Electron diffraction investigation of pulsed supersonic jets

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A pulsed nozzle source has been developed for electron diffraction studies of molecular clusters. Disturbances of the electron beam by the field actuating the pulser have been reduced to a negligible magnitude by introducing magnetic shielding and by carefully timing the electron shutter. Advantages of pulsed operation in diffraction experiments with a Laval nozzle source are considerable. In the Michigan unit stagnation pressures can be increased by an order of magnitude, and pumping requirements are greatly reduced. Moreover, cleaner diffraction patterns can be obtained because exposures can be adjusted to probe a freshly developed jet before gas scattered from the walls can reach the region of sampling. Timing works so effectively that good diffraction patterns can be recorded even when the skimmer isolating the diffraction chamber from the nozzle chamber is removed. Indeed, patterns from unskimmed jets can be particularly informative when cluster beams are composed of mixed structural forms. An unorthodox "vee" skimmer has proven to be useful for examining narrow regions in a jet. Moreover, the vee skimmer makes it possible to measure the diffraction geometry much more precisely than has been the case with conventional skimming configurations. Pulsed operation also facilitates an accurate characterization of the density and velocity distributions in the supersonic jet. The principal design features of a pulsed apparatus are presented together with characteristic results.

INTRODUCTION

Pulsed nozzles offer several attractive potentialities, not the least of which is a means of generating intense supersonic jets without the requirement of large and expensive pumping systems. Although research workers in several areas, especially spectroscopy, have long taken advantage of the desirable features of pulsed jets,[1] electron diffractionists have avoided their use because the electromagnetic triggering of their pulsed valves was perceived to be incompatible with the required stability of electron beams. It is true that unshielded pulsers produce unacceptable disturbances in nearby electron beams. Nevertheless, we have found it to be not only entirely feasible but also highly advantageous to carry out electron diffraction studies on pulsed supersonic jets. Advantages and the experimental means to exploit them are described in the following sections.

I. DESIGN CONSIDERATIONS

Before presenting details of the components of the apparatus, it is helpful first to give a brief overview of the procedures which make it possible to circumvent the undesirable side effects of operating a pulsed nozzle in diffraction studies. First, the electromagnetic disturbance from the pulser can be reduced considerably by magnetic shielding. Second, there is a significant time delay between the strong pulse actuating the nozzle and the emergence of a well-developed jet from the nozzle. This lag is sufficient for the strong pulse to decay almost completely. The weak holding field that remains gives a constant and almost negligible deflection of an electron beam. Therefore, care in the timing of the fast shutter controlling the electron beam can eliminate the principal disturbance. Moreover, it is possible, by keeping electron exposures short, to probe the jet before it can scatter from the walls of the apparatus and return to the probing electron beam as an undesirable background. Consequently, effective timing can lead to diffraction patterns free from the spurious background effects encountered in prior studies in this laboratory of skimmed, continuous jets.[2] Indeed, pulsed operation works so effectively that it is possible to obtain serviceable diffraction patterns even when the skimmer isolating the diffraction chamber from the nozzle chamber is removed altogether. Not only is such operation now possible, it will be seen to be beneficial under certain circumstances.

II. APPARATUS

A schematic diagram of the pulsed diffraction apparatus is given in Fig. 1. Electronic timers in the delay box open the electronic shutter a preset time after energizing the pulser valve and allow a 40-keV beam of electrons to probe the supersonic jet issuing from a Laval nozzle downstream of the pulser. Electrons scattered by clusters in the jet pass through a conventional "rotating sector" before being recorded on a photographic plate. The rotating sector differentially masks the inner part of the diffraction pattern relative to the outer part in order to even out the radial exposure of the photographic plate. Angular evening comes from the averaging of a great many exposures from the periodic pulses. Not shown are a chopper and flight tube which can be introduced to measure velocity distributions in jets and cluster beams.

Details of the diffraction apparatus[3] and supersonic nozzle[4] have been described elsewhere. What distinguishes

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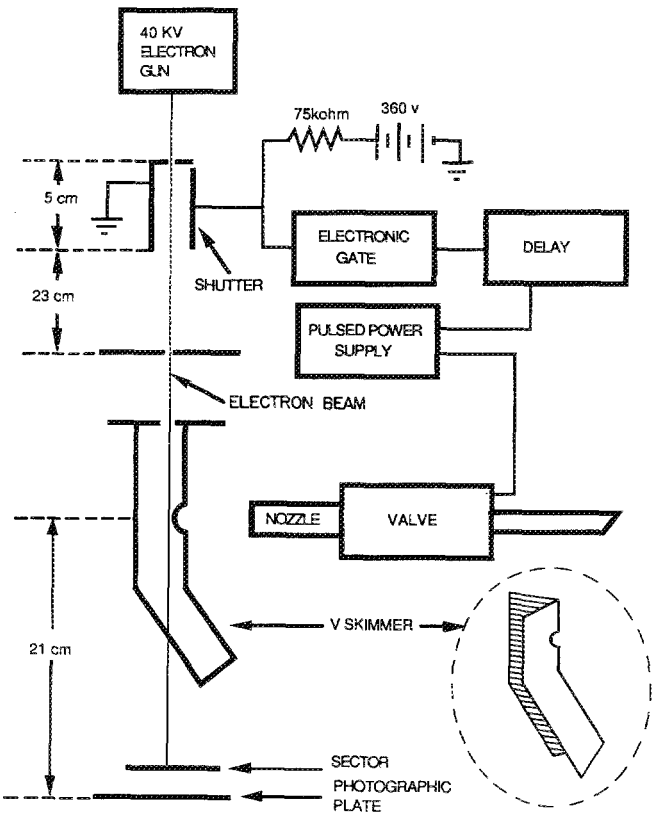

FIG. 1. Schematic diagram of electron diffraction apparatus with pulsed nozzle cluster source. In the most useful configurations either no skimmer at all is introduced or a "vee skimmer" is placed, as shown, with its sharp vertex toward the supersonic jet. Leeward of the jet the skimmer is open along its entire length.

the present configuration from prior configurations is the pulsed valve and its power supply, both of which are conventional components designed for spectroscopic studies by the General Valve Corporation. An Iota-One system was selected because its light weight and small size ($\sim$2.5-cm diameter, 5-cm length) allowed it to be introduced into the existing diffraction apparatus without major changes. A minor modification of the outlet of the valve made it possible to attach a glass Laval nozzle (throat, 0.012-cm diameter), cushioned at both ends by Teflon pads, and sealed by an O ring around the neck. Gas samples are exposed only to Teflon, stainless steel, and Viton. Gas in the 10^{-3}-cm^3 dead space between the valve and the nozzle is exhausted between pulses through the narrow nozzle throat. Because the half-life for emptying after the valve is closed is very short (<1 ms) compared with the usual times between pulses, the dead space contributes no unwanted background gas during the active phases of the cycles.

The pulser is designed to operate at pressures up to 86 bar, increasing the allowable stagnation pressure by an order of magnitude in comparison with previous experiments in this laboratory. This considerably enhances the possibility of nucleating and growing certain condensed phases that could not be produced in prior studies under milder expansion conditions. Valve characteristics of 0.2-ms opening time, 0.4-ms minimum pulse width, and repetition rates in excess of 250 Hz for short pulses offer a convenient range for diffraction experiments. The valve is opened by a 280-V pulse, 0.15-ms FWHM, and is held open for the desired time by a sustained application of 8 V. Three layers of high-permeability alloy (Co-netic AA from the Perfection Mica Company) were wrapped around the body of the pulser to provide magnetic shielding. This reduced the deflection of the electron beam at the strongest part of the pulse to a few hundredths of an s unit in scattering angle. During the brief, reproducibly timed period that the electron beam is normally switched on, any deflection is so small and static that no degradation of the diffraction patterns has been detected.

The shutter controlling the electron beam consists of a pair of circular, parallel plates 5.1 cm in diameter and 0.6 cm apart. Between exposures the beam is deflected away from the 0.02-cm limiting aperture in the magnetic lens by a potential difference of 360 V. Exposures are made by shorting the deflector plates through a transistor for the desired time. Shorting takes less than 1 μs, and recharging to interrupt exposures requires 36 μs to achieve 90% of the final voltage. Termination of exposures occurs more abruptly, however. Satisfactorily timed exposures as short as 0.2 ms are readily obtained. Coordination between the pulser valve and electron beam is achieved by means of a delay box which receives a rectangular timing pulse from the valve driver and produces an output pulse for a preset beam duration after the desired delay. Timers are based on 74LS221 chips. Characteristic times for a gas pulse to pass a probing electron beam or ion gauge, rebound from a wall, and return to the probe are about 0.5 ms. Electron diffraction exposures or measurements of pulse densities can be easily made before this source of interference becomes serious. Therefore, neither cryopumping nor fast diffusion pumps are required to eliminate background gas.

III. SKIMMING CONFIGURATIONS

An ideal skimmer for electron diffraction would serve two purposes. First, it would produce a narrow jet at the electron beam and thereby define the point of scattering. Second, it would divert most of the large throughput normally exiting a supersonic nozzle away from the diffraction chamber and thereby prevent the accumulation of an undesirable background of gas. Molecular beams produced by free jet expansion can be skimmed by appropriate skimmers cleanly enough for the above requirements to be met.[5–7] Research in our laboratory, however, indicates that clusters with the properties we seek are produced more readily by expansion in a Laval nozzle than in free jet expansion.[8] Unfortunately, because gas flux from a Laval nozzle is much more highly directed in the forward direction than that of free jets, Laval jets can be more troublesome to skim cleanly. This is true even when X/D ratios are large compared with those that are well skimmed in the case of free jets. Deleterious skimmer interactions[6,7] characteristically degraded the gas jets transmitted through the skimmer in experiments in this laboratory.[2] Compensating in part for this deterioration of beam quality has been the large size of the clusters produced. Such clusters appear to be able to penetrate the stagnant gas in the skimmer without suffering appreciable change. Nevertheless, velocity profiles of gas jets transmit-

ted through the skimmer have been disrupted too severely for satisfactory inferences to be made about the original gas expansion.

For the above reasons several radical departures from the conventional skimming configuration were tested. First, as explained in Sec. I, a careful timing of electron exposures makes it feasible to dispense with a skimmer entirely. Cluster beams tend to be much narrower than the accompanying jets of carrier gas.[9] This consequence of mass fractionation makes it possible to register quite serviceable electron diffraction patterns in the interval before the gas scattering from walls invades the region of electron scattering. Results are especially favorable when the carrier atoms have a small cross section for scattering electrons. Results of such tests are reviewed in the next section.

An even more promising departure is to introduce a "vee" skimmer, illustrated schematically in Fig. 1. This skimmer, fabricated from brass shim stock in the shape of a V when viewed from the source of the electron beam, is placed as shown with its orifice close to the electron beam. The main body of the skimmer prevents the bulk of the incident jet from intercepting and scattering the electron beam. Skimming is carried out more cleanly in a region of much lower gas density (for a given distance from nozzle to electron beam) than is the case when a standard skimmer, of length 2.5 cm, is used. Moreover, the scattering geometry is much better defined and can be measured an order of magnitude more precisely than with the conventional conical skimmer. An additional bonus is that the orifice can serve to select and sample the clusters in different regions of the cluster beam. This ability has proven to be fruitful, as demonstrated in the next section.

In operation without a skimmer to diminish flow from the nozzle into the diffraction chamber, timing is critical, as indicated above. Illustrated in Fig. 2 is an oscilloscope trace of the development of a neon jet as detected by a fast ion gauge[1,10] at a typical nozzle-to-electron beam distance ($\sim$4.6 cm). For a period after the valve opens, no signal is seen. Then gas density builds up and reaches a plateau. In longer exposures than shown, the pressure can be observed gradually to increase again after gas reflected from the chamber walls returns to the region of the electron beam. The plateau, which is absent when measurements are made close to the back wall of the chamber, identifies the period during which optimum diffraction patterns can be recorded. In the Michigan apparatus this period begins when the magnetic pulse from the solenoid has almost fallen to its holding value. Records of the time profiles of the voltage to the solenoid and the magnetic disturbance from the solenoid are shown in the upper two traces of Fig. 2. Although the temporal sequence of events depicted permits the acquisition of excellent diffraction data, timing would have been rendered less critical if the diffraction chamber had been larger.

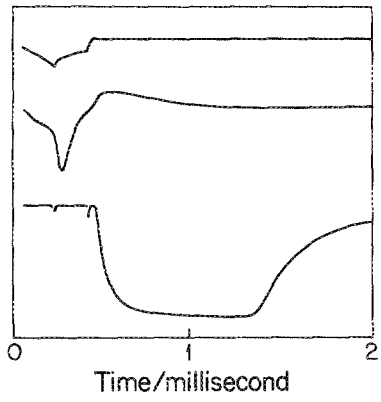

FIG. 2. Oscilloscope traces depicting the timing of the electric, magnetic, and gas pulses associated with the operation of the solenoid valve. The top trace is the "monitor" output from the power supply; it is proportional to the voltage applied to open the valve. The middle trace is the voltage induced in a 1300-turn coil and 500-Ω load resistance placed around the nozzle to measure the rate of change of magnetic field from the pulser (increasing fields, negative signal; decreasing, positive). The bottom trace shows the arrival of a gas pulse at a fast ionization gauge placed at the normal position of the electron beam 4.7 cm from the nozzle exit. Neon at a stagnation pressure of 3.2 bars was the source. Two small spikes before the gas signal are artifacts arising from actuating the valve.

IV. CHARACTERISTIC RESULTS

One of the advantages of operating in the pulsed mode is that the density distribution of the supersonic jet can be measured directly in the diffraction chamber by a fast ion gauge, even when the skimmer is removed. Readings can be made as soon as the flow develops, before background gas distorts the picture. This can be useful in the characterization of the gas dynamics associated with the miniature Laval nozzles adopted in cluster studies. Illustrating the narrowing of supersonic jets of neon as the stagnation pressure increases are the profiles of gas density plotted in Fig. 3. Measurements were made in a plane 7.2 cm from the nozzle tip. No skimmer was present. Argon jets were found to be significantly narrower than those of neon. Shown for comparison with neon is the distribution corresponding to free jet expansion according to the representation of Ashkenas and Sherman.[11] It is the same for any monatomic gas and, for small Knudsen numbers, is independent of stagnation pressure.

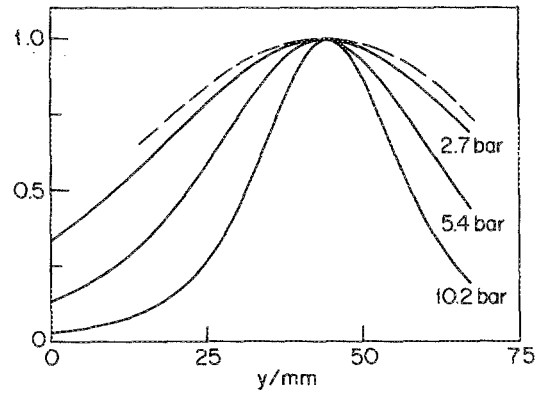

FIG. 3. Density profile ratios $\rho(y)/\rho_{max}$ of neon in a plane 7.2 cm from the nozzle exit, plotted to compare relative breadths as a function of stagnation pressure P_0 identified in right margin. The maximum gas density ρ_{max} increases faster than P_0. Solid lines, observed profile from a Laval nozzle 3.0 cm long, with a 0.012-cm throat and 0.19-cm exit diameter; dashed line, calculated profile from free jet expansion according to Ashkenas and Sherman (Ref. 12). Abscissa y is reckoned from an arbitrary reference position of the gauge.

In order to provide illustrations of the efficacies of the various configurations of skimming when operating with pulsed or continuous jets, a sample of SF_6, mole fraction 0.06 in argon carrier, was selected. This substance is of special interest because the complexity of its low-temperature behavior can aid in the diagnosis of conditions in the supersonic flow. Above 93 K, SF_6 crystallizes in a body-centered cubic (bcc) form.[12] Below that temperature, it is monoclinic in the bulk,[13] although selected area diffraction studies of microcrystals[12] and molecular dynamic computer simulations[14] have indicated the existence of a trigonal phase over an appreciable thermal range between 93 K and the temperature at which the monoclinic form becomes stable. The temperatures of interest are accessible in supersonic flow. A rule of thumb discovered empirically,[15] and later rationalized by unimolecular reaction theory for an evaporative ensemble,[16,17] suggests that the temperatures of clusters generated in supersonic flow are proportional to their condensation energies. Applied by Klots,[17] and by Magnera, David, and Michl[18] to SF_6, these considerations predict a cluster temperature of about 120 K, well above the transition temperature. On the other hand, it has been proposed[8] that additional cooling beyond that provided by evaporation may occur in a medium of expanding carrier gas. Observations bear this out, as small concentrations of monoclinic clusters of SF_6 have been observed.[4] It will be demonstrated below that a judicious choice of skimming can aid in the selection of the type of cluster to be examined and can even reveal forms of clusters eluding previous observations.

In experiments to be described, the diffraction patterns were screened by an r^1 rotating sector. For typical cluster beams, satisfactory patterns could be accumulated with a 40-nA electron beam in 0.5-s net exposure times. Tests in the pulsed mode used pulse parameters of 0.8-ms electron-beam delay, 0.3-ms electron-beam on time, 0.5-ms valve on time, and 10-Hz repetition rate. During individual pulses, exposures through the slowly rotating sector (10–20 Hz) are highly "spoked" snapshots of the two-leafed sector, itself. During the 900–4800 shots corresponding to net exposures of 0.27–1.4 s, sector orientations are averaged, giving circularly symmetric patterns. These patterns suffer negligible degradation from the superposition process because the reciprocity law for photographic emulsions is well obeyed for fast electrons.[19] Control experiments in the orthodox mode used a continuous 0.4-s exposure in conjunction with a conventional Beam Dynamics conical skimmer, 1-mm orifice, which isolated the diffraction chamber from the nozzle chamber. In all runs the tip of the Laval nozzle (glass No. 6, characterized elsewhere[4]) was 4.7 cm from the electron beam.

Typical results of the diagnostic tests are displayed in Fig. 4. When the stagnation pressure of the SF_6/Ar mixture was as low as 2.7 bars, the clusters generated were of the high-temperature bcc phase. The diffraction pattern displayed for such clusters in Fig. 4 was taken with an unskimmed jet. It illustrates that quite satisfactory results can be secured in the absence of a skimmer if attention is paid to timing, even when the net scattering by the relatively heavy carrier exceeds that of the subject vapor (SF_6) by an order of

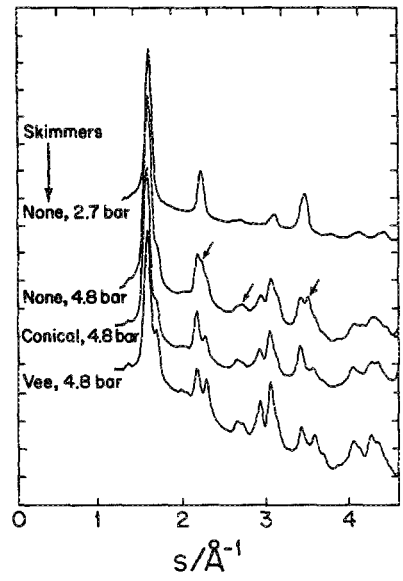

FIG. 4. Electron diffraction patterns of clusters of SF_6 in argon carrier, 0.06 initial mole fraction of SF_6. Skimming configurations and stagnation pressures are identified near left margin. At the lower pressure clusters have bcc structures irrespective of skimmer, and skimmerless conditions produce patterns little degraded in quality from those of skimmed jets. At 4.8 bars the vee skimmer transmits the nearly pure monoclinic form preferentially distributed along the centerline of the jet, while the less selective conventional conical skimmer passes a mixture of monoclinic and bcc. The unskimmed jet allows electrons to probe the full diameter of the cluster beam, disclosing new intensity distributions (identified by arrows) that appear to correspond to trigonal microcrystals.

magnitude in the original mixture. This favorable outcome is due in part to the substantial mass fractionation which concentrates the cluster jet into a beam which is much narrower than that of the carrier jet by the time the nozzle effluent reaches the electron beam.[9] Even better patterns can be obtained with lighter carrier gases which scatter electrons less strongly. Moreover, jets of light carriers are more diffuse and tend to scatter cluster beams less heavily than do heavy carriers, thereby yielding more concentrated clusters.

When the stagnation pressure was increased to 4.7 bars, substantial concentrations of monoclinic clusters appeared. In this case quite different results were obtained with different skimming configurations, as illustrated in Fig. 4. Results reveal that the colder phase is preferentially formed near the center line of the cluster beam, while the warmer phase is to be found at the periphery. Consequently, patterns of the unskimmed jet are a composite of several forms of clusters. A conventional conical skimmer tends to select the central portion of the jet and gives patterns richer in the colder phase. The vee skimmer, intercepting an even narrower zone of the diverging jet, yields a pattern of nearly pure monoclinic clusters. Its capacity for sampling selectively makes it particularly valuable. We conjecture that it affords another advantage in an apparatus limited by pumping constraints similar to those of the Michigan unit (originally designed to study gas molecules, not clusters). It has been shown in Orsay that when the extremely small clusters of monoclinic SF_6 produced in free jet expansion are passed through a shock wave

(Mach disk), they are transformed to bcc microcrystals.[20] The clusters responsible for the patterns in Fig. 4 are more than tenfold larger in bulk. Had they been as small as the Orsay clusters, they would very likely have suffered a substantial modification while traversing the conical skimmer under the poor skimming conditions used in the present experiments with continuous flow. As explained earlier, skimming at the vee skimmer is considerably cleaner.

The most striking result of all, visible in the unskimmed pattern at 4.8 bars, is the appearance of intensity distributions never seen in the many prior studies of SF_6 clusters in three different laboratories.[8] These features are identified by arrows and coincide closely with expected positions for diffraction rings of trigonal SF_6.[21] Other rings of the trigonal form are obscured by those of the other phases. Further tests exploiting the ability of the vee skimmer to isolate individual zones of cluster beams should ascertain the nature of the newly observed clusters.

It may be that the diverse trajectories (and, hence, diverse cluster histories) sampled in unskimmed jets will offer a broad perspective of processes in the jet that have been difficult to detect in prior, narrowly focused investigations. It is certainly true that the selectivity of the vee skimmer in sampling supersonic jets makes it a valuable new tool in cluster studies. Both of these skimming configurations are made possible by operating in the pulsed mode. Augmenting the utility of such studies is the monitoring of the jet density distribution and velocity distribution. These measurements, which are greatly facilitated by pulsed operation, are essential in diagnoses of the characteristics of the gas dynamics. It is evident from the foregoing that in electron diffraction studies of clusters generated in supersonic flow, it is not only possible but also highly advantageous to study jets that are pulsed.

ACKNOWLEDGMENTS

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