Design and characterization of a late-mixing pulsed nozzle

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A pulsed source that allows mixing of two gases without appreciable reaction prior to expansion is constructed for the study of photoinitiated reactions. The source is characterized by the rotational temperature (80 ± 10 K) and translational temperature (<10 K) of HCl in the expansion. The photoinitiated reaction $Cl+CH_3OH$ is studied to illustrate the usefulness of this source. The design is easy to implement and should be effective for a wide range of reaction dynamics experiments requiring the coexpansion of reactive gases. © *2004 American Institute of Physics.*
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Supersonic expansions in chemical reaction dynamics have been of much value because they produce well-collimated beams of molecules having cooled internal degrees of freedom.[1] One such application of the pulsed supersonic expansion is found in photoinitiated reactions that take place within the expanded stream.[2] In this method a suitable molecular precursor AX is mixed with a reactant molecule BC and coexpanded through a pulsed supersonic jet. A laser then photodissociates the AX molecular precursor to initiate the reaction sequence:

$$AX+h\upsilon\rightarrow A+X, \quad (1)$$

$$A+BC\rightarrow AB+C. \quad (2)$$

Owing to the large number densities of the reagents in the molecular beam, this arrangement allows for laser preparation of the reagent quantum states and state specific detection of the products. Both of these tasks are accomplished by spectroscopic means e.g., IR pumping, stimulated Raman pumping (SRP), laser-induced fluorescence (LIF), and resonance enhanced multiphoton ionization (REMPI). In addition, it has been demonstrated that under favorable conditions, this combination of a pulsed supersonic expansion, laser preparation of reagents, and laser detection of products yields determinations of state-to-state resolved differential cross sections (DCS).[3,4]

Two requirements for the successful implementation of this scheme must be met: (1) the reagents must be coexpanded to ensure their relative velocity is close to zero before the arrival of the pulsed beam from the photolysis laser; and (2) the molecular precursor AX and reagent BC must not react with one another. This last requirement has proven to be vexing in numerous applications. Even a reaction between the reagent gases that is slow on the time scale of the experiment is unacceptable because it introduces ambiguities in the reagent concentrations. Thus the power of this technique has hitherto been limited by the fact that many of the most useful precursors (i.e., those whose photofragments are monoenergetic with well-defined anisotropy parameters) are reactive gases, such as Cl_2, HI, and HBr. To allow the use of these precursors with other reactive gases we have designed a late-mixing pulsed nozzle source that allows the reagents to be kept separate until just prior to expansion.

Johnson and co-workers[5] constructed a source using the principle of supersonic entrainment to produce ionic complexes. This technique utilizes the fact that a gas outside the shock-wave boundary of the jet expansion will be drawn into the supersonic flow far from the orifice.[6] They demonstrate the usefulness of this method for bringing small concentrations of gas into the expansion. However, supersonic entrainment is not expected to produce high enough concentrations of the entrained gas a few nozzle diameters away from the orifice, which is where we typically initiate and probe the reaction products. Subsequently, Young and co-workers[7] constructed a late-mixing source for the production of reactive clusters using pulsed concentric valves. This technique proved capable of delivering reactive clusters. Both of these designs utilize two pulsed valves with short opening times to reduce the pumping load of the vacuum system and to concentrate the molecular species during the firing of the laser. While our design uses this essential feature, we choose a variation of these approaches. Instead of using a concentric arrangement of valves, we introduce the second gas upstream of the expansion orifice in an attempt to make sure that the relative translational temperature of the mixed gases is cold. A necessary requirement for obtaining a state-to-state DCS in a photoinitated reaction is that a well-defined collision energy exists between the reagents. Our design is simple to construct and is shown to have excellent performance for studying the reaction dynamics of photoinitiated chemical reactions.

The mixing source, a schematic of which is given in Fig. 1, uses two commercial pulsed solenoid valves (Series 9, Parker Hannifin Corporation, General Valve Division) with Kel-F poppets. Both valves are axial flow and oriented parallel to the molecular beam. The orifice of the first valve (PV1) is 0.8 mm in diameter and has a PEEK capillary tube (Upchurch Scientific, 1/16 in. o.d., 0.030 in. i.d.) attached to the faceplate with a 1/16 in. Swage-lok compression fitting. The second valve (PV2) has a custom machined faceplate

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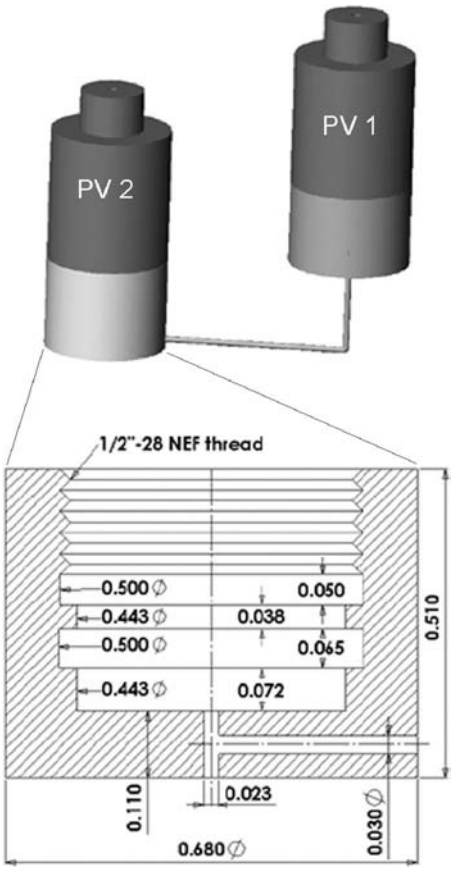

FIG. 1. Schematic of late-mixing pulsed nozzle source and machine drawings of the custom pulsed valve faceplate.

with a 0.8 mm orifice and an additional channel bored into the side that allows connection to the 1/16 in. outer diameter tube. The length of the PEEK tube is 4 cm and is constrained only by the requirement that the new source fit into the space between the electrodes of our existing time of flight (TOF) spectrometer. The advantage of this design is that all parts, except the faceplate for PV2, are commercial components. In addition, the custom part is designed to be compatible with the standard Series 9 valve assembly. The valves, held in place by a set screw, are attached to an XYZ manipulator (MDC Vacuum Products Corporation, 678005) that allows for easy positioning. The manipulator and several electrical and gas feedthroughs are held on an 8 in. CF knife-edge flange and mounted on the existing vacuum chamber. Both pulse valves are controlled by separate homebuilt drivers, capable of producing variable opening times (50–300 μs). The opening of the two separate valves and firing of the lasers is coordinated by a Digital Delay Generator (Stanford Research Systems, DG535).

The rest of the apparatus has been presented previously,[4] so only a brief description is given here. The orifice of PV2 is positioned to be in the extraction region of a linear Wiley-McLaren time of flight (TOF) spectrometer. The expansion is intersected perpendicularly by several lasers, allowing for the photoinitation of the reaction, state selection of the reagents, and spectroscopic probing of the reaction products via REMPI. For the current experiments a Nd:YAG laser (Continuum PL9020) is used to generate 355 nm light (20–50 mJ) and a Nd:YAG (Spectra Physics, DCR-2A) pumped dye laser (Lambda Physik, FL2002 operating with LD489) is used to produce ~2 mJ of 240 nm light after doubling the dye fundamental in a BBO crystal. The spectrometer can be operated in one of two modes. The ''crushed'' mode collects all ions produced in the focal volume of the probing laser by using a large (800 V/cm) extraction field. In the ''velocity-sensitive'' mode ions of a given mass are allowed to separate according to their initial velocity. This is accomplished by operating the mass spectrometer under lower extraction voltages (69 V/cm). A core-extractor is used to reject ions with velocities perpendicular to the flight tube and to simplify the data analysis. Several experiments, discussed in the following, are performed using this apparatus to test our source.

All beam diagnostics were performed under identical conditions as those used for our molecular reaction dynamics experiments. To characterize the rotational temperature, the rotational state distribution of HCl $(v=0)$ in the beam was recorded via 2+1 REMPI on the F-X $(0,0)^{8-10}$ transition around 240 nm. The experimental line strength factors were calibrated by measuring the state distribution of a room temperature sample. After ensuring that the gas streams from PV1 and PV2 were overlapped with the lasers in time and space, the rotational distribution of HCl was recorded by expanding ~1% HCl (Matheson, 99.9%) in He (Liquid Carbonic, 99.995%) with a backing pressure of 800 Torr from PV1 while He flowed through PV2 with a backing pressure of 100 Torr. The lowest J states in the beam $(J=0-4)$, which constitute the majority of the observable HCl, were well characterized by a Boltzmann temperature of 80 ± 10 K.

The translational temperature was characterized by measuring the velocity distribution of HCl using the F-X (0,0), R(1) transition from a single nozzle, the dual nozzle, and a thermal source. This measurement was accomplished by operating our spectrometer in ''velocity-sensitive'' mode, which allows the mass 36 ions (associated with $H^{35}Cl^+$) to separate in time according to their nascent velocities. A Monte Carlo simulation is used to generate the expected experimental response for ions with a given initial speed. The entire speed range can be covered using such ''basis functions,'' thus allowing for a conversion of the measured TOF profile to a speed distribution.[4] In the current experiments we forward convolute a Boltzmann distribution of velocities, using the above basis functions, to obtain the expected TOF profile for a given temperature.[11] Figure 2 shows the TOF profiles that result from HCl seeded in He expanded from the single nozzle, HCl seeded in He expanded from the dual nozzle source, and a thermal sample of HCl. No difference is observed between the single and dual nozzle arrangements [Fig. 2(b)]; thus within our experimental resolution the beam translational temperature of the late-mixing source is similar to that of the single nozzle source. In addition, we note that the jet-expanded TOF profile is significantly narrower than the thermal sample [Fig. 2(a)] indicating that the translational temperature perpendicular to the beam axis is cooled. Using the above forward convolution method, we estimate that the translational temperature is <10 K. We can put only an upper bound on the temperature because the instrument

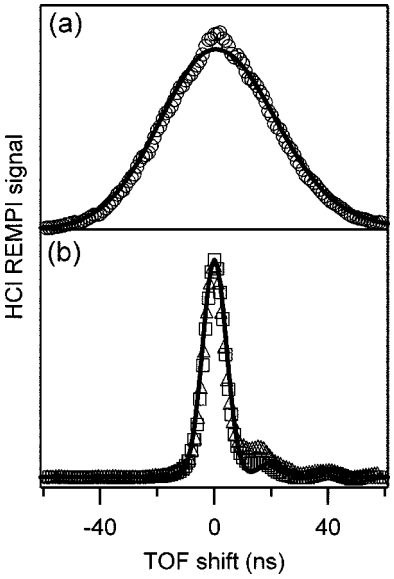

FIG. 2. Time-of flight profiles for (a) a thermal source of HCl (○); and (b) HCl expanded from a single-nozzle source (□) and a dual-nozzle source (△). The solid line is the simulated profile assuming a Boltzmann distribution of velocities at 298 K (a) and 5 K (b).

resolution is not sufficient to differentiate temperatures below this value.

In order to demonstrate the usefulness of this source for a reaction dynamics experiment, we examined the $Cl+CH_3OH$ reaction. This system is difficult to study with a conventional single nozzle arrangement because the reagents (Cl_2 and CH_3OH) cannot be mixed without prereaction. In Fig. 3 we present the REMPI spectrum of the $HCl(v=1)$ products obtained from the $Cl+CH_3OH$ reaction. In this experiment a 1:10 mixture of Cl_2 (Matheson, research grade 99.999%) and He was mixed and expanded from PV1 (backing pressure ~800 Torr) while methanol and He in a ratio of 1:1 was expanded from PV2 (backing pressure ~200 Torr). The third harmonic of a Nd:YAG laser (355 nm) was used for photolysis of the chlorine and provides a center-of-mass collision energy of $1960\pm170\ cm^{-1}$. The given error is taken to be the HWHM of the spread in collision energies and is determined by the initial beam translational temperature.[12] Without the cooling obtained from a supersonic jet the collision energy broadening would be $925\ cm^{-1}$. As seen in Fig. 3, the peaks are well resolved and have an excellent signal-to-noise ratio despite the fact that $HCl(v=1)$ products constitute only $16\pm7\%$ of the total reactive signal. The rotational distributions ($v=0$, $v=1$) and state-selected differential cross sections for this reaction will be the subject of a future publication.[13]

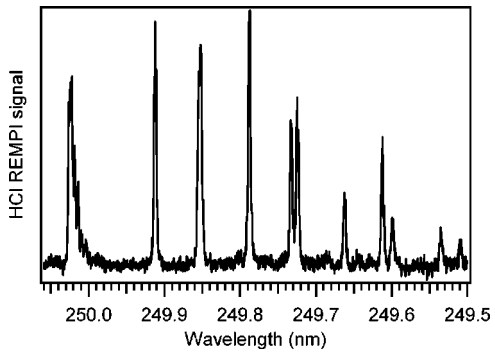

FIG. 3. F-X (0,1) 2+1 REMPI spectrum of $HCl(v=1)$ products from the photoinitiated reaction $Cl+CH_3OH$.

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