Design for improved resolution in a time-of-flight mass spectrometer using a supersonic beam and laser ionization source

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This article describes the design of a time-of-flight mass spectrometer (TOFMS) constructed for optimum use with resonance-enhanced multiphoton ionization spectroscopy in supersonic beams. The use of the supersonic beam results in a great improvement in resolution, i.e., at least 800 at mass 93. Ion packets on the order of 10 ns FWHM or less are observed at our flat dual channel plate detector and the resolution ultimately appears to be laser-pulse-width limited. The design of this TOFMS utilizes fast-pulsed molecular beam techniques to allow the use of reservoir pressures >1 atm with a large orifice (0.5 mm) in order to provide high on-axis intensity for maximizing the photoionization signal produced by our pulsed laser system with the use of only modest pumping capacity. It also uses a skimmed beam, differential pumping, and a liquid-N_2 baffle in order to maintain the flight tube at pressures on the order of 5×10^{-7} Torr and to eliminate organic contamination from the ionization region.

INTRODUCTION

The time-of-flight mass spectrometer (TOFMS) has found utility in many experiments since the full mass spectrum can be displayed on a single ionization pulse. This is particularly important in laser photoionization experiments where the low repetition rates of present laser systems make scanning mass spectrometers impractical for data collection. The TOFMS is also mechanically simple and easy to build and maintain. Its transmission is generally higher than other types of mass spectrometers where transmission may change at the expense of resolution or may vary as a function of mass as in a quadrupole.

The main limitation of TOFMS's has been the limited resolution attainable. The two main factors that limit the resolution are the initial space and energy spread of the ions created in the acceleration region of the TOF device. The space spread is due to the fact that the ionization source has a finite width in space. Therefore, ions starting at different points will reach the detector at different times, consequently limiting the width of the ion peaks observed at the detector. The more serious problem is generally the initial thermal energy of the molecules due to the Boltzmann distribution of resultant-ion energies which may be on the order of 0.09 eV. The original diode source design for a TOF device first published by Wiley and McLaren[1] sought to minimize these problems in order to improve the attainable resolution. However, a resolution of only ~200 could still be achieved. A combination of time-lag focusing and other techniques served to further increase the resolution; however, other solutions to this problem must be found.

In this work we present the use of a skimmed supersonic beam as a means of improving resolution in a TOF mass spectrometer. A TOF system has been constructed to achieve improved resolution using this method and to solve background problems inherent in earlier designs. The key to improving the resolution is to narrow the velocity spread of the molecules in the acceleration region of the TOF. This can be accomplished by the use of a supersonic molecular beam,[2,3] in which atoms or molecules are forced to expand through an orifice into vacuum. The result is a Maxwellian distribution which is strongly peaked around an average velocity,[4,5] so that to first approximation the molecules are now traveling in the same direction with the same velocities and there is minimal energy spread to limit the resolution.

I. DESIGN OF TIME-OF-FLIGHT SYSTEM

The production of a supersonic jet involves seeding a small percentage of a molecule of interest in a flow of a light carrier gas such as Ar, He, etc., so that the large organic species are carried along with the flow of light atoms. In order to obtain improved resolution the maximum translational cooling obtainable is desired. The translational temperature lowering is related to the Mach number M, where $M\alpha(V_s/\sqrt{T_s})$ and V_s is the stream velocity and T_s is the local temperature in the beam.[4,5] The terminal Mach number reached in the beam under free flow conditions is given for argon as $M_T = 133(P_0D)^{0.4}$, where D is the diameter of the nozzle orifice and P_0 is the reservoir pressure. The ability to reach high M_T thus depends on maximizing the reservoir pressure and diameter of the nozzle. However, this would place high demands on the pumping capacity of the vacuum system. Thus, a pulsed molecular beam modulator or pulsed valve[6–8] is used to pulse the beam in order to reduce the duty cycle and thus the gas load to be pumped. The molecular beam is pulsed at the repetition rate of our pulsed laser source which is 10 Hz. The pulsed valve has an opening time of 55 μs at "choked flow" so that it is only open for 550 μ s

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during every second of operation, producing a reduction in the duty cycle by nearly 2000×. The use of this pulsed valve allows reservoir pressures on the order of 1 atm and a nozzle diameter of 0.5 mm, so that a terminal Mach number for Ar on the order of 40 can be achieved and a significant reduction in the velocity spread thus results.

The supersonic beam is designed for use with a skimmed, differentially pumped TOF design shown in Fig. 1. The beam from the pulsed valve enters horizontally from one side of a standard 8-in. conflat six-sided cross while the TOF mass spectrometer sits vertically on top of the cross. The laser ionization source enters through the other set of orthogonal ports through quartz windows which transmit the UV light beam. An important feature of this device is the differential pumping design in which a liquid-N_2 baffled 6-in. diffusion pump station pumps the main throughput of the beam so that under the operating conditions described above the pressure in the main chamber is 1.8×10^{-5} Torr when the pulsed valve is operating. However, the TOF acceleration region is enclosed by a structure with apertures for the molecular beam and laser beam which are conductance limited as shown in Fig. 2. The acceleration region and flight tube are pumped by a liquid-N_2 baffled 2-in. diffusion pump so that during operation the pressure in the TOF device is $\sim6\times10^{-7}$ Torr or a factor of 30× lower than the main chamber. Thus, the TOF device remains relatively clean and the electron multiplier lifetime is extended by operating at lower pressure. The really significant point is that a liquid-N_2 trap is connected to this enclosed structure in order to keep the ionization region clean from organic contamination. This was found to be a serious problem in earlier designs in which background laser ionization was detected from at least two sources: (1) backstreaming diffusion pump oil; (2) molecules from the jet which collide with the walls and become thermalized and then backscatter into the ionization region. This second source of background provides a thermalized signal whose mass spectral peak is broadened compared to that of the cold species in the jet. However, the ionization region is kept clean from organics by the use of liquid-N_2 baffling to trap out contamination. The walls of the Dewar container are constructed of thin 0.020-in. stainless steel in order to minimize heat conduction to the walls and thus boil off of liquid N_2. The TOF is designed vertically in order to allow construction of the liquid-N_2 trap.

The design of the acceleration region is shown in Fig. 2 and is a modified version of the diode source of Ref. 1. The source contains three plates where the voltage on $f_1 = 4181$ V, on $f_2 = 3866$ V, and f_3 is at ground. The distances between the plates are $d_1 = 1$ cm and $d_2 = 1$ cm. The apertures in the plates are 1 cm and are covered by 50 lines/in. stainless-steel

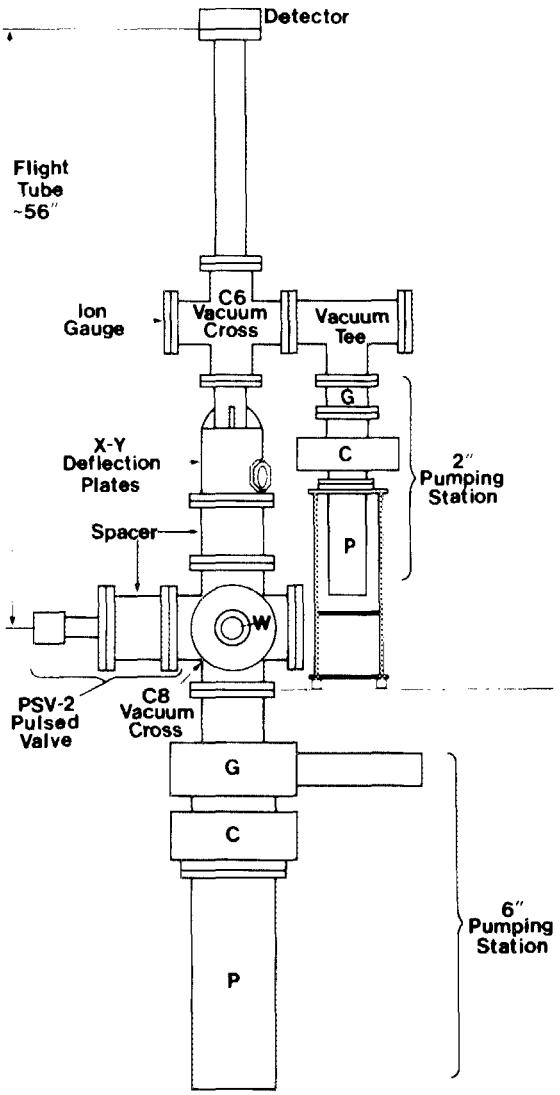

FIG. 1. Schematic of the TOFMS and vacuum components, where C8 = 8-in. conflat six-way cross, C6 = 6-in. conflat four-way cross, G = gate valve, C = liquid-nitrogen cold trap, P = diffusion pump, W = polished quartz windows.

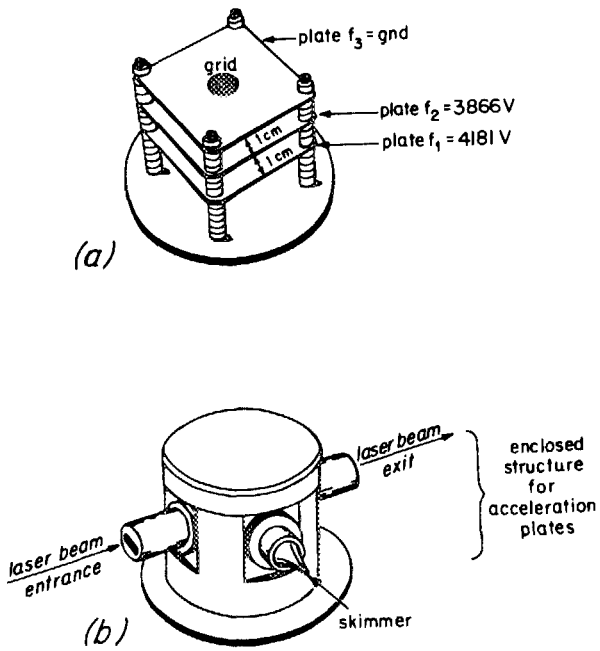

FIG. 2. (a) Sideview of the ionization region of the TOFMS according to the original design of Wiley and McLaren. (b) View of the structure surrounding the ionization region shown in (a). Note the two ports for allowing passage of the laser beam through the ionization region and the skimmer for skimming the molecular beam orthogonal to the laser beam.

grids with 90% transmission each. The acceleration region is enclosed by a structure with apertures to allow the laser beam to pass through the ionization region (i.e., between f_1 and f_2). The other set of orthogonal sides of the structure have openings for the molecular beam. On the entrance side the beam is skimmed by a skimmer (Beam Dynamics, Inc.) with a 0.040-in. orifice. The skimmer collimates the molecular beam so that it passes through the ionization region cleanly without interacting with the plates, which might cause turbulence and disrupt the surpersonic flow. The opposite side uses an extended tube as a beam dump. It should be noted that the space resolution from Ref. 1 is $\propto (S_0/\Delta S)^2$, where S_0 = initial position of the ions about the average position and ΔS is basically the size of the ionization region. The resolution can be increased by spreading apart the acceleration plates f_1 and f_2 to increase S_0 or by decreasing the laser ionization region to decrease ΔS. However, if ΔS is decreased then the ionization interaction volume will decrease as the (radius)^2 and the signal will drop accordingly. In this design the plates have been spread apart to eliminate the space resolution problem.

The TOF device is constructed according to the dimensions shown in Fig. 1. In order to position the ionization region to the correct height so that the laser beam passes through the interaction region, an 8-in. conflat nipple spacer is used. Above this spacer located in the four-sided cross marked X–Y are the X–Y deflection plates. Since the supersonic molecular beam provides a directed flow in one direction, a low-voltage deflection must be applied to the plates in order to correct for the transverse velocity component that results. This correction is mass dependent and the plates have been placed in the center of the flight path to allow the ions time to spread out in space so that the plate voltage can in principle be programmed and swept so that each ion mass is equally corrected.

The detector is a dual microchannel plate which provides a gain of 10^7 and is terminated with a special 50-Ω connector. Its rise time is subnanosecond which is essential for the fast pulses arriving at the detector. A grid is placed in front of the detector to create a truly fieldfree drift region in the flight tube since the front surface of our device is operated at a high negative potential. The output connector should also be properly terminated for 50 Ω.

This TOF design will provide high resolution when used properly in conjunction with the supersonic beam technique. Figure 3 shows a TOF mass spectrum of the parent peak of aniline. This was taken using laser photoionization at 293.77 nm which is at the peak of the origin of the $^1A_1 \rightarrow {}^1B_2$ transition. The resolution is defined as $R = T/(2\Delta T)$, where T is the total flight time of the ion packet and ΔT is the FWHM of the peak. In this case $R = 16 \times 10^3$ ns/20 ns = 800 resolution. With careful adjustment of the voltages and beam to skimmer distance to prevent turbulence on the skimmer, we have observed ion packet widths of ~5 ns which appear to be laser limited in resolution. According to the equations of Ref. 1 the space resolution should be M_s ~5300 assuming a laser beam diameter of 2 mm so that the space resolution is not a factor in these results. Further, assuming a Mach number of 40 for Ar a translational temperature of ~0.5 K is obtained. This would result in an energy resolution of M_θ ~9300 so that this is not a limiting factor either. This should also be true if He is used as the carrier gas, although here the temperature reaches only 6.7 K and M_θ ~2500. In fact a laser with a narrower pulse should be able to improve the resolution further.

The signal in Fig. 3 is huge at nearly 20 V full scale into 50 Ω. If the detector has a gain of $10^7\times$ then 2000 ions are produced per laser pulse. Assuming an initial aniline concentration of 30 ppm in 1 atm He then the density of aniline molecules in our interaction region is $\sim 3 \times 10^{10}$ molecules/cm^3 in the molecular beam at the interaction region (0.03 cm^3) and if we assume an ionization efficiency of 10%, then the total efficiency of the supersonic beam-laser ionization TOF device is ~0.002%. Approximately 10% of this number is due to the fact that the molecular beam is spread out over 2.2 cm at the ionization region and the laser beam which intersects this is only 0.2 cm in diameter. This number could be improved by using a laser beam which is an expanded sheet parallel to the detector to increase the number of molecules excited without losing resolution.

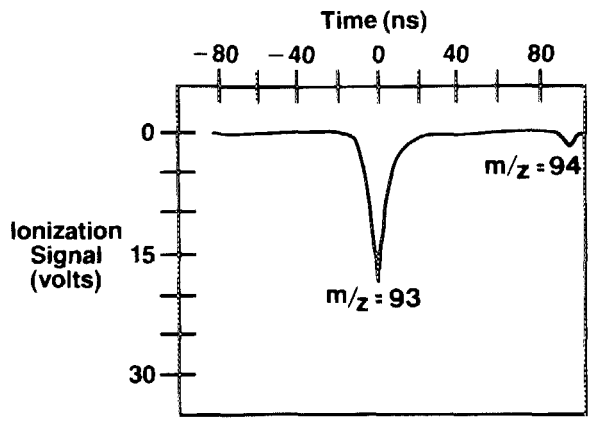

FIG. 3. TOF mass spectrum of the parent peak ($m/z = 93$) of aniline. No fragmentation was observed over the rest of the mass range. The small peak present at higher mass is the C_{13} isotope of aniline at ($m/z = 94$).

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