Generation and detection of intense cluster beams

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Generation and Detection of Intense Cluster Beams

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An improved method for generating intense, collimated cluster beams is described. The beam mass distribution is interrogated by a single-photon ionizer and a novel time-of-flight mass spectrometer, optimized for very high mass detection.

Introduction

Extensive research has produced various methods of generating cluster beams (see, for instance, the excellent review article of ref 1). Most of these methods create a supersaturation of vapors (generated by temperature gradients). Methods such as laser beam evaporation,[2] condensation cells,[3,4] and supersonic beam expansion[5] are well-known representatives.

Very intense cluster beams have been produced by using shaped supersonic expansion, as pioneered by Becker,[6] Hagena,[7] and Gspann[8] and developed by Stein.[9] The extreme difficulty in mathematical modeling of flow and cooling in shaped supersonic expansion have led to complex empirical design of the nozzle contour, detracting potential users from its wider application.

We find that a simple conically shaped nozzle influences the expansion in such a way as to produce a controlled distribution of relatively cold clusters in the beam.

The detection or mass separation of neutral cluster is difficult;[10] thus detection is usually achieved by ionization. Several methods of ionization are currently employed, all leading to a distortion of the original neutral distribution by inducing fragmentation. Electron impact, the most popular method, is probably the worst offender in this respect.[11] Similar problems are encountered with multiphoton ionization.[12] Threshold single photon ionization is probably the least destructive method of cluster detection.[13] In what follows we shall highlight several components, involving the production and detection of large clusters, in an experimental system dedicated to the investigation of large molecular clusters. These components include: (a) a high temperature (up to 470 °C) pulsed conical nozzle; (b) a subnanosecond, vacuum UV, high brightness lamp for the single-photon soft-ionization of large clusters; and (c) a modified Wiley and McLaren TOF mass spectrometer[14] which enables high transmission of perpendicular propagating cluster beam. It is equipped with a high efficiency detector for large masses.

The Experimental System

A brief description will be given indicating the integration of the various components described in the following sections. The system consists of three vacuum chambers separated by skimmers. The molecular beam source chamber equipped with the pulsed nozzle is pumped by a 2400 L/s diffusion pump (Varian VHS6). The central core of the beam is skimmed with a 1-mm-diameter skimmer into a differential pumping chamber equipped with a 200 L/s diffusion pump (Alcatel crystal 63). The beam is skimmed again 30 mm downstream into a third work chamber. This is an ultrahigh vacuum chamber pumped by a trapped 300 L/sec diffusion pump (Alcatel crystal UHV100). The base pressure is better than 4×10^{-9} Torr. During experiment the pressure consisting mainly of the molecular beam carrier gas reaches 1×10^{-7} Torr. The last chamber contains a time-of-flight mass spectrometer equipped with a subnanosecond vacuum UV lamp as the ionization means. The chamber is also equipped with instrumentation for the interrogation of cluster–surface interactions, and two-color-ionization spectroscopy of large clusters.

Conical Nozzle Cluster Source

We are currently using nozzles (both pulsed and continuous) of a simple conical shape. The conical expansion hole is machined in stainless steel, boron nitride, or quartz. The throat diameter varies between 0.1 (for CW nozzle) and 0.6 mm (for pulsed operation) and the length varies between 3 and 8 mm. The apex cone angle is varied between 10 and 60°. The hole is drilled by a tool and honed.

We find that the supersonic jet profile (stagnation pressure between 0.1 and 3 bar) follows roughly the cone shape. Thus a collimated supersonic beam is produced. We have visualized the flow profile by maintaining a glow discharge between the nozzle and electrode in the vacuum chamber. Another method consists of seeding the noble gas beam with a larger molecule (like tetracene or porphirine) and monitoring the deposition pattern on a glass slide in front of the nozzle. The narrow cones produced a beam of such intensity that special attention in skimmer design is essential. (The skimmer is made from electroformed copper, sharpened to a razor edge.) At present skimmer interference is the limiting factor in raising the beam intensity. Beam intensity improvement of at least one order of magnitude is possible (as compared to standard circular hole nozzles under similar throughput conditions).

These high beam intensities (10^{21} atoms/(s sr) for a CW nozzle and 10^{23} atom/(s sr) for a pulsed valve, all at moderate pumping throughput of 1 scm^3/s) incorporate in a high number of binary collisions (responsible for cooling in the supersonic expansion) and three-body collisions (required for cluster growth).

The efficient cooling achievable in such an expansion is depicted in Figure 1 and 2. Notice that the cooling of aniline at a given distance from the nozzle is more efficient, and that the terminal internal temperature is lower with the conical nozzle than with a planar source.[15] The conical nozzle gives the highest cooling for a given flow.

The influence of apex cone angle on cluster producing efficiency can be seen in Figure 3, where two conical nozzles are compared. Under similar expansion conditions, aniline cluster formation is enhanced for the smaller apex angle cone.

The pulsed value is a home-built magnetic actuated device (Figure 4). It is machined from stainless steel and has glass-fiber-insulated coil and "Kapton" polyimide seals. The changeable end piece nozzle is made of hardened steel. This valve produces

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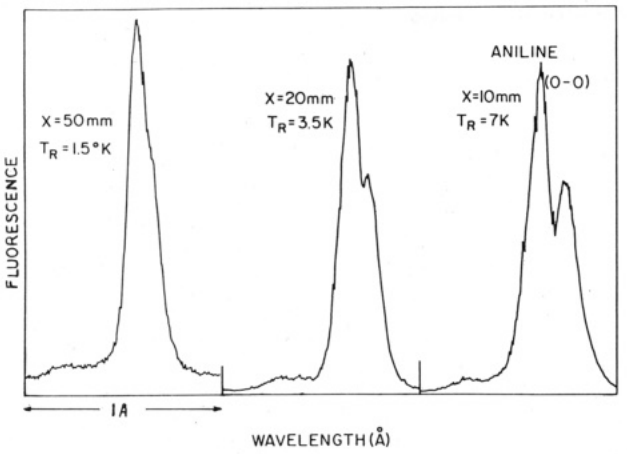

Figure 1. Laser-induced fluorescence of aniline in a conical expansion: carrier gas, He at 1 bar; cone angle, 30°; throat diameter, 0.3 mm. Notice the large distances from the nozzle and the derived rotational temperatures.

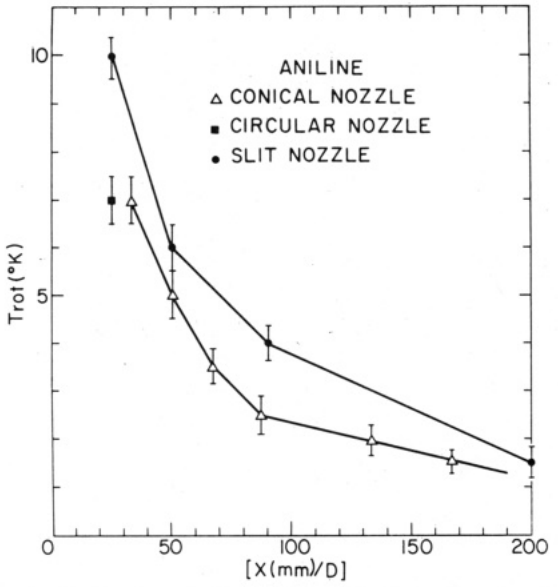

Figure 2. Cooling in conical expansion. The derived rotational temperatures of aniline as a function of distance, for different nozzles. The circular nozzle is 0.6 mm diameter at 7.5 bar. The slit nozzle is 2 × 0.2 mm at 2 bar and the conical nozzle is 0.3 mm diameter, 30° apex angle at 3 bar. The throughput is 0.55 cm^3/s for the circular nozzle, 0.8 cm^3/s for the slit, and 0.3 cm^3/s for the conical nozzle. The conical nozzle gives the highest cooling for a given flow.

a pulse of gas 200 μs long, at 20 Hz, and can be heated to 470 °C. The high temperature achievable in these valves allows the investigation of large, low vapor pressure molecules. An example of the laser-induced fluorescence of a tetrabenzoporphyrin produced at 470 °C nozzle temperature is displayed in Figure 5.

Single-Photon Ionizer

To bypass the multiphoton ionization process (which opens up intermediate states that can lead to cluster fragmentation) we chose single-photon ionization with a light source in the vacuum UV. This is a broad band light source so that photon energy can be tuned to the threshold of ionization, minimizing the excess energy in the cluster. We developed a very fast discharge light source in high pressure noble gas (or gas mixtures), Figure 6. It provides a bright spark source (with an area of 0.2 mm^2) which is focused by a CaF_2 lense onto the center acceleration region of the time-of-flight mass spectrometer (each pulse lasting less than 1 ns at 20–40 kHz; 5–10 bar of gas (hydrogen, Ar, Xe, or mixtures of these)) to yield photon energies between 2 and 10 eV. The broad band emission, containing some sharp lines as well as the excimer emission bands (depending on gas fill mixtures) can be

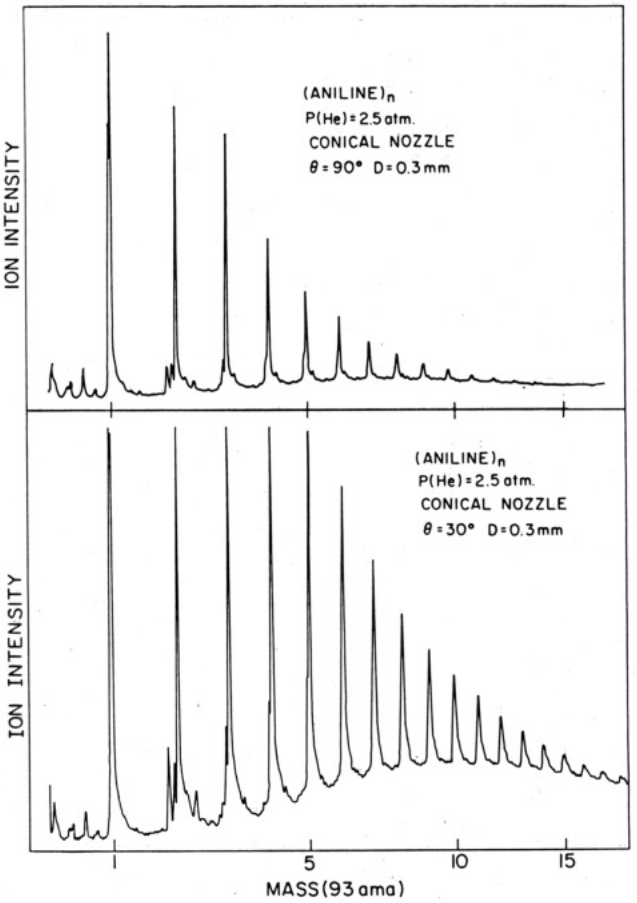

Figure 3. Cluster mass spectra of aniline obtained with a 90° and 30° conical nozzles under similar experimental conditions.

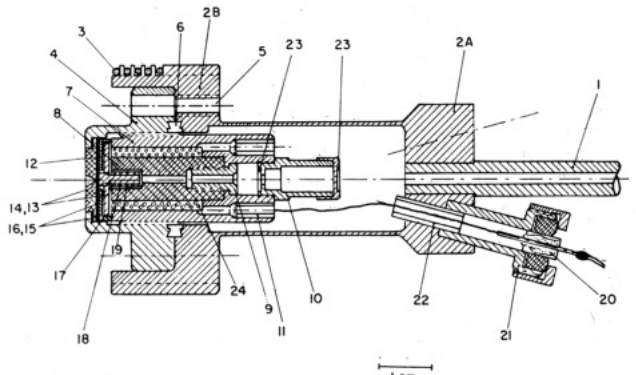

Figure 4. Pulsed valve for high temperatures: 1, gas feedthrough; 2, stainless valve body; 3, mineral-insulated heater wire; 4, valve front end flange; 5, tightening screws; 6, copper gasket seal; 7, coil housing made of soft iron; 8, coil core made of soft iron; 9, tightening nut; 10, cartridge containing sample; 11, electrical connection to coil; 12, replacable nozzle end piece; 13,14, moving valve stem made of soft iron disk and carbide center piece; 15,16 "KAPTON" seals (replaceable); 17, retaining disk for valve stem; 18, return spring made of Mo–Re alloy. 19, hardened steel sleeve to guide reciprocating stem; 20,21, electrical feedthrough and housing, 22; ceramic tube for insulation; 23, sample container cover cap; 24, glass braided sleeve insulated copper wire (20 turns).

tuned rougly by a suitable UV filter or changing gas mixture.[18] The fast pulsing is achieved by utilizing coaxial geometry in the capacitor discharge circuit. The self-capacitance of the lamp coaxial electrodes is about 100 pF. Typical operating voltage is 5–7 kV; a series charging resistor of 2 mΩ and current of 5 mA

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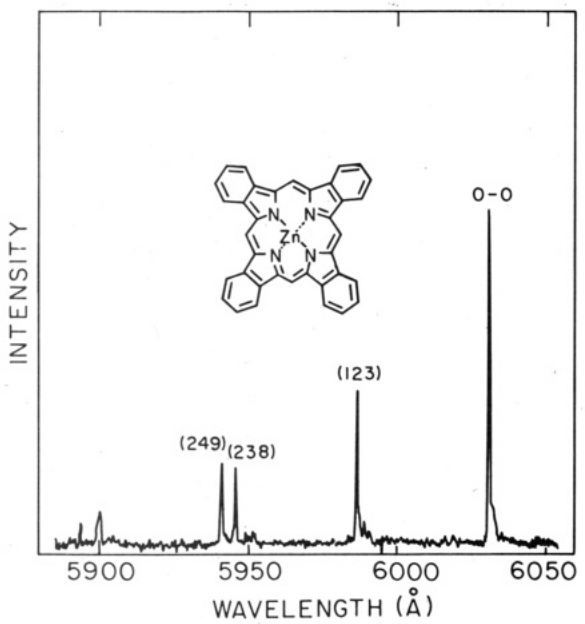

Figure 5. LIF spectrum of zinc tetrabenzoporphyrin obtained at 470 °C nozzle temperature with 1 bar of He stagnation pressure.

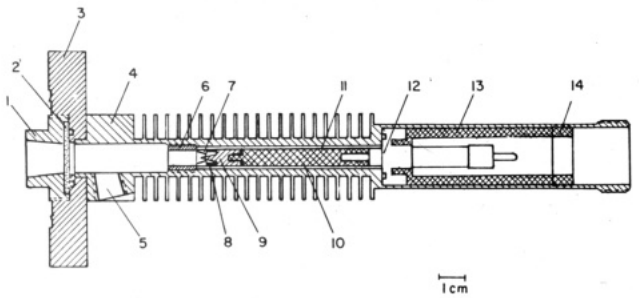

Figure 6. Vacuum UV short pulse lamp: 1, window tightening nut; 2, window (fluoride of lithium, calcium, or Mg); 3, "Conflat" copper gasket flange (stainless); 4, lamp stainless housing; 5, gas inlet; 6, adjustable threaded spacer; 7, tungsten copper alloy; bottom electrode; 8, macor insulating bead and electrode spacer; 9, upper spark electrode—tungsten copper; 10, high voltage side of coaxial capacitor—stainless; 11, alumina dielectric of capacitor; 12, gas seal with high voltage feedthrough; 13, Teflon insulator (atmosphere side); 14, tightening nut of assembled lamp.

will generate about 30 000 free running pulses per second in 10 atm of H_2.

The low peak power, high repetition rate source allows the use of single-photon-counting techniques to accumulate mass spectra in short time. A background pressure of 10^{-7} Torr of aniline will generate 5000 counts/s. The light pulse and the drifting ion hitting the detector trigger a start–stop time-to-amplitude converter, to generated a time-of-flight mass spectrum on a multichannel analyzer. Time resolution of 1 ns or better are commonly achieved with these techniques, making our light source a good match for generating TOF mass spectra.

Time-of-Flight Mass Spectrometer for Heavy Clusters

Time-of-flight (TOF) mass spectrometer are usually configured so that the ion flight direction is perpendicular to the collimated neutral beam axis. The unfavored axial configuration suffers from a loss in resolution resulting from the longitudinal velocity spread in the beam and its associated spread in kinetic energy. This resolution loss is more severe for the higher masses. In the perpendicular configuration this problem is practically avoided; however, it suffers from a high mass transmission loss. Since neutrals of different mass move all at similar velocity (determined mostly by the carrier gas), the kinetic energy of each cluster rises linearly with its mass. Thus the trajectory of the accelerated ions in the perpendicular configuration depends on its mass, imposing a high mass limit on the transmission of the flight tube. Deflection plates were commonly used to overcome this effect allowing the

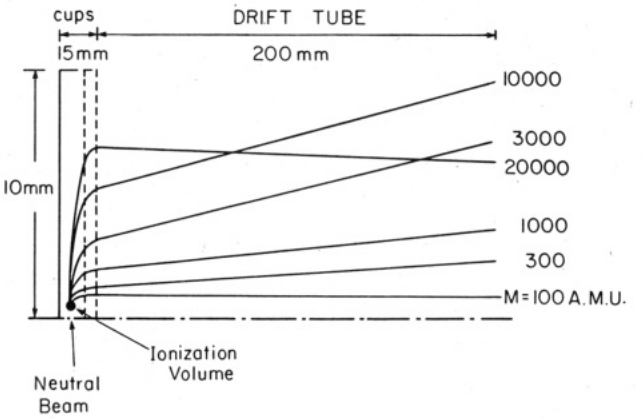

Figure 7. Trajectory simulation in the TOF mass spectrometer for difficult masses. Neutral beam velocity is 1000 m/s and the total acceleration voltage is 3000 V. Notice the complete transmission up to mass 20000 amu.

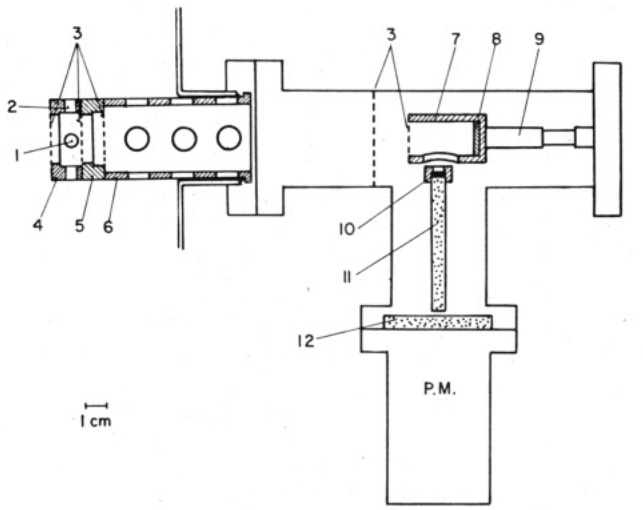

Figure 8. Time-of-flight mass spectrometer: 1,2, molecular beam and light roles in lower cup of mass spectrometer; 3, high transparency stainless mesh; 4, lower cup; 5, upper cup; 6, drift tube; 7, "Daley" converter cup; 8, magnesium coated target plate; 9, high voltage feedthrough; 10, plastic scintillator, coated with Al; 11, light guide; 12, glass window.

measurment of mass spectra in discrete overlapping segments.

We have modified he standard TOF Willey–McLaren configuratin[14] to counteract this effect. The modification involves replacing the two lower plates of the acceleration region by two focusing "cups". A computer simulation procedure (solving the potential distribution and calculating trajectories) shows that small and large ion clusters can be focused, with little loss in resolution, and transmission through the drift tube (Figure 7), i.e. a constant transmission up to mass 10000 amu, is achieved, with a resolution larger than 200, using a short drift tube (200 mm).

Detection of charged ions is usually achieved by monitoring the secondary electrons emission resulting from the ion collisions with an appropriate surface. This process is velocity dependent, requiring a velocity of 10^4–10^5 m/s for the primary ion.[16] Since the ions in the mass spectrometer are all accelerated at constant voltage (2–3 kV) the large clusters would lack the necessary velocity to be efficiently detected. A "Daley" converter[17] overcomes this limitation. It consists of a stainless steel cup, maintained at high negative potential (−20 kV). Ions are accelerated to a Mg coated surface where they release two or three secondary electrons. These electrons are accelerated to a grounded fast scintillator, located in front of a photomultiplier, emitting 5–10 photons each. This large area detector proved to be highly efficient, almost without background, unaffected by multiple exposure to air or intense beams (Figure 8).

Registry No. Zn tetrabenzophorphyrin, 14586-52-8; aniline, 62-53-3.