

Design of a pulsed valve for high-pressure NH₃ injection into supersonic beam/mass spectrometry

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A novel design of a pulsed valve for high-pressure injection of NH₃ for supersonic jet expansions is presented. This valve can operate up to 200-atm reservoir pressure at 180 °C with a pulse width down to 100 μs. This valve has been designed so that the solenoid core is not in contact with the carrier fluid so that it can be used with highly polar corrosive liquids or supercritical fluids. The ability to use supercritical NH₃ as a means of injecting small thermally labile biological molecules into supersonic jet expansions for analysis by resonant two-photon ionization in a time-of-flight mass spectrometer is demonstrated.

INTRODUCTION

Supersonic jet expansions have served as a means of producing ultracold molecules for spectroscopy¹ and as an injection technique for mass spectrometry.² This method has been limited largely to molecules which are sufficiently volatile to be heated into the gas phase where they can be mixed with a light carrier gas such as Ar. The focus of recent work, though, has been to extend the supersonic jet technique to nonvolatile and thermally labile molecules.³⁻⁸ A number of techniques have been developed for entrainment of nonvolatiles into jet expansions including pulsed laser desorption,³⁻⁸ thermospray,^{7,9,10} direct liquid injection,¹¹ and supercritical fluid injection.¹²⁻¹⁴

Supercritical fluids have the property that enables them to dissolve many nonvolatile molecules like a liquid; however, upon injection into vacuum, as in a supersonic jet, they expand like a gas. Thus, this serves as a convenient means of injecting molecules into a mass spectrometer without the severe clustering problems often associated with liquid injection methods. In previous work,¹²⁻¹⁴ relatively nonvolatile compounds have been entrained in supersonic expansions from supercritical CO₂ and N₂O. Molecules such as polynuclear aromatic hydrocarbons (PNAHs) were often studied since these nonpolar species dissolve readily in these nonpolar solvents. However, polar biological molecules have been shown to have very low solubility in these bulk solvents.¹⁵

In our previous work,¹² a pulsed method for supercritical fluid injection in supersonic beams was introduced which involved a custom-designed valve capable of withstanding the required supercritical fluid conditions. This pulsed method resulted in a reduced duty cycle for pumping of the supercritical solvent when used in combination with a pulsed excitation/ionization source such as laser-induced resonant two-photon ionization (R2PI). A large (200 μm) orifice could thus be used for enhanced sensitivity relative to continuous expansions. Most significantly, though, it was shown that by correctly synchronizing the laser pulse to the molecular beam pulse one could minimize the formation of clusters even at a relatively low temperature (40 °C).^{12,16}

In these initial experiments, however, the pulsed valve injection source used has several distinct disadvantages in-

cluding: (1) a large dead volume and surface area which required a heavy-duty stainless-steel construction in order to withstand the high pressure and as a consequence often resulted in a serious memory effect and; (2) a solenoid coil exposed to the solvent that was susceptible to damage from the corrosive highly polar fluids.

In this work, we present the design of a simple pulsed valve which is capable of operating with supercritical NH₃ up to 200 atm and 180 °C with a pulse width as short as 100 μs. This valve uses a simple construction based upon a small dead volume and small surface area. The use of supercritical NH₃ as the solvent is shown to provide a promising sample introduction method for polar biologicals into a mass spectrometer under relatively mild conditions in order to prevent decomposition of these fragile species. In the experiments presented herein, liquid NH₃ is used to initially dissolve polar samples. The liquid is then converted to supercritical conditions in the valve and injected as a supersonic jet into a time-of-flight mass spectrometer where the sample is selectively ionized by R2PI.

I. EXPERIMENT

A. System design

The experimental setup has been described previously.¹² It consists of a differentially pumped vacuum system with a time-of-flight mass spectrometer (TOFMS) sitting vertically on top of the chamber. The laser beam enters the chamber through a quartz window and R2PI is produced in the acceleration region of the TOFMS. The molecular beam is introduced through a pulsed valve in the source chamber, which is pumped by a 4-in. diffusion pump and cryobaffle. The main load of pumping the condensable NH₃ supercritical fluid carrier is performed with four liquid nitrogen (LN₂) traps, which extend from the top of the chamber into vacuum. The ionization chamber is pumped by a 6-in. diffusion pump and cryobaffle and is separated from the source chamber by a liquid N₂-cooled partition plate with a skimmer. The skimmer was designed with a sharp edge to slice the beam and with a shape to deflect molecules not transmitted through the orifice, thus minimizing shock waves. If a

330- μm orifice is used in the pulsed valve with a 10-Hz repetition rate, 100- μs pulse width, and 150-atm backpressure of NH_3 , then the pressure in the first chamber does not rise above 1×10^{-4} Torr and in the second chamber remains less than 1×10^{-5} Torr.

B. High-pressure pulsed valve design

The design of the high-pressure pulsed valve is shown in Fig. 1. It consists of two basic sections: (a) the solenoid and (b) the plunger and body enclosure. The solenoid provides the magnetic field to move the plunger. It is prepared by winding ~ 150 ft of 28 gauge magnetic wire (Belden heavy armored poly thermaleze insulation) to a steel tube (7.1 mm in diameter) originally cut from a Bosch fuel injector valve (Bosch O 280 150 045) and silver soldered to a stainless-steel body. In this design the solenoid is not in contact with the fluid so that corrosive gases such as NH_3 may be used. The surface of the steel tubing and the main body are coated with a thin Teflon resin film (Whitford Corporation) in order to prevent electrical leakage from the solenoid wire due to imperfect insulation on the wire.

The plunger is spring loaded and is pulled back from its seal with the orifice during the magnetic solenoid pulse. The spring is located inside the steel tube and sits against a piece of 3-mm-diam copper tubing. The sharp plunger tip forms a metal-metal seal which is seated in the exit aperture due to the force of the spring when the magnetic pulse is off. The exit aperture is 330 μm in diameter and is drilled into a 7-mm-thick stainless-steel front plate which is fastened to the main body using eight (8-32) steel screws. A graphite filled Teflon ring (Bal Seal Static Faces) serves as the seal between the main body and front plate. This Teflon ring can sustain over 200-atm NH_3 at 250 $^\circ\text{C}$ for over several months of operation. In contrast, a KaptonTM (polyimide) seal decomposed after several minutes of use with NH_3 .

The plunger is a stainless-steel rod ~ 2 cm long $\times 0.3$ cm in diameter with a sharp tip at the end which when polished

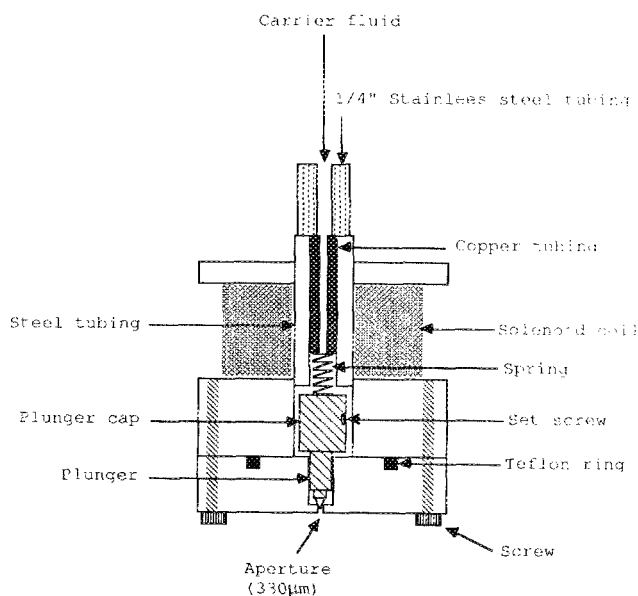


FIG. 1. The design of pulsed valve.

properly with metal grinding compound provided a metal-metal seal with the aperture. The leakage of this seal is negligible even at 200-atm backpressure. The length of the plunger can be adjusted by addition of a plunger cap which is held to the plunger by a set screw. As the plunger cap changes the plunger length, the distance between the plunger cap and solenoid is also changed. If the set distance is too large, the spring does not provide sufficient force to push the plunger against the front plate aperture so that a leak may result. If the plunger is too long, there is not enough room to allow the plunger to move and the nozzle cannot open. The correct spacing is critical to proper valve operation. The pulse width of this valve will vary depending on the stiffness of the spring, the length of the plunger, and the voltage applied to the solenoid. Presently, the pulse width is optimized at 100 μs (FWHM) and shown in Fig. 2. The molecular beam pulse profile was obtained by monitoring the aniline 0-0 transition signal intensity injected from supercritical NH_3 at 120 atm and 150 $^\circ\text{C}$ as a function of the delay between the laser pulse and valve pulse.

The dead volume of this valve is ~ 0.2 ml, which can be reduced significantly by narrowing down the inner diameter of the solenoid coil steel tubing. The low dead volume allows a simple construction which can withstand the high fluid pressure without the risk of explosion. The nozzle has been tested successfully to over 200 atm pressure. The nozzle can be heated to ~ 140 $^\circ\text{C}$ with a thermocoax heater wound around the valve. The maximum operating temperature is 180 $^\circ\text{C}$ and is limited by the insulation on the solenoid wire.

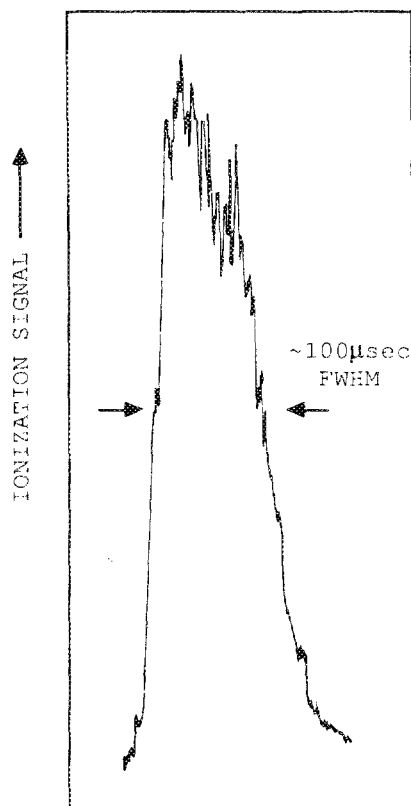


FIG. 2. The superionic jet profile obtained with supercritical NH_3 injection at 120 atm and 150 $^\circ\text{C}$.

In order to increase the operational temperature, a Teflon coated wire may be used instead. However, a temperature of 140–150 °C is sufficient to generate supercritical NH₃ conditions for these experiments. A higher temperature may result in thermal degradation of the sample. The temperature is monitored by use of a Chromel-Alumel thermocouple. An electrical drive circuit similar to that of Ref. 12 was used to pulse the valve.

High-pressure liquid NH₃ (~120–150 atm, 25 °C) was delivered by a Varian 8500 syringe pump and passed through a high-pressure inline filter (NUPRO SS-4F10-7) in which the sample was placed and maintained at room temperature. Molecules from the sample were extracted by the NH₃ and carried to the pulsed valve for injection. In the nozzle the liquid NH₃ was converted to supercritical NH₃ ($T_c = 131$ °C) and a supersonic jet was formed upon expansion into vacuum. The liquid ammonia was obtained from Scott Speciality Gases (Troy, MI). All samples used in this experiment were obtained from the Sigma Chemical Company and used without further purification.

The ionization source for generating the mass spectra was a frequency quadrupled (266 nm) Nd:YAG laser at a power density of $\sim 5 \times 10^6$ W/cm². A frequency-doubled Nd:YAG pumped dye laser was used to produce 324.5-nm radiation ($P \sim 2 \times 10^6$ W/cm²) for ionization of carbazole at its 0–0 band. The laser beam, collimated to a ~ 3 mm beam by a positive-negative lens combination, intersects with the molecular beam ~ 22 cm from the nozzle source. Thus, for proper synchronization the laser beam must be delayed by about 600 μ s with respect to the valve pulse. The ions produced by R2PI were mass analyzed in the TOF mass spectrometer and recorded by a Lecroy 9400 digital oscilloscope. The spectra in Figs. 3–5 were signal averaged over 100 laser pulses.

II. RESULTS AND DISCUSSION

R2PI mass spectra of adenine and adenosine introduced into the TOFMS using pulsed supercritical NH₃ injection at

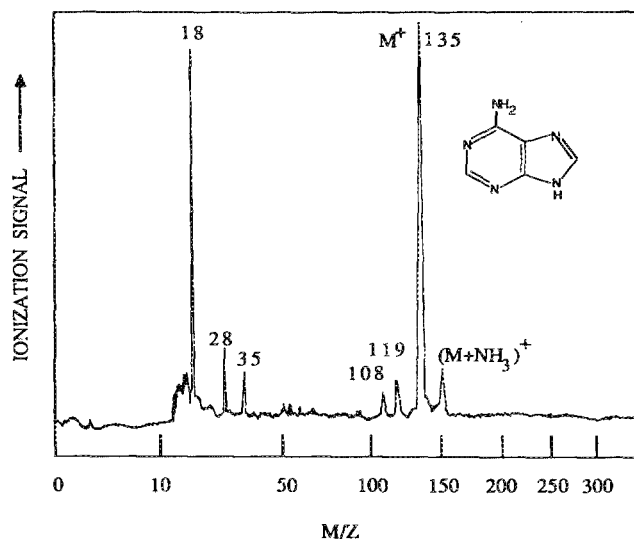


FIG. 3. The R2PI mass spectrum of adenine obtained by supercritical NH₃ expansion at 120 atm and 150 °C.

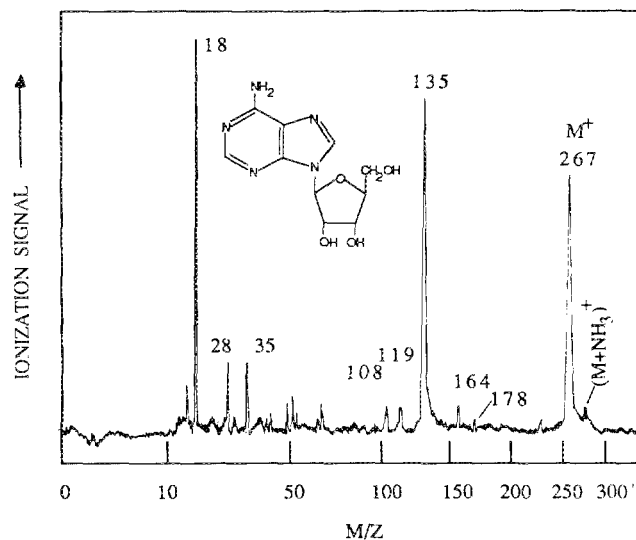


FIG. 4. The R2PI mass spectrum of adenosine obtained by supercritical NH₃ expansion at 120 atm and 150 °C.

120 atm and 150 °C are shown in Figs. 3 and 4. In each case R2PI at 266 nm produces the molecular ion, M^+ , with relatively high abundance compared to other easily formed fragments. This is especially difficult to achieve for adenosine and other nucleosides even with relatively soft desorption/ionization methods such as chemical ionization (CI),¹⁷ fast atom bombardment (FAB),¹⁸ and field ionization (FI) or field desorption (FD) mass spectrometry.¹⁹ These methods often yield characteristic fragments for such fragile species that may dominate the mass spectrum with only weak production of the molecular ion. The salient point is that supercritical NH₃ extraction offers a means to inject relatively labile polar molecules into the mass spectrometer without extensive decomposition prior to ionization.

A feature of the R2PI induced mass spectra of these compounds (Figs. 3 and 4) expanded in NH₃ carrier is that

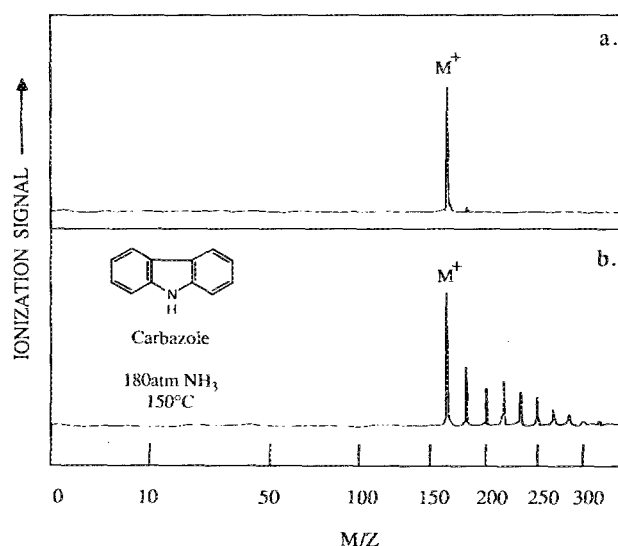


FIG. 5. The R2PI mass spectra of carbazole obtained by supercritical NH₃ expansion at 180 atm and 160 °C using 324.5 nm laser radiation: (a) 40 μ s delay; (b) 100 μ s delay.

additional peaks may result due to charge exchange with NH_3 or due to MPI induced fragmentation. In the case of the R2PI induced adenine (m.p. 360 °C) mass spectrum at 266 nm shown in Fig. 3, a strong molecular ion, M^+ , results, and also a peak at m/z 18 which corresponds to NH_4^+ . Under the conditions of these experiments, we have shown that NH_3 is not directly ionized efficiently. The NH_4^+ signal appears to be the result of charge transfer in the ionization region of the TOFMS. Indeed, the abundance of the m/z 18 peak appears to be strongly related to the background pressure and the number of ions produced by R2PI. The ion signals of m/z 18, 28, and 35 are also observed in all these supercritical NH_3 injection experiments where m/z 35 is the protonated ammonia dimer ion $(\text{NH}_3)_2\text{H}^+$. There are also minor fragments at m/z 119 and 108 which correspond to M-16 (loss of an amino group) and expulsion of HCN, respectively. It should be noted that in the early experiments of Giddings,²⁰ adenine could not be detected by SF NH_3 injection with FID detection. However, with R2PI at 266 nm, this compound is readily detected.

Figure 4 shows a laser-induced mass spectrum ($\lambda = 266$ nm) of the nucleoside adenosine. This compound is much more prone to decomposition upon heating than the very stable adenine base, thus illustrating the utility of this method. In addition to the molecular ion M^+ at m/z 267, one observes the base peak BH^+ at m/z 135 which is generally the dominant peak in the mass spectrum of this compound using other ionization methods and NH_4^+ at m/z 18. There are also minor fragment peaks at m/z 119 and 108 as in adenine.

One drawback of high-pressure NH_3 injection is that a solvent-solute ($M + \text{NH}_3$) cluster ion is observed in all spectra. The cluster formation is greater than that observed in high-pressure CO_2 or N_2O expansions. The enhanced cluster formation might be expected due to the strong tendency for hydrogen bonding to occur between NH_3 and the highly polar solute compounds. Nevertheless, the degree of cluster formation is still relatively low.

This low degree of clustering may be partially due to formation of a transient shock wave induced in the high-pressure pulse of gas emitted by the valve which destroys the weakly bound clusters. However, a second effect observed is that the degree of clustering is minimized when the laser pulse intercepts the rising edge of the molecular beam pulse. As the laser pulse probes further into the molecular beam pulse, the degree of clustering becomes much more extensive. For example, note the lack of clustering in Fig. 5(a) for carbazole expanded from supercritical NH_3 at 180 atm and 160 °C when the laser probes 40 μs into the molecular beam pulse. This appears to be due to a kinetic effect where at the beginning of the molecular beam pulse there is insufficient time for three-body collisions to occur in the nozzle to produce clustering. If the delay is changed by only 60 μs so that the laser probes 100 μs into the jet pulse then extensive clustering of carbazole with ammonia is observed as shown in Fig. 5(b). Thus, by timing our laser probe pulse accordingly, the clustering effect can be minimized. On the other hand, in the expansion of Fig. 5(b), clusters up to $M + 9 \text{NH}_3$ are formed and detected at 324.5 nm (0-0 band of carbazole). It

should be noted that the intensity of the peaks of the cluster masses in Fig. 5(b) may or may not correspond to the distribution of neutral clusters in the beam. Since MPI often produces ions well above the ionization threshold, there is likely to be a significant amount of fragmentation of the clusters.

In summary, this novel pulsed valve design permits the use of supercritical or high-pressure liquid NH_3 for injection of small thermally labile molecules into a mass spectrometer. The short pulses permit the use of NH_3 at pressures up to 200 atm behind a large (330 μm) orifice into a TOFMS system with only a modest-sized pumping station. This gives a high on-axis density and the resulting R2PI mass spectra exhibit relatively strong molecular ion abundances accompanied by some characteristic fragmentation for small biological nucleosides that are quite polar and difficult to volatilize without extensive decomposition.

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