can decay under H atom loss (Sec. III A and Ref. 41). These H atoms start with the higher benzyl velocity and lead to higher energy H atoms, so that the overall Doppler profile broadens.

A possible explanation for the observed difference between SACM calculation and experiment for the benzyl channel might be the existence of a small barrier in the exit channel. A barrier of height E_B can be simulated by a shift of the distribution with E_B to higher translational energies.⁵⁷ It was found that a barrier of less than 500 cm⁻¹ height is sufficient to reproduce the measured spectra with the SACM/ PST calculations.⁴⁰ On the other hand, measurements of the thermal recombination rate constant for benzyl+H→toluene contradict this assumption.²⁴ Further theoretical as well as experimental studies are necessary to resolve this open question.

In contrast to the benzyl channel, a good agreement between SACM/PST theory and experiment is found for the reaction path R_2 to phenyl and methyl. Mean translational energies of $\langle E_T \rangle = (900^{+175}_{-90}) \text{ cm}^{-1}$ after exciting toluene at 193 nm and $\langle E_T \rangle = (1240^{+120}_{-150}) \text{ cm}^{-1}$ after exciting cycloheptatriene at 193 nm were measured. Besides the measurements presented in this work, a further experiment of the Lee group³⁸ has been performed, which is in excellent agreement with our results (see Fig. 8 and Table IV).

B. Branching ratio

The branching ratio of two reaction channels can be directly expressed by the ratio of the specific rate constants and is therefore as well a sensitive observable to be compared with statistical models.

In this work, relative reaction efficiencies Q_2 of 0.23 ±0.05 after excitation of cycloheptatriene at 248 nm, 0.22 ±0.05 after excitation of toluene at 193 nm and 0.21±0.05 after excitation of cycloheptatriene at 193 nm were determined. The major source for the given errors are due to uncertainties in ionization cross section and fragmentation probabilities, which were considered in the given errors. Table V summarizes the experimental results of this work and other groups with a SACM calculation fitted to a measured branching ratio at $E_{\rm ex}$ =52 700 cm^{-1.33}

The group of Troe determined a relative reaction efficiency of $Q_1 = 1 - Q_2 = 0.75 \pm 0.2$ following laser excitation of toluene at $\lambda = 193$ nm from the benzyl yield via the known absorption cross section of the benzyl radical.^{8,26} In further experiments of this group, the methyl product (channel R_2) was detected with resonant-enhanced multiphoton ionization (REMPI) and nonresonant one photon ionization of the methyl radical.^{33,34} The ion signal was converted into a reaction efficiency by calibrating the product yield with a photoreactions of a known yield of methyl radicals. For this



FIG. 8. Mean product translational energy of the reaction toluene \rightarrow phenyl+CH₃. Experimental results of this work (\bullet) and from Lee *et al.* (∇) Ref. 38 are shown together with a SACM/PST calculation (—).

purpose the photodissociation of ethylbenzene to benzyl +methyl was used. The uncertainty in the methyl yield in this reaction (75%–100%) determined their value as well as the error in the relative yield to $Q_2=0.17\pm0.06$ after laser excitation of toluene at $\lambda=193$ nm.³³ New results in Refs. 34 and 40, 58 indicate, that the relative reaction efficiency for the methyl channel in ethylbenzene is larger than 96%, so that the published value can be recalculated to $Q_2=0.19\pm0.07$. In addition, the methyl yield after laser excitation of cycloheptatriene at $\lambda=193$ nm was investigated with nonresonant one photon ionization at 121 nm,³⁴ leading to the same relative reaction efficiency at a 11 000 cm⁻¹ higher internal energy;³⁴ i.e., the relative efficiency is constant in this considered energy range.

Molecular beam investigations in Lee's group determined branching ratios of BR= 6.56^{37} and BR= $(8.4^{+4.4}_{-2.5})^{38}$ after laser excitation of cycloheptatriene at λ =248 nm and λ =266 nm, respectively. The branching ratios can be converted into relative reaction efficiencies of Q_2 =0.13 and Q_2 =(0.11±0.04).

The results for the relative reaction efficiencies of channel R_2 obtained with the different experimental techniques of about 10% to 20% are in a surprisingly good accordance by taking into account the uncertainties in the different calibration procedures. The results of this work together with the results from Ref. 34 indicate a reaction efficiency which is



FIG. 9. Relative reaction efficiency Q_2 for the photodissociation of toluene to phenyl and methyl. Experimental results of this work (\bullet), Refs. 37, 38 (\Box , \triangle), Ref. 33 (∇) and Ref. 34 (∇) are shown together with a SACM/PST calculation (—) (Ref. 33).

constant in the energy range between 50 000 and 65 000 cm^{-1} . This is in contrast to results of the SACM theory which predicts a smooth increase.

V. CONCLUSIONS

In this work the photodissociation of toluene to benzyl+H and $phenyl+CH_3$ after laser excitation was investigated in a molecular beam experiment. For this system the advantages of the photofragment translational spectroscopy together with selective ionization using low energy electrons detection in forward direction were illustrated. The reaction pathways, their branching ratio as well as the translational energy distributions of the products were determined. Calculations based on statistical theories were used to reproduce the measured spectra.

The primary advantage of the experimental method used here is its universal detection ability for even very slowly recoiling reaction products and the simultaneous reduction in

TABLE IV. Mean product translational energies for toluene \rightarrow phenyl+CH₃ obtained from photofragment translational spectroscopy measurements.

$E_T^{\max^a}$ (cm ⁻¹)	$\langle E_T \rangle$ (cm ⁻¹)	Used distribution	Reference
16 240	(900^{+60}_{-90})	SACM/PST	This work
27 240	(1240^{+120}_{-150})	(RRK with $q = 16^{+1}_{-1}$) SACM/PST (RRK with $q = 20^{+3}$)	This work
15 214	(845^{+240}_{-285})	RRK with $q = 12^{+2.5}_{-2.0}$	38

^aMaximum translational energy $E_{\text{max}} = E_{\text{ex}} - E_0$.

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TABLE V. Comparison of measured and calculated relative reaction efficiencies Q_2 for toluene \rightarrow phenyl+CH₃.

$E_{\rm ex}$ (cm ⁻¹)	Relative efficiency Q_2 (10 ⁻²)	Observation method	Reference
51 590	23±5	Photofragment translational spectroscopy	This work
52 240	22±5	Photofragment translational spectroscopy	This work
63 240	21±5	Photofragment translational spectroscopy	This work
52 730	$100 - (75 \pm 20)$	UV Absorption of benzyl	8
52 730	17±6	REMPI of Methyl	33
52 730	19 ± 7^{a}	REMPI of Methyl	33
63 510	19 ± 7^{b}	VUV 1 Photon ionization	33, 34
53 500	13	Photofragment translational spectroscopy	37
50 900	$10.6^{+3.9}_{-3.4}$	Photofragment translational spectroscopy	38

^aCorrected for the methyl reaction efficiency from ethylbenzene determined in recent experiments to be $Q_{EthB} = 0.96 \pm 0.04$ (Refs. 34 and 40).

^bCalculated from the corrected value of Ref. 33 by using the constancy of the branching ratio in this energy range (Ref. 34).

experimental requirements (no UHV detection chamber or rotatable detector required) compared to standard photofragment translational spectroscopy. Therefore, this method can be used for investigations of a widespread range of unimolecular processes. It is especially advantageous for processes in which products arise which are difficult to investigate via laser spectroscopy, e.g., large, internally hot products and/or with unknown spectroscopy. Examples are the photoinduced dissociations of large molecules or isomerization reactions.¹⁷ In a forthcoming publication the investigation of laser induced unimolecular reactions of methyl as well as alkylsubstituted benzenes using this technique will be presented.⁵⁸

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APPENDIX: PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY

Unimolecular reaction products arise with a certain amount of both internal and translational energy,^{5,14} the latter being measurable by photofragment translational spectroscopy.^{12,13} Assume a molecule *AB* to be excited with a photon of energy $E_{ex} = h\nu$ and to dissociate into two products, *A* and *B*. Energy conservation claims the excess energy E_{tot} , i.e., the sum of internal E_{int} and translational energies E_T of the products, to be given by the difference between E_{ex} and the dissociation energy E_0 Due to conservation of momentum $m_A \cdot \mathbf{u}_A = -m_B \cdot \mathbf{u}_B$, and since $E_T = (1/2)m_A \cdot \mathbf{u}_A^2 + (1/2)m_B \cdot \mathbf{u}_B^2$, where m_A , m_B , and \mathbf{u}_A , \mathbf{u}_B are the masses and velocities in the center-of-mass system of A and B, respectively, the c.m. velocity can be expressed by

$$u_A = \sqrt{2 \cdot \frac{m_B}{m_A} \frac{1}{m_{AB}} \cdot E_T}.$$
 (A2)

The velocity of the product molecules in the laboratory frame \mathbf{w} is the vector sum of the reactant velocity \mathbf{v} and the product c.m. velocity **u**. In the experiment **w** is measured by recording the flight time for a certain distance. The goal is to extract from the measured time-of-flight spectra in the laboratory frame the c.m. translational energy distributions by a forward convolution formula.^{40,46,47} To do so, a trial product translational energy distribution $P_E(E_T)$ is assumed and transformed into a c.m. velocity distribution Q(u). Q(u) is then convoluted with the initial reactant velocity distribution P(v) (determined from the reactant time-of-flight distribution) and the apparatus function (finite detection angle and length of the ionizer) to yield the velocity distribution on a certain angle in the laboratory frame, which is directly converted to a time-of-flight distribution T'(t). T'(t) is compared with the measured time-of-flight spectra T(t). This procedure is repeated until a good agreement between theory and experiment is achieved.

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$$E_{\rm tot} = E_{\rm ex} - E_0 = E_{\rm int} + E_T.$$
 (A1)

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