Effusive molecular beam-sampled Knudsen flow reactor coupled to vacuum ultraviolet single photon ionization mass spectrometry using an external free radical source

N. Leplat and M. J. Rossi^{a)}

Laboratory of Atmospheric Chemistry (LAC), Paul Scherrer Institute (PSI), CH-5232 Villigen PSI, Switzerland

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A new apparatus using vacuum ultraviolet single photon ionization mass spectrometry (VUV SPIMS) of an effusive molecular beam emanating from a Knudsen flow reactor is described. It was designed to study free radical-molecule kinetics over a significant temperature range (300–630 K). Its salient features are: (1) external free radical source, (2) counterpropagating molecular beam and diffuse VUV photon beam meeting in a crossed-beam ion source of a quadrupole mass spectrometer with perpendicular ion extraction, (3) analog detection of the photocurrent of the free radical molecular cation, and (4) possibility of detecting both free radicals and closed shell species in the same apparatus and under identical reaction conditions owing to the presence of photoelectrons generated by the photoelectric effect of the used VUV-photons. The measured thermal molecular beam-to-background ratio was 6.35 ± 0.39 for Ar and 10.86 ± 1.59 for $i\text{-C}_4\text{H}_{10}$ at 300 K, a factor of 2.52 and 1.50 smaller, respectively, than predicted from basic gas-dynamic considerations. Operating parameters as well as the performance of key elements of the instrument are presented and discussed. Coupled to an external free radical source a steady-state specific exit flow of 1.6×10^{11} and 5.0×10^{11} molecule $\text{s}^{-1} \text{ cm}^{-3}$ of $\text{C}_2\text{H}_5^\bullet$ (ethyl) and $t\text{-C}_4\text{H}_9^\bullet$ (*t*-butyl) free radicals have been detected using VUV SPIMS at their molecular ion m/z 29 and 57, respectively, at 300 K. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829879>]

I. INTRODUCTION

Thermochemical parameters, namely the standard heats of formation $\Delta H_{298}^0(\text{R}^\bullet)$ and absolute entropies $S_{298}(\text{R}^\bullet)$ for hydrocarbon free radicals ($\text{R}^\bullet$) are baseline quantities that determine the thermochemistry of complex processes such as combustion, atmospheric chemistry, and plasma processing, to name just a few. Free radicals such as ethyl ($\text{C}_2\text{H}_5^\bullet$), hydroxyl ($\text{OH}^\bullet$), and *t*-butyl ($t\text{-C}_4\text{H}_9^\bullet$) are reactive species that react both with themselves as well as with other gases encountered in the reaction system. The measurement of $\Delta H_{298}^0(\text{R}^\bullet)$ and $S_{298}(\text{R}^\bullet)$ therefore poses a considerable experimental problem given the free radical reactivity and its transient character. Three methods have been used to determine free radical thermochemistry, namely the positive and negative ion cycles as well as the study of temperature-dependent chemical halogenation equilibria given in Eq. (1)¹:

HX, $\text{X}^\bullet$, and R-H represent the hydrohalic acid, the atomic halogen, and the parent hydrocarbon, respectively. Of the three listed methods of thermochemical measurement the latter is by far the most accurate when the temperature dependence of the forward and backward reaction is measured which leads to individual rate constants as a function of temperature. This obtains the kinetic (Arrhenius) parameters for both k_1 and k_{-1} providing a T-dependent equilibrium constant $K_1 = k_1/k_{-1}$ measured over some temperature range. This so-

called Second Law approach leads to an independent determination of the enthalpy and absolute entropy of reaction, $\Delta_r H^0$ and $\Delta_r S$, respectively. Alternatively, a single value of K_1 at a given temperature leads to $\Delta_r H^0$ as well if the reaction entropy is known or assumed (Third Law approach). Taking $\Delta_r H^0$ and $\Delta_r S$ as a starting point the thermochemical parameters of $\text{R}^\bullet$ may be calculated from the known parameters of all other reactants listed in a thermodynamic database except for the radical in question.

The reverse reaction k_{-1} has been measured by many researchers over the years for many hydrocarbons yielding the corresponding free radicals.² This led to thermochemical parameters for many free radicals $\text{R}^\bullet$ using assumed Arrhenius parameters for k_1 . More recently, however, reaction k_1 has been measured experimentally by several research groups,^{3–8} whereby one group of researchers obtained large values of k_1 at 300 K coupled to small, but significantly negative activation energies.^{3,4} In contrast, the other group^{5–7} measured low values for k_1 associated with expected positive activation energies (E_a). The forward rate constant k_1 resulting in a negative Arrhenius activation energy ($E_a < 0$) was measured in a laminar flow tube by monitoring the decay of $\text{R}^\bullet$ using vacuum ultraviolet (VUV)-single photon ionization mass spectrometry (SPIMS)³ or the formation of atomic $\text{Br}^\bullet$ (reaction 1) using flash photolysis resonance fluorescence.⁴ In contrast, the group finding positive activation energies ($E_a > 0$) all dealt with thermal free radicals generated using a chemical reaction, and for the most part monitored the closed shell product RH after titration with HX (equation (1)). The two sets of results significantly differ in one respect: $E_a < 0$ was obtained exclusively upon photolytic generation of free radicals

^{a)} Author to whom correspondence should be addressed. Electronic mail: michel.rossi@psi.ch

reacting in a laminar flow tube in the presence of a few up to 100 mbar He carrier gas using a pulsed excimer or Nd:YAG laser at 193, 248, or 266 nm.^{3,4} In contrast, $E_a > 0$ was found when the reaction was studied using thermal free radicals with HX in a Knudsen flow reactor.^{5–7} Negative activation energies and too-fast H-transfer reactions were criticized by Benson and Dobis for fundamental kinetic reasons.⁸ In addition to H-transfer reactions, other metathetical reactions having unexpected small negative activation energies, such as Cl-transfer reactions, have been found.^{9–11}

In order to bridge the gap between both groups of experiments we decided to build an instrument based on a Knudsen reactor having the capability to both monitor the decay of $R^\bullet$ using VUV-SPIMS^{3,4} as well as the accumulation of closed shell products using electron-impact (EI) ionization^{5–7} in the same apparatus and at identical experimental conditions. We have emphasized the use of the Knudsen reactor because $R^\bullet$ is undergoing many, mostly “hard,” collisions with the vessel walls, thereby minimizing possible residual excitation energy in $R^\bullet$ regardless of the generating method, either by chemical reaction or photolysis from a suitable precursor. In practice the use of a Knudsen flow reactor generates thermal free radicals or other transients.

Tunable single VUV photon ionization from synchrotron radiation is increasingly used in conjunction with mass spectrometric detection of the resulting molecular ion in the context of both gas phase as well as aerosol composition studies because the resulting mass spectrometric signals are fragment-free and therefore make identification of the parent compounds easier.^{12,13} Because synchrotron-based experiments place high demands on infrastructure and personal resources, laboratory-based approaches using fixed-frequency VUV SPIMS are being pursued as well.^{14,15} With the ad-

vent of high energy electron-beam pumped rare gas lamps the implementation of brilliant VUV single photon ionization sources became once again easier for laboratory-based techniques of mass spectrometry.^{16,17} Both quadrupole as well as time-of-flight mass spectrometers have been equipped with these types of lamps with great success,^{17,18} and hyphenation with other analytical techniques such as thermogravimetry has demonstrated the analytical value of such an approach.¹⁹

II. DESCRIPTION OF INSTRUMENT

In order to achieve the mentioned objective, a new experimental apparatus was constructed (Figure 1). It consists of a Knudsen flow reactor coupled to (VUV) SPIMS in “line-of-sight” geometry.²⁰ Hydrocarbon free radicals are generated upstream of their introduction into the Knudsen flow reactor shown on the left side in Figure 1, according to several different chemical schemes displayed in reactions (2)–(4) for the generation of thermal ethyl ($C_2H_5^\bullet$) radical:

Reactions (2)–(4) generate thermalized free radicals through chemical reactions, namely $H^\bullet$, $I^\bullet$, abstraction and $H^\bullet$ addition, respectively, in contrast to photolytic generation that led to free radicals in various degrees of internal excitation depending on experimental conditions. It is thought that the internal degree of excitation of free radicals has a significant effect on its reactivity, especially in cases where small reaction

FIG. 1. Schematic diagram of VUV Single Photon Ionization Mass Spectrometer (SPIMS) for free radical detection using an external free radical source with the microwave discharge (2.46 GHz) creating H or Cl atoms. Gas handling vacuum line (left) is not shown. Three PTFE capillary inserts of 1–2 mm diameter (ID) and 10–20 mm length are displayed on the free radical source (left). P-, CC-, and ion gauges are thermocouple (Pirani), cold cathode, and hot cathode gauges, respectively. V1–V3 are shut-off valves mentioned in the text.

barriers are involved, such as reaction (1). As an example of reactions (2) and (3), a flow of 2%–5% Cl_2/Ar or 20% H_2/Ar is established across a 14 mm O.D./12 mm I.D. Pyrex tube excited by a 2.45 GHz ($\lambda = 12.2$ cm) microwave discharge (Opthos Inc., Evenson cavity). When the μ -wave discharge is set to 40 W, approximately 70% and 50% of Cl_2 and H_2 , respectively, undergo bond scission and generate $\text{Cl}^\bullet$ and $\text{H}^\bullet$ atoms. This flow of atomic radicals react downstream in a second 14 mm O.D. Pyrex tube with a free radical precursor in order to generate the hydrocarbon free radical of interest according to reactions (2)–(4). There are essentially two reasons that enable the generation of thermal free radicals $\text{R}^\bullet$: (i) no direct interaction of the radical precursors (RH, RI, or olefin) with the diffuse microwave plasma and (ii) removal of the potential excess internal energy in $\text{R}^\bullet$ through numerous collisions of $\text{R}^\bullet$ with the internal (coated or passivated) wall of both the free radical source (second flow tube, see above) as well as the Knudsen flow reactor. It is therefore expected that $\text{R}^\bullet$ flowing into the Knudsen flow reactor are thermalized free radicals on account of the many gas-wall collisions. Artifacts that may perhaps lead to negative values of E_a and the associated abnormally large rate constants (see Introduction) are thus minimized or are absent in view of the chemical generation scheme in this free radical source external to the Knudsen reactor.

The so produced free radicals generated at a typical total pressure of 0.1–0.3 Torr flow into the Knudsen reactor via a 1 mm diameter and 10 mm long PTFE capillary insert and react with HX admitted across a separate inlet in an accurately measured flow. The gases escape from the reactor in an effusive molecular beam across an orifice of 1.5, 3.5, or 7 mm nominal diameter into the mass spectrometry chamber and are identified and quantitatively analyzed using VUV-SPIMS. Table I provides characteristic gas-kinetic parameters as a function of the geometry of the Knudsen reactor. The Knudsen number λ/Φ , where λ is the mean free path and Φ is the orifice diameter (Table I), is 45 when an average molecule of 60 dalton (amu) with a molecular diameter of 6 Å²¹ and a typical limiting concentration of 4×10^{12} molecule cm^{-3} are assumed. This ensures that molecular flow conditions prevail even under conditions when molecular densities up to 5×10^{13} molecule cm^{-3} for a nominal exit orifice diameter of 3.5 mm (reactor a, Table I) are used. Table I also displays characteristic gas-kinetic parameters for the external free radical source which corresponds to the radical formation tube in

Figure 1 that is second in series with the microwave discharge tube.

In contrast to previous embodiments of Knudsen flow reactors that were equipped with a differentially pumped electron-impact quadrupole mass spectrometer and made use of phase-sensitive detection by electron-impact (EI) of the effusive molecular beam formed at the exit orifice of the reactor,²² the present design foregoes differential pumping while preserving line-of-sight geometry.²⁰ A key feature of the present experimental design is the close proximity of the beam-forming orifice of the Knudsen reactor to the ionization volume of the quadrupole mass spectrometer (Balzers/Pfeiffer QMG421 with QMA400 analyzer) in which on average 90% of the beam intensity enters the ionization volume of the MS owing to an opening angle in excess of 74° (see Sec. III B). Specifically, the beam-forming orifice is contiguous to the ionization volume which is part of a commercially available EI “cross beam” ion source. If used in EI mode the molecular and thermionic electron beam intersect at a 90° angle. Its design affords an ion yield that is expected to be independent of molecular mass owing to a constant collection/ionization volume coupled to a suitable ion extraction field. The substitution of the EI with the VUV-source is expected to leave the ion collection volume unchanged because the VUV photon flux counterpropagating to the effusive molecular beam and the electron beam are arranged perpendicular to each other, but are located in the same plane perpendicular to the cross section of the apparatus displayed in Figure 1. In region II of Figure 1 the VUV flux and the thermionic electron beam propagate in and perpendicular to the paper plane, respectively. The ionizer consists of a stainless-steel box open on a pair of opposite sides located in close proximity to the beam-forming escape orifice of the Knudsen reactor at a distance of 0–1 mm in order to capture as much of the effusive (thermal) beam intensity as possible. A 700 l s^{-1} (N_2) 8 in. nominal diameter cryopump keeps the pressure in the single detection chamber to acceptably low levels even at flow rates of H_2 and *i*-butane ($\text{i-C}_4\text{H}_{10}$) as high as 3×10^{17} and 2.2×10^{16} molecule s^{-1} , respectively (see below).

Single-Photon VUV Ionization (SPI) was used in conjunction with quadrupole mass spectrometry (QMS) as it allows a more specific and sensitive detection of $\text{R}^\bullet$ and selected stable closed shell molecules compared to electron impact MS (EIMS). The microwave-powered discharge lamp equipped with an Evenson cavity has been installed

TABLE I. Important parameters of the used Knudsen reactors and the free radical formation tube (temperature T/K, molecular mass M/g).

	Reactor “a”	Reactor “a”	Reactor “b”	Radical formation tube
Volume (ml)	213	213	286	30
Internal surface area (cm^2)	256	256	275.5	102.3
Nominal diameter Φ of exit aperture (mm)	1.5	3.5	7.0	1.0
k_e (s^{-1})	$0.226^*(\text{T/M})^{1/2}$	$1.034^*(\text{T/M})^{1/2}$	$2.367^*(\text{T/M})^{1/2}$	$0.724^*(\text{T/M})^{1/2\text{a}}$ $1.716^*(\text{T/M})^{1/2\text{b}}$
ω (s^{-1})	$4386^*(\text{T/M})^{1/2}$	$4386^*(\text{T/M})^{1/2}$	$3509^*(\text{T/M})^{1/2}$	...

^aValve V3 closed.

^bMaximum pumping by mechanical pump of external free radical source (Valve V3 open, see Figure 1).

opposite the MS ionizer in line-of-sight geometry at 40 mm distance from the 2 mm thick and 1 in. diameter MgF_2 window that was occasionally replaced by a 1 in. diameter 40 mm f.l. plano-convex MgF_2 lens in some experiments. In operation, a thin beam of combined VUV/Visible photons entered the Knudsen flow reactor owing to direct line-of-sight but did not affect the gas composition in the reactor. This was confirmed by using several photon energies by changing the discharged gas from (pure) H_2 to Cl_2/He and Br_2/He without detectable change in results. However, the generation of photoelectrons is unavoidable for the present design when using a diffuse discharge in contrast to using VUV synchrotron radiation where the VUV photons are delivered in a collimated beam.²³ These photoelectrons of undefined, but of maximum energy of 50 V (ion reference voltage of cross-beam ion source) enabled the electron-impact ionization of closed-shell molecules but led to fragmentation of some free radicals and closed-shell species whose ionization and/or appearance potential exceeded the photon energy. This feature, albeit originally thought to be a nuisance, proved helpful in the present case because it made the detection of stable reaction products possible at comparable sensitivities in the presence of free radicals. Certain classes of organic molecules such as aromatic hydrocarbons (toluene) and ketones (acetone) did not show any or a very limited extent of fragmentation (see examples below) in contrast to pure hydrocarbons, and especially iodohydrocarbons which underwent fragmentation to some degree.

Figure 1 summarizes the schematic diagram of SPIMS detection for the Knudsen flow reactor measurement of the kinetics of reactions such as $\text{R}^\bullet + \text{HX}$ ($\text{X} = \text{I}, \text{Br}$) $\rightarrow \text{RH} + \text{X}^\bullet$. To summarize, the salient features of this apparatus are the following:

- Close or minimal proximity of the beam-forming orifice of the Knudsen flow reactor to the ionization volume of the QMS, either used in electron-impact (EI) or single photon ionization (SPI) mode using VUV photons from a μ -wave discharge lamp. This arrangement affords a maximum contribution of the beam to the MS signal as well as a sufficient dynamic range that proved to be compatible with analog detection of the ionization current and made ion counting unnecessary.
- Low background gas density MS signal levels compared to concentrations within the molecular beam on the order of 10% (see below) or so owing to the high volumetric pumping rate of approximately 700 l s^{-1} (for N_2). This makes molecular-beam modulation and phase-sensitive detection unnecessary but may occasionally require corrections for background signal and fragmentation contributions.
- Operation of EI and SPIMS under identical experimental conditions in the same apparatus for both free radical detection using SPIMS or closed shell product analysis using EI. This enables true chemical mass balance to be established which is of critical importance for the validation of the kinetic scheme.
- An innovative external chemical generation of free radicals using a chemical reaction scheme in conjunc-

tion with the use of a Knudsen flow reactor. Free radicals generated are thermally distributed because, (i) no precursors of the radical (RH, RI, or alkene R-1H) interact with the microwave discharge plasma and (ii) any excess internal energy is efficiently removed by collisional relaxation in numerous collisions of the free radical with the walls of the radical generation tube and/or the Knudsen flow reactor before reaction.

III. DETAILED CHARACTERIZATION AND PERFORMANCE OF KEY ELEMENTS

This section will present three key aspects of the new apparatus owing to the fact that we did forego the implementation of differential pumping that is usually encountered in conjunction with molecular beam detection using MS. We have chosen this option in order to enable the close proximity of the plane of the exit orifice of the Knudsen reactor to the entrance of the ionization volume of the mass spectrometer in order to minimize the distance. It is wise to design the apparatus with this notion in mind because the density of a thermal (effusive) molecular beam decreases with the square of the distance. Section III A presents basic considerations of the effusive beam in relation to the chosen geometry for molecular detection. Section III B describes experiments designed to probe the interaction of the MS detection with the background gases caused by the molecular beam. Experiments have been performed in order to quantitatively determine the crucial issue of the background level for a monoatomic (Ar) and polyatomic ($\text{i-C}_4\text{H}_{10}$) gas, that is, the non-beam contribution of the MS signal in the high vacuum chamber owing to the absence of differential pumping. These quantitative features are compared to a semiquantitative model of pressure cascading across the different elements traversed by the effusive beam. We attach great importance to these issues because they determine the quality of the expected experimental data. Section c presents some example SPIMS spectra serving as an illustration. Finally, additional issues regarding the diffuse discharge lamps are entirely dealt with in Appendix A, whereas Appendices B and C present additional data regarding Sec. III B.

A. Geometrical arrangement and molecular beam sampling

Figure 1 schematically presents the three spatial elements in conjunction with molecular beam sampling in the present arrangement. Regions I, II, and III correspond to the Knudsen flow reactor, the SPIMS ionization region, and the high vacuum chamber, respectively. This leads to a cascade of pressures that is exhibited in Table II for an Ar inflow of $5 \times 10^{15} \text{ molecule s}^{-1}$. Equation (5) displays the analytical expression for the

$$f = (1 - \cos^2(\theta)), \quad (5)$$

intensity fraction f of the effusing molecular beam as a function of conical opening angle θ .²⁴ The minimum opening angle of 74° corresponding to the maximum distance of 1 mm between the plane containing the exit orifice of the Knudsen

TABLE II. Concentration (number cm^{-3}) of Ar and corresponding pressure (Torr) in Regions I, II, and III at an inlet flow into the Knudsen reactor $F_i(\text{Ar}) = 5.0 \times 10^{15} \text{ molecule s}^{-1}$ at ambient temperature. The upper number in column 3 corresponds to number density (molecule cm^{-3}), the lower to partial pressure in Torr.

Nominal Φ (mm) of exit aperture (mm)	Measured Effusion rate constant (s^{-1}) ^a	Region I Knudsen reactor	Ratio ^b I/IIA I/IIB	Region IIA ^{b,c} IIB	Ratio ^b IIA/III IIB/III	Region III ^d
1.5	$0.226*(T/M)^{1/2}$	3.8×10^{13}	67	1.8×10^{-5}	67	2.7×10^{-7}
Reactor a	0.619 (Ar)	1.2×10^{-3}	273	4.4×10^{-6}	16.3	
3.5	$1.034*(T/M)^{1/2}$	8.3×10^{12}	14.4	1.8×10^{-5}	67	2.7×10^{-7}
Reactor a	2.832 (Ar)	2.6×10^{-4}	59	4.4×10^{-6}	16.3	
7.0	$2.367*(T/M)^{1/2}$	3.6×10^{12}	6.1	1.8×10^{-5}	67	2.7×10^{-7}
Reactor b	6.482 (Ar)	1.1×10^{-4}	25	4.4×10^{-6}	16.3	

^aMeasured effusion rate constant using (i) sudden halt of inlet flow into Knudsen reactor and (ii) increase of static pressure upon increase of admitted flow.

^bModel A of region II (ionization volume) corresponds to a Knudsen reactor in series with $k_e = 5752 \text{ s}^{-1}$ (gas residence time of 174 ms); in Model B region II is a box guiding the molecular beam without undergoing wall collisions. The gas residence time $t = \text{length}/c = 1.73/4 \times 10^4 = 43.3 \times 10^{-6}$ corresponding to an effective $k_e = 2.3 \times 10^4 \text{ s}^{-1}$, where c is the mean molecular speed of Ar at 300 K.

^cRegion II is a volume element approximated as a flow reactor with the following (approximated) dimensions/mm: $6.6 \times 13.3 \times 17.3 = \text{height} \times \text{width} \times \text{length}$ (ionization volume). This is an approximation to the real shape whose cross section resembles a compressed hexagon. The calculated escape rate constant is $k_e = 5782 \text{ s}^{-1}$ for Ar, 300 K.

^dRegion III is the SPIMS chamber housing the MS instrument with the following measured volumetric pumping rate (8 in. nominal diameter cryopump Oerlikon Leybold COOLVAC 800 BL (CF): The specified volumetric pumping rate S of the cryopump alone for N_2 is 800 l s^{-1} whereas the measured value in the present instrument is 680 l s^{-1} using a Varian nude ion gauge coupled to a SenTorr readout unit. The measured value for Ar is $S(\text{Ar}) = (5.80 \pm 10) \times 10^5 \text{ cm}^3 \text{ s}^{-1}$.

flow reactor, region I (relevant parameters may be found in Table I) and the outer edge of the ionization box, region II, leads to a calculated value of 0.92 which corresponds to a lower limit of the degree of interception of the effusive beam by the ionizer box. It will be higher for the case where the Pyrex finger of the Knudsen reactor is in physical contact with the ionizing volume, region II. The distance between the exit plane of the molecular beam-forming orifice and the entrance plane to the ionization volume of the quadrupole mass spectrometer is critical: increasing the distance by 1 or 2 additional mm will lead to a SPIMS signal loss of approximately a factor of two.

The ionization volume, region II, is approximated by a rectangular open-ended box on opposite sides of dimension length $\times$ width $\times$ height of $17.3 \times 13.3 \times 6.6 \text{ mm}^3$ whose $13.3 \times 6.6 = 87.7 \text{ mm}^2$ opening may be regarded as an exit orifice of a Knudsen flow reactor put in series to the one upstream represented by region I. We call this arrangement Model A which leads to an estimated effusion rate constant of $k_{\text{esc}} = 5752 \text{ s}^{-1}$ corresponding to a gas residence time of 174 μs for Ar at 300 K if the ionization volume is considered as a small volume free molecular flow reactor (Model A). This has to be contrasted with Model B that lets the molecular beam cross region II without formally undergoing a single collision. In this case the effective residence time drops from 174 to 43.5 μs for Ar at 300 K corresponding to an effective rate constant for effusion of $k_{\text{esc}} = 2.3 \times 10^4 \text{ s}^{-1}$. These two points of view represent two extremes because part of the thermal beam passes the ionization volume without undergoing a wall collision corresponding to Model B, whereas the other part collides with the container walls corresponding to Model A when region II is understood as being a free molecular flow reactor. Detailed calculations would be necessary to evaluate the two fractions as well as the degree to which the ionization volume could be treated either as a molecular flow reactor or simply as a beam containment element. More collisions with the container wall will slow-down molecular effusion and thus emphasize the character of region II as a flow reactor.

Table II summarizes the pressure cascade in regions I, II, and III for Ar, 300 K for Knudsen flow reactors “a” and “b” as well as for Model A and B regarding the ionization volume, region II. The pressure drop between regions I and II is largest for the smallest exit orifice and drops from a factor of 67 to 6.1 and from a factor of 273 to 25 in going from the 1.5 to 7.0 mm nominal diameter exit orifice for Model A and B, respectively. The effective volumetric pumping speed for Ar is calculated as $S = 592 \text{ l s}^{-1}$ when the ion gauge reading is corrected from N_2 to Ar by dividing the readout by 1.2.²⁵ This has to be compared to a measured value of $S = 680$ and 580 l s^{-1} for N_2 and Ar, respectively, for the present instrumental arrangement which is marginally lower than the manufacturer’s specifications owing to a change of geometry between the actual instrument at hand and the standard calibration configuration. The pressures in region III have been calculated using the measured values of $S(\text{Ar})$. In anticipation of what will be presented and discussed in Sec. III C we emphasize that Model B is more in agreement with experimental evidence presented in Figure 2(a) and 2(b) compared to Model A.

B. Molecular beam vs. background SPIMS signals

This section deals with the potential perturbation of the effusing molecular beam by the presence of background gas that is building up as a consequence of the beam flux into the chamber and the finite pumping speed of the main (cryo) pump. In one set of experiments we have left the effusive beam intensity constant and varied the background level by increasing the flow directly into the chamber across the bypass valve V2 displayed in Figure 1. In another set of experiments we have chosen a given flow across the Knudsen reactor and sampled the effusive beam in comparison with letting in the same flow directly into the chamber across the bypass valve V2. In this way the effusive molecular beam intensity and the background gas density may be independently varied

FIG. 2. SPIMS signal for ratios r of Ar flow through bypass (V2, V1 closed) and Knudsen reactor (V1, V2 closed) monitored at m/z 40 using 0.25 Torr of H_2 in a 70 W microwave discharge and 3000 V SEM voltage, (a) reactor "a" ($\Phi = 3.5$ mm nominal diameter orifice) and (b) reactor "a'" ($\Phi = 1.5$ mm nominal diameter orifice).

and therefore decoupled or compared at the same flow for a single probe gas.

Figure 3(a) shows the SPIMS signal of isobutane ($i-C_4H_{10}$) at m/z 58 flowing across the Knudsen flow reactor as a function of the measured inflow of isobutane. Using reactor "a" the H_2 pressure in the 70 W discharge lamp was 0.25 Torr and the SEM voltage was 3000 V. A straight line going through zero is obtained, as expected, whose slope is the SPIMS calibration factor that defines the mass spectral overall sensitivity depending on the mentioned experimental parameters. Figure 3(b) displays the Ar SPIMS signal at m/z 40 at a constant inflow across the bypass valve V2 of 1.43×10^{16} molecule s^{-1} as a function of isobutane flow across the Knudsen flow reactor (V1 open). A constant SPIMS signal at m/z 40 is expected; however, an increase of approximately 20% is observed at the highest isobutane inflow of 2.14×10^{16} molecule s^{-1} which is attributed to flow entrainment of background Ar into the mass spectrometer by the molecular beam of isobutane. We have consciously taken reactor "a" with the 3.5 instead of the 7 mm diameter exit orifice in order to increase the density of isobutane in the effusive molecular beam so as to maximize the interaction of the effusive molecular beam with the background gas in the ionization volume of the SPIMS instrument.

Figure 4 shows the inverse of Figure 3(b), namely the SPIMS signal of isobutane effusing from the Knudsen flow

FIG. 3. (Top) Linear dependence of MS signal at m/z 58 of $i-C_4H_{10}$ on measured isobutane inflow through the inlet valve V1 into the Knudsen flow reactor at a constant flow of $F_i(Ar) = 1.43 \times 10^{16}$ molecule s^{-1} , correlation line parameters: $y = 1.01 \times 10^{-16} x - 3.62 \times 10^{-2}$, $R^2 = 0.98$; (bottom) dependence of MS signal for Ar at m/z 40 flowing into the MS chamber through the bypass valve V2 at a constant flow of $F_i(Ar) = 1.43 \times 10^{16}$ molecule s^{-1} as a function of the measured inflow of $i-C_4H_{10}$ through the Knudsen flow reactor; 0.25 Torr in H_2 discharge lamp at 70 W, SEM voltage of 3000 V, reactor a (3.5 mm nominal Φ exit orifice), correlation line parameters: $y = 1.10 \times 10^{-18} x + 8.22 \times 10^{-2}$, $R^2 = 0.90$.

reactor "a" (3.5 mm diameter exit orifice) as a function of inflow of Ar across the bypass valve V2. A small, but significant decrease of the isobutane SPIMS signal of 5% may be observed that is interpreted as scattering of the isobutane

FIG. 4. Dependence of MS signal for $i-C_4H_{10}$ at m/z 58 flowing into the MS chamber through the Knudsen flow reactor across the inlet valve V1 at a constant flow of $F_i(i-C_4H_{10}) = 4.13 \times 10^{15}$ molecule s^{-1} as a function of the measured inflow of Ar through the bypass valve V2. 0.25 Torr in H_2 discharge lamp at 70 W, SEM voltage of 3000 V, reactor "a" (3.5 mm exit orifice), correlation line parameters: $y = 3.49 \times 10^{-19} x + 3.99 \times 10^{-1}$.

effusive beam by an increased background concentration in Ar. The small decrease in SPIMS signal of the effusive beam intensity is of the same order as the standard deviation of the signal and is usually not taken into account in the data evaluation. It is interpreted as attenuation of the effusive beam of isobutane by the increasing Ar background pressure by a beam-gas scattering processes. We would like to stress that the Knudsen number Kn is well within the molecular flow limit at the highest used flow rates of isobutane. Specifically, $Kn = 6.0$ with an estimated hard sphere collision cross section of $\sigma = 5 \text{ \AA}$ for isobutane²¹ and $F_{i,\text{max}}(\text{isobutane}) = 2.14 \times 10^{16} \text{ molecule s}^{-1}$ corresponding to a number density $[i\text{-C}_4\text{H}_{10}] = 4.3 \times 10^{13} \text{ molecule cm}^{-3}$ for reactor “a” ($\Phi = 3.5 \text{ mm}$). The original criterion for molecular flow stipulated by Knudsen, namely $Kn = 10$, has been relaxed in practice to $Kn = 3$ as a result of extensive work in Knudsen flow reactors.²⁶ Tables V and VI provide additional quantitative information regarding data displayed in Figures 3 and 4.

In order to explore the parameter space regarding the degree of flow entrainment (Figure 3(b)) and molecular scattering (Figure 4) we took an additional pair of molecules, namely H_2 (2 amu) and SF_6 (146 amu) with substantially differing masses compared to the pair $i\text{-C}_4\text{H}_{10}$ (58 amu) and Ar (40 amu). Figures 5 and 6 show analogous results to Figures 3 and 4. Figure 5 shows a similar flow entrainment of the pair H_2/SF_6 compared to the case $i\text{-C}_4\text{H}_{10}/\text{Ar}$ (discussed above) that manifests itself in an increase of the background SPIMS signal of approximately 25%. Figure 6 displays the small scattering effect of SF_6 on the molecular beam of effusing H_2 that manifests itself as a 3.4% decrease of the SPIMS signal of H_2 in the presence of the highest flow $F_i(\text{SF}_6) = 2.24 \times 10^{16} \text{ molecule s}^{-1}$ through the bypass valve V2. This small SPIMS signal decrease of the H_2 effusive beam intensity was neglected in view of the larger standard deviation of the SPIMS signals. Although the highest value of $F_i(\text{H}_2) = 3.0 \times 10^{17} \text{ molecule s}^{-1}$ appears excessive (see Figure 7) we obtain $Kn = 10.9$ with $\sigma = 2.3 \text{ \AA}$ and $[\text{H}_2] = 1.11 \times 10^{14} \text{ molecule cm}^{-3}$ (reactor “a,” 3.5 mm nominal diameter exit orifice) and conclude that the experiment at the

FIG. 5. Dependence of MS signal for SF_6 at m/z 146 flowing into the MS chamber through the bypass valve V2 at a constant flow of $F_i(\text{SF}_6) = 6.06 \times 10^{15} \text{ molecule s}^{-1}$ as a function of the measured inflow of H_2 through the Knudsen flow reactor. 0.25 Torr in H_2 discharge lamp at 70 W, SEM voltage of 3000 V, reactor “a” (3.5 mm exit orifice), correlation line parameters: $y = 4.99 \times 10^{-22} x + 4.52 \times 10^{-2}$, $R^2 = 0.74$.

FIG. 6. Dependence of MS signal for H_2 at m/z 2 flowing into the MS chamber through the Knudsen flow reactor at a constant flow of $F_i(\text{H}_2) = 9.54 \times 10^{16} \text{ molecule s}^{-1}$ as a function of the measured inflow of SF_6 through the bypass valve V2. 0.25 Torr in H_2 discharge lamp at 70 W, SEM voltage of 3000 V, reactor “a” (3.5 mm exit orifice), correlation line parameters: $y = 2.77 \times 10^{-19} x + 1.93 \times 10^{-1}$.

highest inlet flow of H_2 still is in the molecular flow regime. Tables VII and VIII provide additional data pertaining to Figures 5 and 6.

The last experiment of this series concerns the situation where a chosen but identical flow of Ar has been directed either through the bypass valve V2 or the inlet valve V1 into the Knudsen flow reactor in order to quantitatively determine the background contribution relative to the beam intensity under realistic pumping conditions. SPIMS signals have been recorded using a 70 W H_2 discharge at 0.25 Torr total pressure (pure H_2) and a SEM voltage of 3000 V. Figures 2(a) and 2(b) display the results of the SPIMS signal ratio of bypass (b) (V1 closed, V2 open) to Knudsen reactor Ar flow (a) (V1 open, V2 closed) as a function of Ar inlet flow when either the bypass (V2) or reactor flow (V1) is chosen as the inlet flow. In this case either the inlet valve V1 to the Knudsen reactor or the vacuum chamber (bypass, V2) is opened (see Figure 1) such that an identical flow is dispensed either through the Knudsen reactor or to the vacuum chamber. The bypass flow across V2 only contributes to the background SPIMS signal whereas the same flow directed across the Knudsen flow reactor through

FIG. 7. SPIMS signal for ratios r of $i\text{-C}_4\text{H}_{10}$ flow through bypass and Knudsen reactor monitored at m/z 58 using 0.25 Torr of H_2 in a 70 W microwave discharge and 3000 V SEM voltage, reactor “a” ($\Phi = 3.5 \text{ mm}$ nominal diameter exit orifice).

TABLE III. Bypass to Knudsen reactor SPIMS signal ratio and corresponding effusive molecular beam-to-background ratio for Ar and isobutane ($i\text{-C}_4\text{H}_{10}$). 0.25 Torr of H_2 were flowing in a 70 W microwave discharge, SEM voltage set at 3000 V.

Nominal Φ of exit aperture (mm)	Type of gas (detected ion mass)	Ratio of SPIMS signals	Ratio a/b (beam/background)
1.5 (reactor a)	Ar (40)	0.136 ± 0.072	6.35 ± 0.39
1.5	$i\text{-C}_4\text{H}_{10}$ (58)	0.0843 ± 0.0110	10.86 ± 1.59
3.5 (reactor a)	Ar (40)	0.147 ± 0.018	5.81 ± 0.81
3.5	$i\text{-C}_4\text{H}_{10}$ (58)	0.0847 ± 0.0174	10.80 ± 2.53

V1 comprises the sum of the beam plus the background signal. Comparison (ratio r displayed in Table III) of both SPIMS signals affords the separation of the background contribution to the total SPIMS signal. The average values of r are 0.147 ± 0.018 and 0.136 ± 0.072 for the 3.5 and 1.5 mm exit orifice reactor, respectively, if no systematic trend with $F_i(\text{Ar})$ is assumed (Table III). This ratio is expected to be somewhat molecule dependent because it depends on the pumping speed of the cryopump which controls the background pressure in the chamber. Indeed, Table III displays values for signal ratios of $i\text{-butane}$ ($i\text{-C}_4\text{H}_{10}$) that are smaller by approximately a factor of two. The contribution of the background and the molecular beam are expected to be additive owing to molecular flow conditions in regions I, II, and III (see Figure 1) such that a simple separation scheme between background and beam contribution may be applied (see below).

The measured ratio of the background to molecular beam SPIMS signal is given in Eq. (6) in which r is the measured SPIMS signal ratio and b and a are the true (separated) contributions to the background and molecular beam SPIMS signals.

$$r = b/(a + b), \quad (6)$$

$$a/b = (1 - r)/r. \quad (7)$$

The molecular beam signal is the sum of the beam and the background contribution whereas there is no beam contribution for the background SPIMS signal when the identical inflow is admitted across the bypass valve V2. The ratio given above results in $a/b = 5.81 \pm 0.81$ and 6.35 ± 0.39 for the 3.5 and 1.5 mm diameter exit orifice reactors, respectively, for Ar according to Eq. (7) which has to be confronted with the two different models of regions I, II (molecular beam contribution), and III (background) presented above. The data in Figure 2(a) and 2(b) may be compared to either one of the ratios II/III displayed in Table II. Using the absolute background pressure of 2.7×10^{-7} Torr (region III) displayed in Table II we arrive at an absolute pressure in region II of 1.8×10^{-6} Torr corresponding to a molecular density of 5.8×10^{10} molecule cm^{-3} . Table II reveals an absolute pressure of 1.8×10^{-5} and 4.4×10^{-6} Torr in region II for Models A and B, respectively. On that basis we choose Model B as being suitable for the description of the collisional environment despite the fact that the experimentally derived Ar pressure is lower by a factor of 2.6 compared to a factor of 10.6 for Model A when taking the beam-to-bypass ratios for the 1.5 mm exit orifice reactor.

The agreement is satisfactory in view of the semiquantitative nature of the calculation summarized in Table II and outlined in Sec. III A. The agreement of the measured beam-to-background ratio is even more favorable for isobutane as the sample gas leading to a beam-to-background ratio $a/b = 10.86 \pm 1.59$ and 10.80 ± 2.53 for the 3.5 and 1.5 mm exit orifice, respectively. These data lead to an $i\text{-butane}$ partial pressure in volume II smaller by a factor of 1.50 compared to the expectation value based on simple gas-dynamic considerations. The isobutane data set is displayed in Figures 7 and 8 as well as in Tables XI and XII, respectively. As expected, there is no significant difference in the a/b ratio between both apertures as the flows are identical at a set flow rate. The largest uncertainty stems from the assumption regarding the nature of the gas dynamics in the ionization volume, region II, as alluded to above because part of the beam undergoes a small number of collisions whereas the other (smaller) part does not. In addition, there are a finite number of gas-gas collisions within an effusing thermal molecular beam as outlined by Lubman *et al.*²⁷ owing to velocity spread such that collisionless beams are a strongly idealized case.

Tables IX and X provide additional data in support of the results plotted in Figure 2(a), and for the highest Ar flow of 3.7×10^{16} molecule s^{-1} the Knudsen number Kn is calculated to be 12.4 for reactor “a” ($\Phi = 3.5$ mm) with $\sigma = 2.9$ Å for Ar.²¹ This means that for this total inflow of Ar into the Knudsen reactor the background contribution is approximately 17% of the total SPIMS signal for the 3.5 mm diameter orifice reactor “a,” independent of the type of molecule or free radical as long as we do not have too high

FIG. 8. SPIMS signal for ratios r of $i\text{-C}_4\text{H}_{10}$ flow through bypass and Knudsen reactor monitored at m/z 58 using 0.25 Torr of H_2 in a 70 W microwave discharge and 3000 V SEM voltage, reactor “a” ($\Phi = 1.5$ mm nominal diameter orifice).

a pressure in the ionization volume which may lead to beam-gas interaction at increasing gas-gas collision frequency. For isobutane a background contribution of approximately 9.3% has been established according to Table III and results displayed in Figures 7 and 8, Tables XI and XII. In practice, the background contribution to the VUV SPIMS signal will be accounted for when using closed shell species detection in the 3.5 mm diameter orifice reactor.^{28,29} When free radicals such as ethyl²⁸ or propyl²⁹ are detected, it is usually unnecessary to apply a correction because ratios of free radical concentrations are used for the extraction of the relevant kinetic information. In addition, free radicals will hardly survive gas-surface collisions with the stainless steel chamber walls so their contribution to the background intensity will be minimal. However, this latter point needs additional experimental verification using a reliable free radical source.

C. SPIMS spectra

In this section several SPIMS spectra are displayed for illustration purposes in terms of sensitivity at a given resolution. Figure 9(a) displays a mass scan of a SPIMS signal for toluene (C_7H_8) at an inflow $F_i(C_7H_8) = 3.03 \times 10^{15}$ molecule

FIG. 9. SPIMS signal of (a) toluene (C_7H_8) at $F_i(C_7H_8) = 3.03 \times 10^{15}$ molecule/s at $P = 1 \times 10^{-6}$ Torr (ion gauge), SEM voltage of 1500 V, reactor a ($\Phi = 3.5$ mm nominal orifice diameter). The pressure in the H_2 lamp was 1 Torr at 40 W; (b) acetone (C_3H_6O) at $F_i(C_3H_6O) = 7.49 \times 10^{15}$ molecule/s at identical conditions as for (a).

FIG. 10. Calibration plot for toluene SPIMS signal as a function of the inflow $F_i(C_7H_8)$: full circles, pure H_2 (correlation line parameters: $y = 3.25 \times 10^{-16} x + 1.73 \times 10^{-1}$, $R^2 = 0.99$) and empty circles, Cl_2/He (0.1%) (correlation line parameters: $y = 1.20 \times 10^{-16} x + 3.24 \times 10^{-1}$, $R^2 = 0.99$) microwave discharge lamp at 1 Torr total pressure and 40 W; SEM voltage of 1500 V, reactor "a" ($\Phi = 3.5$ mm nominal orifice diameter). The SPIMS spectrum displayed in Figure 10 has been taken at the same experimental conditions and corresponds to the seventh (blue) data point from the left.

s^{-1} obtained using a H_2 discharge lamp at 1 Torr/40 W and a SEM voltage of 1500 V. Except for the isotope peak at m/z 93 which comprises 7% of the molecular ion at m/z 92 as expected, no other masses were detected at significant intensity. Figure 10 exhibits a calibration plot of the SPIMS signal intensity as a function of inflow of toluene using both H_2 and Cl_2 (Cl_2/He (0.1% v/v) discharge lamps for comparison. The experimental conditions for the VUV sources were 1 Torr total pressure at 40 W with the SEM voltage set at 1500 V as for the conditions of Figure 9(a). The ratio of the slopes are 3:1 in favor of single VUV photon ionization by radiation emitted from the H_2 lamp compared to the Cl_2 lamp under the chosen experimental conditions. Figure 10 also shows a small positive intercept for this case which may be attributed to a small background contribution at m/z 92 at the time the data were obtained. Figure 9(b) displays the molecular ion of acetone (CH_3COCH_3) at m/z 58 at an inflow of 7.5×10^{15} molecule/s into reactor "a" using the 3.5 mm nominal diameter orifice and Lyman- α radiation from a 1 Torr H_2 microwave discharge lamp at 40 W. For both toluene and acetone possible SPIMS fragment masses were not observed at a significant intensity at the prevailing noise level.

We intended to improve the single photon VUV ionization by focusing the radiation into the middle of the ionization volume by replacing the planar MgF_2 window by a 1 in. diameter 40 mm f.l. length plano-concave MgF_2 lens which serves as a sealing element at the same time. Moreover, we attempted to reduce the photoelectron yield by applying a thin coating of a high electron affinity compound (EA = 1.9 eV)³⁰ to the stainless steel ionization box described above. To this end we dissolved pyromellitic dianhydride ($C_{10}H_2O_6$) in acetone, immersed the ionization box after thorough cleaning and mounted the part on top of the cross-beam ionization source of the mass spectrometer after prior solvent evaporation. Figure 11 displays the result using the free radical precursor $i-C_3H_7I$ as a test because electron impact fragmentation is responsible for the m/z 43 ($C_3H_7^+$) fragment

FIG. 11. SPIMS scan of $i\text{-C}_3\text{H}_8\text{I}$ using either flat MgF_2 window or 40 mm f.l. MgF_2 lens; with and without PMDA coating of the ionization volume. The color codes and assignment of the scans may be found in Table IV.

being the base peak. The observed peak ratio 43/170 in $i\text{-C}_3\text{H}_7\text{I}$ in Figure 11 is equal to electron impact ionization³¹ within the uncertainty limits. It is possible, however, that $i\text{-C}_3\text{H}_7\text{I}$ undergoes fragmentation upon photoionization at 10.2 eV because the appearance potential of $i\text{-C}_3\text{H}_7^+$ is listed at approximately 9.8 eV.³¹ In this case ionization of $i\text{-C}_3\text{H}_7\text{I}$ would not constitute a secure diagnostic for the occurrence of concurrent EI and VUV-Single Photon Ionization owing to the formation of secondary electrons. Table IV displays the corresponding experimental conditions and results compared to the base case, i.e., no lens and no coating, which led to the conclusion that neither led to a significant improvement of the MS detection. Focusing the diffuse VUV radiation emitted by the discharge lamp did not improve the ion yield nor did the coating lead to a suppression of the secondary electron yield that should have changed the SPIMS intensity ratio between the molecular ion (m/z 170) to fragment ion signal (m/z 43). Similar results and conclusions have been obtained using C_2H_6 as a test molecule.

IV. PERFORMANCE OF THE EXTERNAL FREE RADICAL SOURCE: TWO EXAMPLES

Figures 12(a) and 12(b) display the performance of the external free radical source coupled to VUV SPIMS detection of the free radical as well as closed shell product molecular cations in the present apparatus. Figure 12(a) describes the system performance for the ethyl free radical using reaction (2). Roughly 70% of $[\text{Cl}_2]$ are removed through the microwave discharge and converted into atomic $\text{Cl}^\bullet$ that quickly reacts with C_2H_6 and decreases its concentration in order to generate $\text{C}_2\text{H}_5^\bullet$ free radicals and HCl . This initial free radical density $[\text{C}_2\text{H}_5^\bullet]_0$ is distributed across recombination (head-to-head dimerization resulting in $n\text{-C}_4\text{H}_{10}$) and disproportionation (head-to-tail H-transfer resulting in $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$) products that are unwanted, but unavoidable owing to free radical reactivity. Equations (8) and (9) provide a simplified mass balance for ethyl free radical whose extent of reaction strongly depends on gas phase residence time, recombination/disproportionation rate constants³¹ and total

TABLE IV. Mass scan of SPIMS signal for $i\text{-C}_3\text{H}_7\text{I}$ using either flat MgF_2 window or 40 mm f.l. MgF_2 lens; with and without PMDA coating of the ionization volume box.^c

	Lamp	Lens (MgF_2)	PMDA coating ^b	Peak area ($\text{V}\cdot\text{amu}$)		
				$m/z = 43$	$m/z = 170$	Mass ratio 43/170
Blue ●	H_2			0.68	0.18	3.80
Maroon ●	H_2	Yes		0.48	0.13	3.71
Red ▲	Cl_2	Yes		0.32	0.08	3.90
Dark green ●	H_2	Yes	Yes	0.56	0.14	3.88
Light green ▲	Cl_2	Yes	Yes	0.39	0.10	3.74
Electron impact (70 eV) MS ^a						3.94

^aNIST chemistry WebBook (<http://webbook.nist.gov/chemistry/>).

^bPMDA is Pyromellitic Dianhydride ($\text{C}_{10}\text{H}_2\text{O}_6$).

^cExperimental conditions: Discharge lamp pressure of 0.25 Torr at 70 W; inflow rate $F_i(i\text{-C}_3\text{H}_7\text{I}) = 1.32 \times 10^{16}$ molecule s^{-1} ; pressure in MS chamber (ion gauge) of 1.0×10^{-6} Torr; SEM voltage of 2400 V, reactor “b” (7 mm nominal Φ for escape orifice).

FIG. 12. (a) SPIMS signals or calibrated exit flows between μ -wave discharge switched off and on for chemical compounds that are consumed or produced in the generation scheme of $\text{C}_2\text{H}_5^\bullet$ radicals involving: $\text{Cl}_2 + \mu\text{-wave dc} \rightarrow 2\text{Cl}^\bullet$ and $\text{C}_2\text{H}_6 + \text{Cl}^\bullet \rightarrow \text{C}_2\text{H}_5^\bullet + \text{HCl}$. (reactor “a,” 3.5 mm exit orifice, $F_i(\text{Cl}_2) = 5.60 \times 10^{13} \text{ molec s}^{-1}$, $F_i(\text{C}_2\text{H}_6) = 6.25 \times 10^{14} \text{ molec s}^{-1}$, SEM voltage 2500 V, 0.25 Torr in H_2 discharge lamp at 70 W). (b) Calibrated exit flows between μ -wave discharge switched off and on for chemical compounds that are consumed or produced in the generation scheme of $\text{t-C}_4\text{H}_9^\bullet$ radicals involving: $\text{H}_2 + \mu\text{-wave dc} \rightarrow 2\text{H}^\bullet$ and $\text{t-C}_4\text{H}_9\text{I} + \text{H}^\bullet \rightarrow \text{t-C}_4\text{H}_9^\bullet + \text{HI}$. (reactor “a,” 3.5 mm exit orifice, $F_i(\text{H}_2) = 2.05 \times 10^{14} \text{ molec s}^{-1}$, $F_i(\text{t-C}_4\text{H}_9\text{I}) = 1.08 \times 10^{15} \text{ molec s}^{-1}$, SEM voltage 2500 V, 0.25 Torr in H_2 discharge lamp at 70 W).

pressure:

$$\Delta[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_5^\bullet]_0, \quad (8)$$

$$[\text{C}_2\text{H}_5^\bullet]_0 = [\text{C}_2\text{H}_5^\bullet]_{\text{ss}} + [\text{C}_2\text{H}_4]_{\text{ss}} + [\text{C}_2\text{H}_6]_{\text{ss}} + 2[\text{n-C}_4\text{H}_{10}]_{\text{ss}}, \quad (9)$$

where Δ corresponds to the difference in species concentrations between microwave discharge “on” and “off” and the subscript “ss” denotes steady-state conditions that correspond to outflow of the named species. According to Figure 12(a) we obtain an ethyl free radical specific exit flow of $1.6 \times 10^{11} \text{ molecule s}^{-1} \text{ cm}^{-3}$ that is amenable to spectroscopic identification or chemical reaction, as the case may be. Using $k_{\text{esc}} = 3.31 \text{ s}^{-1}$ from Table I for ethyl free radical at 298 K we end up with an ethyl radical concentration of $4.83 \times 10^{10} \text{ molecule cm}^{-3}$. Figure 12(b) displays the case of the tertiary

butyl ($\text{t-C}_4\text{H}_9^\bullet$) free radical generated using atomic hydrogen in reaction (10):

In this case we observe roughly a 10%–15% consumption of the free radical precursor t-butyl iodide leading to a steady-state exit flow of $5.0 \times 10^{11} \text{ molecule s}^{-1} \text{ cm}^{-3}$ of t-butyl free radicals along with the disproportionation ($\text{i-C}_4\text{H}_{10}$, $\text{i-C}_4\text{H}_8$) and recombination (C_8H_{18} , hexamethylethane or equivalently, 2,2',3,3'-tetramethylbutane) products.

The above-listed exit flows emanate from the 3.5 mm diameter exit orifice of the used Knudsen flow reactor “a.” A typical measured flow of ethyl free radical at 300 K³¹ into the Knudsen flow reactor of $7 \times 10^{13} \text{ molecule s}^{-1}$ corresponds to an ethyl radical concentration of 4.2×10^{11} and $1.0 \times 10^{12} \text{ molecule cm}^{-3}$ for pumping at full speed and

mechanical pump turned off, respectively. This calculation made use of k_{esc} for the radical formation tube displayed in Table I, namely $k_{\text{esc}} = 5.50 \text{ s}^{-1}$ (full pumping, V3 open) and 2.32 s^{-1} (V3 closed), respectively, using the mechanical pump on the free radical source (left-hand side of Figure 1). Using the rate constant for ethyl radical recombination to $n\text{-C}_4\text{H}_{10}$ of Dobis and Benson,³² $k_{\text{rec}} = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, we calculate a first order free radical decay $k^{\text{I}} = 5.88$ (full pumping, V3 open) and 14.0 s^{-1} (V3 closed) that must be compared to the above k_{esc} values. It is clear that full pumping (V3 open) significantly decreases the radical-radical reaction rates such as recombination and disproportionation. If one compares $[\text{C}_2\text{H}_5^{\bullet}]$ in the free radical source vs. the 3.5 mm diameter exit orifice reactor “a” (4.2×10^{11} vs. $4.8 \times 10^{10} \text{ molecule cm}^{-3}$) one comes to the conclusion that $[\text{C}_2\text{H}_5^{\bullet}]$ is higher by roughly an order of magnitude in the free radical source given that no radical recombination/disproportionation occurs in the free radical source owing to the fact that the residence time is small at full pumping (V3 open). The presented thermal free radical source is indeed promising and will be used in kinetics experiments in the near future.

V. CONCLUSIONS AND PERSPECTIVES

The new SPIMS instrument presented herein has been successfully used for the determination of the chemical kinetics of reaction (1) for ethyl free radical ($\text{C}_2\text{H}_5^{\bullet}$).³⁰ Both the activation (Arrhenius) parameters as well as the thermochemical consequences (thermochemical parameters $\Delta_f H^0(\text{C}_2\text{H}_5^{\bullet})$ and $S_0(\text{C}_2\text{H}_5^{\bullet})$) have been determined when the kinetic parameters of the reverse reaction has been taken into account. At variance with recent determinations of the same kinetic parameters of reaction (1)^{3,4,9,10} we have obtained a small, but significant positive activation energy and a preexponential A-factor that is consistent with “low” values of the rate constant k_1 .²⁸ The decisive advantage of this kinetic measurement has been enabled by the following new features embodied in the new SPIMS instrument: (i) free radical source external to the Knudsen flow reactor providing thermal free radicals generated using chemical methods of abstraction and addition from suitable free radical precursors. In addition, it removes the possibility of secondary chemistry inside the Knudsen flow reactor; (ii) established mass balance in the chemical kinetic scheme by observing the ethyl free radical decay and the accumulation of the ethane product under identical experimental conditions; (iii) use of several physically different Knudsen flow reactors enabling the separate determination of free radical wall losses, thereby settling a question debated in the literature; and (iv) use of analog detection techniques owing to sufficient sensitivity of the free radical SPIMS signal thereby saving time during signal accumulation. However, the use of microwave discharges for both VUV photon generation as well as in the free radical generation schemes leads to unwanted noise in the experimental data that may be circumvented, at least partly, by the use of synchrotron radiation for single tunable photon ionization of free radicals.

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APPENDIX A: DISCHARGE LAMP PERFORMANCE

Microwave-powered discharge lamps emit diffuse albeit intense line radiation in the VUV spectral region according to the nature of the discharged gas that often is mixed with He or Ar in a per cent or so by volume concentration.³³ Owing to the diffuse nature of the emission a critical design parameter is the distance between the MgF_2 entrance window of the VUV radiation and the center of the ionization region II of the quadrupole mass spectrometer. In the present design this distance has been minimized to 49 mm by recessing the flange by approximately 100 mm from the outer cylindrical surface of the chamber towards the cylindrical axis of the chamber (Figure 1). As discussed above, VUV photons generate secondary photoelectrons on the interior walls of the stainless steel chamber that have been detected using a diode detector for the electron density (concentration). This diode detector was installed at the location of the ionization volume (see Figure 1) after removal of the quadrupole mass spectrometer and consisted of two copper ring electrodes of approximately 5 cm diameter spaced 3 cm apart and connected to a transient electrometer-amplifier described in the literature.^{34,35} The copper ring electrodes were chosen instead of solid metal electrodes in order to minimize the metal surface exposed to VUV radiation, a design proven in the past in the detection of ions and electrons generated through laser-based (resonance-enhanced multiphoton) ionization (REMPI).³ Figures 13 and

FIG. 13. Relative photoelectron density caused by VUV radiation emitted by pure H_2 microwave discharge as a function of hydrogen total pressure in discharge lamp at 40 W with removed quadrupole MS, correlation line parameters: $y = 1.49x + 2.88$, $R^2 = 0.97$.

FIG. 14. Relative photoelectron density caused by VUV radiation emitted by Cl₂/He (0.1% v/v) microwave discharge as a function of He total pressure in discharge lamp at 40 W with removed quadrupole MS, correlation line parameters: $y = 6.05 \times 10^{-1} x + 9.10 \times 10^{-4}$, $R^2 = 0.98$.

FIG. 15. Relative photoelectron density caused by VUV radiation emitted by Cl₂/He (0.1% v/v) microwave discharge as a function of discharge power at 0.95 Torr total pressure in discharge lamp with removed quadrupole MS, correlation line parameters: $y = 9.90 \times 10^{-3} x + 2.12 \times 10^{-1}$, $R^2 = 0.97$.

14 display the dependence of the amplified electron signal as a function of the lamp pressure for pure H₂ and 0.1% (v/v) Cl₂/He, respectively, whereas Figure 15 displays the dependence of the relative electron density as a function of discharge power for a 0.1% (v/v) Cl₂/He gas mixture. The supply voltage for the transient electrometer-amplifier was set at ± 6.4 V based on rechargeable batteries that were constantly recharged by a dc power supply while in operation. The voltage on the copper ring electrodes was set at ± 27.4 V which corresponded to a value close to saturation of the electron current. Figures 13 and 14 display a linear relationship of the relative electron density with total pressure in the discharge lamp above 0.2 and 0.4 Torr for H₂ and Cl₂/He, respectively. Figure 15 shows the corresponding dependence on discharge power for Cl₂/He at 0.95 Torr total pressure in the discharge lamp. These data show a linear dependence of lamp perfor-

mance on both total pressure and microwave power using the relative photoelectron density in the presence of VUV photons as a proxy. The primary purpose of the secondary photoelectron detection was to provide a proxy for monitoring the VUV flux as well as its temporal stability, notwithstanding the fact that the insertion of the quadrupole mass spectrometer would represent a perturbation to the signal.

APPENDIX B: SPIMS SIGNAL AND BACKGROUND CONSIDERATIONS

Tables V and VI provide additional quantitative information regarding data displayed in Figures 3 and 4. Tables VII and VIII provide additional data pertaining to Figures 5 and 6.

TABLE V. i-C₄H₁₀ and Ar MS signals at a constant flow of Ar through the bypass and variable flow of i-C₄H₁₀ through the Knudsen flow reactor.^a

Pressure (Torr)	Flow Ar (molecule/s)	Flow i-C ₄ H ₁₀ (molecule/s)	Signal i-C ₄ H ₁₀ (V)	Signal Ar (V)
1.00×10^{-06}	$1.43 \times 10^{+16}$	0	0.00	8.33×10^{-02}
1.40×10^{-06}	$1.43 \times 10^{+16}$	$4.17 \times 10^{+15}$	0.292	8.48×10^{-02}
1.40×10^{-06}	$1.43 \times 10^{+16}$	$3.44 \times 10^{+15}$	0.307	8.20×10^{-02}
1.70×10^{-06}	$1.43 \times 10^{+16}$	$6.55 \times 10^{+15}$	0.568	9.02×10^{-02}
1.90×10^{-06}	$1.43 \times 10^{+16}$	$7.16 \times 10^{+15}$	0.722	9.24×10^{-02}
2.30×10^{-06}	$1.43 \times 10^{+16}$	$1.15 \times 10^{+16}$	1.02	9.35×10^{-02}
2.40×10^{-06}	$1.43 \times 10^{+16}$	$1.04 \times 10^{+16}$	1.09	9.71×10^{-02}
2.50×10^{-06}	$1.43 \times 10^{+16}$	$1.06 \times 10^{+16}$	1.20	9.42×10^{-02}
2.80×10^{-06}	$1.43 \times 10^{+16}$	$1.51 \times 10^{+16}$	1.44	1.00×10^{-01}
3.60×10^{-06}	$1.43 \times 10^{+16}$	$2.14 \times 10^{+16}$	2.12	1.04×10^{-01}

^aH₂ discharge lamp at 0.25 Torr, 70 W, SEM set at 3000 V, reactor “a.”

TABLE VI. $i\text{-C}_4\text{H}_{10}$ MS signal at a variable flow of Ar through the bypass and a constant flow of $i\text{-C}_4\text{H}_{10}$ through the Knudsen flow reactor.^a

Pressure (Torr)	Flow Ar (molecule/s)	Flow $i\text{-C}_4\text{H}_{10}$ (molecule/s)	Signal $i\text{-C}_4\text{H}_{10}$ (V)
6.70×10^{-07}	$1.05 \times 10^{+15}$	$4.13 \times 10^{+15}$	3.89×10^{-01}
8.00×10^{-07}	$3.10 \times 10^{+15}$	$4.13 \times 10^{+15}$	4.04×10^{-01}
1.10×10^{-06}	$7.19 \times 10^{+15}$	$4.13 \times 10^{+15}$	4.00×10^{-01}
1.30×10^{-06}	$1.14 \times 10^{+16}$	$4.13 \times 10^{+15}$	4.09×10^{-01}
1.40×10^{-06}	$1.16 \times 10^{+16}$	$4.13 \times 10^{+15}$	3.74×10^{-01}
1.70×10^{-06}	$1.58 \times 10^{+16}$	$4.13 \times 10^{+15}$	4.15×10^{-01}
2.10×10^{-06}	$2.14 \times 10^{+16}$	$4.13 \times 10^{+15}$	3.85×10^{-01}
2.20×10^{-06}	$2.35 \times 10^{+16}$	$4.13 \times 10^{+15}$	3.87×10^{-01}
3.10×10^{-06}	$3.30 \times 10^{+16}$	$4.13 \times 10^{+15}$	3.79×10^{-01}
4.10×10^{-06}	$4.55 \times 10^{+16}$	$4.13 \times 10^{+15}$	3.88×10^{-01}

^aH₂ discharge lamp at 0.25 Torr, 70 W, SEM set at 3000V, reactor "a."TABLE VII. SF₆ and H₂ MS signals at a constant flow of SF₆ through the bypass and variable flow of H₂ through the Knudsen flow reactor.

Pressure (Torr)	Flow SF ₆ (molecule/s)	Flow H ₂ (molecule/s)	Signal H ₂ (V)	Signal SF ₆ (V)
7.80×10^{-07}	$6.06 \times 10^{+15}$	0	1.13×10^{-01}	4.45×10^{-02}
9.90×10^{-07}	$6.06 \times 10^{+15}$	$1.67 \times 10^{+16}$	1.20×10^{-01}	4.87×10^{-02}
1.00×10^{-06}	$6.06 \times 10^{+15}$	$2.28 \times 10^{+16}$	1.24×10^{-01}	4.45×10^{-02}
1.10×10^{-06}	$6.06 \times 10^{+15}$	$3.75 \times 10^{+16}$	1.40×10^{-01}	4.46×10^{-02}
1.40×10^{-06}	$6.06 \times 10^{+15}$	$6.63 \times 10^{+16}$	1.40×10^{-01}	4.76×10^{-02}
1.50×10^{-06}	$6.06 \times 10^{+15}$	$9.53 \times 10^{+16}$	1.80×10^{-01}	5.04×10^{-02}
1.50×10^{-06}	$6.06 \times 10^{+15}$	$7.72 \times 10^{+16}$	1.37×10^{-01}	5.33×10^{-02}
1.80×10^{-06}	$6.06 \times 10^{+15}$	$1.01 \times 10^{+17}$	1.56×10^{-01}	5.07×10^{-02}
2.10×10^{-06}	$6.06 \times 10^{+15}$	$1.43 \times 10^{+17}$	1.79×10^{-01}	4.97×10^{-02}
2.30×10^{-06}	$6.06 \times 10^{+15}$	$1.48 \times 10^{+17}$	2.15×10^{-01}	5.74×10^{-02}
2.30×10^{-06}	$6.06 \times 10^{+15}$	$2.03 \times 10^{+17}$	2.01×10^{-01}	5.50×10^{-02}
3.30×10^{-06}	$6.06 \times 10^{+15}$	$2.99 \times 10^{+17}$	2.14×10^{-01}	6.12×10^{-02}
2.40×10^{-06}	$6.06 \times 10^{+15}$	$2.00 \times 10^{+17}$	2.17×10^{-01}	5.08×10^{-02}
2.60×10^{-06}	$6.06 \times 10^{+15}$	$2.25 \times 10^{+17}$	2.26×10^{-01}	5.28×10^{-02}
3.10×10^{-06}	$6.06 \times 10^{+15}$	$2.61 \times 10^{+17}$	2.75×10^{-01}	6.14×10^{-02}

TABLE VIII. H₂ MS signal at variable flow of SF₆ through the bypass and at constant flow of H₂ through the Knudsen flow reactor.

Pressure (Torr)	Flow SF ₆ (molecule/s)	Flow H ₂ (molecule/s)	Signal H ₂ (V)
1.60×10^{-06}	$3.89 \times 10^{+15}$	$9.54 \times 10^{+16}$	1.93×10^{-01}
1.80×10^{-06}	$5.49 \times 10^{+15}$	$9.54 \times 10^{+16}$	1.93×10^{-01}
2.00×10^{-06}	$7.90 \times 10^{+15}$	$9.54 \times 10^{+16}$	1.86×10^{-01}
2.30×10^{-06}	$9.51 \times 10^{+15}$	$9.54 \times 10^{+16}$	1.89×10^{-01}
2.40×10^{-06}	$1.09 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.90×10^{-01}
2.60×10^{-06}	$1.19 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.91×10^{-01}
2.70×10^{-06}	$1.36 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.95×10^{-01}
3.00×10^{-06}	$1.49 \times 10^{+16}$	$9.54 \times 10^{+16}$	2.02×10^{-01}
3.30×10^{-06}	$1.71 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.75×10^{-01}
3.60×10^{-06}	$2.09 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.91×10^{-01}
3.70×10^{-06}	$2.09 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.88×10^{-01}
3.90×10^{-06}	$2.24 \times 10^{+16}$	$9.54 \times 10^{+16}$	1.85×10^{-01}

APPENDIX C: MOLECULAR BEAM VS. BACKGROUND RATIO FOR Ar AND i-C₄H₁₀

Tables IX and X provide additional data in support of the results plotted in Figure 2(a) and 2(b). The isobutane data set is shown in Tables XI and XII plotted in Figures 7 and 8 in the text.

TABLE IX. Measured ratio of Ar SPIMS signals of the flow through the bypass valve to the Knudsen reactor using a 70 W pure H₂ discharge at 0.25 Torr, 3000 V SEM voltage, and reactor a ($\Phi = 3.5$ mm nominal exit orifice).

Pressure (Torr)	Flow Ar (molecule/s)	SPIMS signal from K-cell (V)	SPIMS signal bypass (V)	Ratio (%) bypass/K-cell
3.70×10^{-7}	2.60×10^{15}	1.47×10^{-1}	2.59×10^{-2}	17.6
5.20×10^{-7}	5.00×10^{15}	2.25×10^{-1}	3.56×10^{-2}	15.8
8.30×10^{-7}	9.20×10^{15}	4.03×10^{-1}	5.56×10^{-2}	13.8
1.30×10^{-6}	1.79×10^{16}	7.20×10^{-1}	9.82×10^{-2}	13.6
2.00×10^{-6}	2.78×10^{16}	1.09	1.36×10^{-1}	12.6
2.60×10^{-6}	3.71×10^{16}	1.35	2.03×10^{-1}	15.0

TABLE X. Measured ratio of Ar SPIMS signals of the flow through the bypass valve to the Knudsen reactor using a 70 W pure H₂ discharge at 0.25 Torr, 3000 V SEM voltage, and reactor a ($\Phi = 1.5$ mm nominal exit orifice).

Pressure (Torr)	Flow Ar (molecule/s)	SPIMS signal from K-cell (V)	SPIMS signal bypass (V)	Ratio (%) bypass/K-cell
4.00×10^{-7}	3.75×10^{15}	2.23×10^{-01}	3.40×10^{-02}	15.2
6.00×10^{-7}	6.28×10^{15}	3.18×10^{-01}	4.55×10^{-02}	14.3
6.00×10^{-7}	6.76×10^{15}	2.91×10^{-01}	3.82×10^{-02}	13.1
9.00×10^{-7}	1.04×10^{16}	4.47×10^{-01}	5.71×10^{-02}	12.8
1.20×10^{-6}	1.63×10^{16}	7.35×10^{-01}	9.88×10^{-02}	13.4
1.20×10^{-6}	1.55×10^{16}	6.60×10^{-01}	8.62×10^{-02}	13.1
1.40×10^{-6}	1.87×10^{16}	8.09×10^{-01}	1.14×10^{-01}	14.1
1.60×10^{-6}	2.18×10^{16}	9.04×10^{-01}	1.25×10^{-01}	13.8
1.80×10^{-6}	2.79×10^{16}	1.26×10^{00}	1.62×10^{-01}	12.8
2.50×10^{-6}	3.54×10^{16}	1.44×10^{00}	1.93×10^{-01}	13.4

TABLE XI. Measured ratio of i-C₄H₁₀ SPIMS signals of the flow through the bypass valve to the Knudsen reactor using a 70 W pure H₂ discharge at 0.25 Torr, 3000 V SEM voltage and reactor "a" ($\Phi = 3.5$ mm nominal Φ exit orifice).

Pressure (Torr)	Flow of i-C ₄ H ₁₀ (molecule/s)	SPIMS signal from K-cell (V)	SPIMS signal bypass (V)	Ratio (%) bypass/K-cell
7.90×10^{-7}	5.41×10^{15}	5.82×10^{-01}	3.70×10^{-02}	6.4
8.10×10^{-7}	4.72×10^{15}	4.48×10^{-01}	3.20×10^{-02}	7.1
9.00×10^{-7}	6.69×10^{15}	6.21×10^{-01}	6.63×10^{-02}	10.7
1.00×10^{-6}	6.86×10^{15}	7.09×10^{-01}	4.76×10^{-02}	6.7
1.30×10^{-6}	9.39×10^{15}	8.53×10^{-01}	5.53×10^{-02}	6.5
2.10×10^{-6}	1.56×10^{16}	1.29×10^{00}	1.00×10^{-01}	7.8
2.90×10^{-6}	2.32×10^{16}	1.67×10^{00}	1.52×10^{-01}	9.1
3.50×10^{-6}	2.60×10^{16}	1.79×10^{00}	1.83×10^{-01}	10.3
4.10×10^{-6}	2.97×10^{16}	1.92×10^{00}	1.89×10^{-01}	9.9
4.70×10^{-6}	3.53×10^{16}	2.07×10^{00}	2.10×10^{-01}	10.2

TABLE XII. Measured ratio of $i\text{-C}_4\text{H}_{10}$ SPIMS signals of the flow through the bypass valve to the Knudsen reactor using a 70 W pure H_2 discharge at 0.25 Torr, 3000 V SEM voltage, and reactor "a" ($\Phi = 1.5$ mm nominal exit orifice).

Pressure (Torr)	Flow of $i\text{-C}_4\text{H}_{10}$ (molecule/s)	SPIMS signal from K-cell (V)	SPIMS signal bypass (V)	Ratio (%) bypass/K-cell
7.00×10^{-07}	5.44×10^{15}	6.36×10^{-01}	4.25×10^{-02}	6.7
9.00×10^{-07}	6.12×10^{15}	7.36×10^{-01}	5.95×10^{-02}	8.1
1.00×10^{-06}	7.02×10^{15}	8.62×10^{-01}	5.77×10^{-02}	6.7
1.10×10^{-06}	8.67×10^{15}	9.02×10^{-01}	7.97×10^{-02}	8.8
1.70×10^{-06}	1.34×10^{16}	1.28×10^{00}	1.02×10^{-01}	7.9
1.90×10^{-06}	1.62×10^{16}	1.34×10^{00}	1.14×10^{-01}	8.5
2.30×10^{-06}	1.88×10^{16}	1.50×10^{00}	1.34×10^{-01}	8.9
2.90×10^{-06}	2.43×10^{16}	1.73×10^{00}	1.57×10^{-01}	9.1
3.40×10^{-06}	2.55×10^{16}	1.80×10^{00}	1.71×10^{-01}	9.5
4.30×10^{-06}	3.30×10^{16}	2.03×10^{00}	2.04×10^{-01}	10.1

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