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FORMATION OF MIXED MOLECULAR CLUSTERS IN FREE-JET EXPANSIONS

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VON KÁRMÁN GAS DYNAMICS FACILITY
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To determine the concentrations of jet engine pollutants in the stratosphere, it is necessary to obtain information concerning the molecular clustering characteristics of pollutant species. In the present investigation, a simulation of jet engine exhaust emissions has been accomplished by expanding various gas/water mixtures from a molecular beam source and mass analyzing the resulting molecular beam. It was found possible to produce

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clusters of the following types: $(N_2)_n^+$, $(NO)_n^+$, $(CO_2)_n^+$, $(SO_2)_n^+$, $(CH_4)_n^+$, $N_2^+(H_2O)_n$, $NO^+(H_2O)_n$, $SO_2^+(H_2O)_n$, $(SO_2)_2^+(H_2O)_n$, $CO_2^+(H_2O)_n$, $(CO_2)_2^+ (H_2O)_n$, $SO_2^+N_2$, NO^+N_2, NO^+SO_2, $NO^+N_2\ H_2O$, $NO^+\ SO_2\ H_2O$, $CO_2^+\ SO_2$, $(CO_2)_2^+\ SO_2$, and $NO^+\ CO_2$. The purpose of nitrogen in the gas mixtures was to simulate the major air fraction of the jet exhaust.

PREFACE

The research reported herein was conducted by the Arnold Engineering Development Center (AEDC) for Air Force Cambridge Research Laboratories (AFCRL), Air Force Systems Command (AFSC), under Program Element 62101F. The results presented herein were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC, AFSC, Arnold Air Force Station, Tennessee. The work was done under ARO Project No. VF224. The manuscript (ARO Control No. ARO-VKF-TR-74-14) was submitted for publication on January 29, 1974.

Captain J. Calo (AFCRL) formulated the test program and assisted with some of the experimental work. The conclusions presented in this report in no way reflect those of Capt J. Calo or AFCRL.

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1.0 INTRODUCTION

Recently mass spectra have been obtained from cluster beams formed by the expansions of various water/gas mixtures (Ref. 1). Cluster ions of the following types were observed: $H^+(H_2O)_n$, $(SO_2)_n^+$, $(NO)_n^+$ $SO_2^+ (H_2O)_n$, $(SO_2)_2^+ (H_2O)_n$, $(NO)^+ (H_2O)_n$, $NO^+ (SO_2)_n$, $NO^+ (SO_2) (H_2O)_n$, $(Ar)_n^+$, $AR^+ (H_2O)_n$, and $Ar^+ (SO_2)_n$. As a result of a presentation of these data to the Department of Transportation (DOT), by Air Force Cambridge Research Laboratories (AFCRL), Calo has defined the objectives of the present investigation.

The present program evolves into essentially two subprograms: (1) a Mixed Molecular Cluster Program, which is concerned with jet engine pollutant species and is basically stratospheric in scope and (2) an Ionospheric Cluster Program, which is concerned with NO^+/H_2O cluster interactions and appearance potentials of the oxides of sulphur from mixed clusters of H_2O and SO_2 and H_2SO_4.

The simulation of jet engine exhaust emissions will be accomplished by controlling the temperature, pressure,, and relative composition of the source gas. The species to be considered will be SO_2, NO, CO, CO_2, H_2O, and CH_4 in pure nitrogen carrier gas. Mass spectra will be obtained for both neutral and pre-ionized expansions in order to observe possible shifts in mixed cluster composition, from which a determination as to the relative importance of neutral and ionic clustering may be obtained. In the pre-ionized mode of operation the mass spectrometer ion source filament will have to be deactivated while the focusing and extractor potentials will still be required.

An attempt to study the conversion of NO^+ to water cluster ions in the absence of sunlight will be made by crossing a thermal NO^+ beam with a neutral water cluster beam. It is anticipated that the concentration of possible reactive products will be low and that some effort will have to be devoted to the development of the photon-counting technique.

An investigation of the species formed upon expansions of H_2O/SO_2 mixtures and weak H_2SO_4 solutions will be undertaken in an attempt to determine the mechanisms responsible for the existence of the sulphur oxide series in the Lower D region of the ionosphere. As a result of these measurements, it may be possible to determine whether this series (i.e., sulphur oxide) results from SO_2/H_2O interactions or from the direct ionization of sulfates.

2.0 APPARATUS

2.1 MOLECULAR BEAM CHAMBER MODIFICATIONS

A complete description of the AEDC-VKF Aerodynamic Molecular Beam Chamber (Fig. 1) and the associated beam detection systems is given in Ref. 2. The modifications made to the chamber and associated detection systems are summarized in Ref. 3.

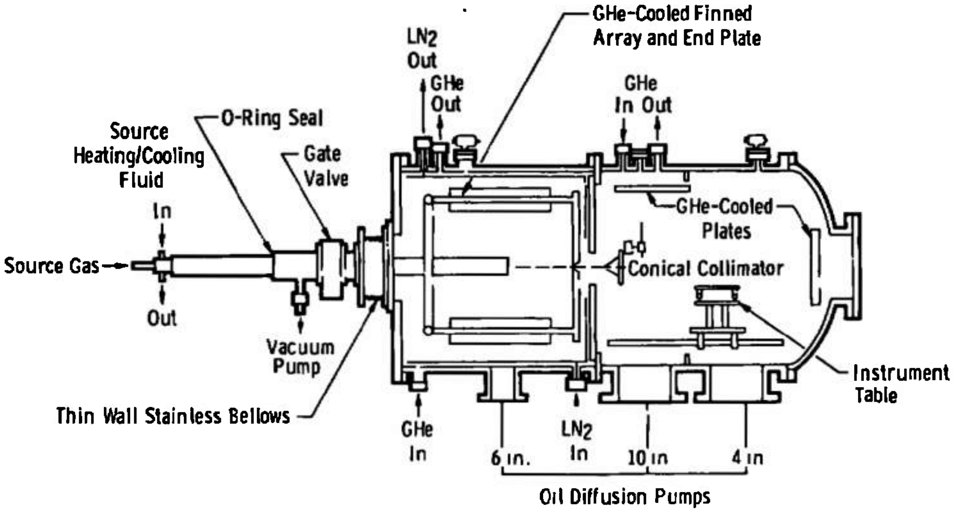


Figure 1. Schematic of Molecular Beam Chamber.

The molecular beam source is described in Ref. 2. The test gas flows through an approximately 1-m-long tube, which vents into a settling chamber prior to exiting from a sonic orifice into the chamber. Heating (or cooling) fluid passing through two tubes concentric with the gas supply tube effectively controls the temperature of the test gas. Gas temperature is measured with a copper-constantan thermocouple located at the upstream end of the settling chamber. The source orifice used in the present study has a diameter of 0. 0343 cm.

A schematic of the gas inlet system used to produce mixtures of water and the gases of interest is shown in Fig. 2. In the present application, the temperature of the water boiler was held constant at approximately 295°K. In the preparation of the test gas mixtures of interest, the following procedures were utilized: (1) the pressure of the gas leaving the gas bottles was regulated to 30 psi, (2) the gas flow rate from each of the gas bottles was set at the desired value by adjusting

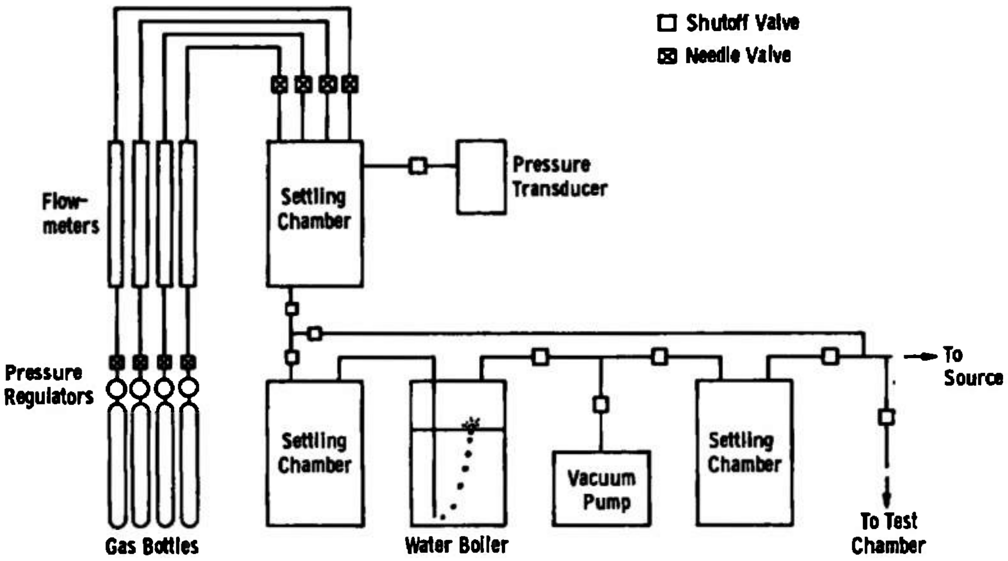


Figure 2. Schematic of gas addition system.

the needle valve downstream of the flow meter, and (3) as each of the gas flow rates was established, the pressure in the first settling chamber was measured with the pressure transducer.

In an earlier study involving gas/water mixtures, some problems were encountered with the flow of water out of the water boiler. These problems have been resolved by the installation of two settling chambers, one upstream and the other downstream of the water boiler (see Fig. 2). Provision has been made to evacuate the gas addition system with a small mechanical vacuum pump and the molecular beam chamber cryopumps. The molecular beam cryopumps are used to purge the gas addition system after the use of toxic gases. Thus, in this manner all the toxic gases used in this investigation were pumped by the cryosurfaces in the molecular beam chamber. At the end of a test series as these surfaces warm up, the gases evolve and in the past have been pumped by the chamber diffusion and mechanical pumps. On completion of the earlier test program (Ref. 1), it was found that this pumping system had suffered considerable damage as a result of pumping these gas/water mixtures. As a result of this, modifications have been made to the purging procedures to minimize damage of this type. Dry nitrogen is bled into the test section, and when the chamber pressure reaches 600 torr, an air ejector exhaust pump is used to evacuate the test chamber. This ejector is able to maintain a pressure of approximately 550 torr with a continuous inbleed of dry nitrogen and the gas evolving from the cryosurfaces. The exhaust from the air ejector is vented 20 ft above the laboratory roof. It is of interest to note that this has proven to be a highly effective means of minimizing damage to the diffusion and mechanical pumps. However, with gas mixtures of the types used previously (Ref. 1) and those considered in the present investigation, contamination of the cryosurfaces does occur, and all the cryosurfaces have to be removed from the chamber and cleaned. The mechanical and oil diffusion pumping system has been completely redesigned so that (1) the time to pump the chamber to 0.050 torr has been considerably reduced, (2) in the event of a power failure the chamber is automatically isolated from the pumping system, and (3) the liquid nitrogen traps on the 6- and 4-in. diffusion pumps have been replaced with a freon refrigerator which permits the continuous operation of the pumps.

In the present study the molecular beam has been formed with a 0.635-cm-diam cryogenically-cooled (20°K gaseous helium) skimmer and a nonpumping 0.193-cm conical collimator.

2.2 DETECTOR SYSTEM

A description of the modulated beam detection system used to measure specie concentration in the molecular beam is contained in Ref. 4. It consists of (1) a two-slot mechanical chopper which gives equal beam on and off times, (2) an EAI quadrupole mass spectrometer modified so that it has a range from 14 to 176 atomic mass units (AMU), and (3) a lock-in (narrow bandpass) amplifier. The pulsed molecular beam is crossed with an electron beam, and the resulting ionized molecules are drawn into the quadrupole section of the mass spectrometer. The resulting ion current is amplified by a 17-stage copper-beryllium (Cu-Be) electron multiplier.

In an earlier experimental study of expansions of this type (Ref. 1), the mass spectra were obtained by manually scanning the mass range and recording the voltmeter signal at the mass numbers of interest. Through the use of a suitably programmed PDP-8® minicomputer in conjunction with a teleprinter and the mass spectrometer, the mass number of interest can be selected, and the corresponding intensity is automatically recorded.

The mass range from 14 to 176 was calibrated by (1) bleeding SF_6 into the test chamber and observing the mass spectrometer settings for S^+, SF^+, SF_2^+, SF_3^+, and SF_4^+ and by (2) observing the mass spectrometer setting for CO^+, CO_2^+, $(CO_2)_2^+$, $(CO_2)_3^+$, and $(CO_2)_4^+$ in a CO_2

expansion. Provided the operating characteristics of the mass spectrometer were not changed, it was found that this mass calibration did not change over the time period of this investigation.

An alternate technique for obtaining mass spectra has been developed which involves the adaptation of conventional pulse-counting techniques to the EAI mass spectrometer. In this application, the PDP-8 minicomputer has been programmed to scan the mass range of interest and identify the mass peaks occurring over this range.

3.0 DISCUSSION OF EXPERIMENTAL RESULTS

3.1 PRELIMINARY EVALUATION OF EXPERIMENTAL PROGRAM REQUIREMENTS

One requirement of the test program is to obtain mass spectra from neutral and pre-ionized expansions. The scope of this portion of the test program is summarized in Table 1. In the course of the present investigation, some additional mixtures not listed in this original test schedule were evaluated.

In considering the need for a pre-ionized expansion and the production of a thermal NO^+ ion beam, an attempt was made to use a common source to satisfy both of these requirements. A review of the available literature (e.g., Ref. 5) revealed that the fabrication of a source designed specifically for the production of a thermal NO^+ ion beam was beyond the scope of the present investigation and would not necessarily be suitable for both of the above requirements. An alternate method of producing ions in the expansion was suggested by the work of Barreto (Ref. 6). Barreto was able to produce a large supply of ions in an expanding flow by maintaining a corona discharge upstream of a nozzle throat. In this technique (see Ref. 6), a tungsten needle is supported concentric with and slightly upstream of the throat and electrically insulated from it. A high voltage power supply is connected between this needle and the nozzle, thus maintaining a corona discharge. The gas in the region of the corona becomes ionized, and ions are fed into the expanding flow. A source of this type was evaluated in the present investigation.

In operation, a corona discharge upstream of the sonic orifice was clearly visible. As a result of Baretto's work, this discharge was taken to be an indication of ions in the initial portion of the subsequent expansion.

Table 1. Test Schedule*

Series	Run	Gas (Pressure, torr)		Water	Information to be Gained
0	0	N_2(2000)		-	Determine the Effects of N_2 Carrier Gas
		N_2(2000)		x	
I	1	A(2000)		-	Determine Variation of $SO_2(H_2O)_n$ with SO_2 Concentration
	2	A(2000)		x	
	3	B(2000)		x	
	4	C(2000)		x	
	5	D(2000)		x	
II	1	E(2000)		-	Determine Variation of NO $(H_2O)_n$ with NO Concentration
	2	E(2000)		x	
	3	E(1500)	N_2(500)	x	
	4	E(1000)	N_2(1000)	x	
	5	E(500)	N_2(1500)	x	
III	1	F(2000)		-	Determine Variation of CO $(H_2O)_n$ with CO Concentration
	2	F(2000)		x	
	3	F(1500)	N_2(500)	x	
	4	F(1000)	N_2(1000)	x	
	5	F(500)	N_2(1500)	x	
IV	1	G(2000)		-	Determine Variation of CO_2 $(H_2O)_n$ with CO_2 Concentration
	2	G(2000)		x	
	3	G(1500)	N_2(500)	x	
	4	G(1000)	N_2(1000)	x	
	5	G(500)	N_2(1500)	x	
V	1	E(1000)	A(1000)	-	Determine Variation of NO SO_2 $(H_2O)_n$ with SO_2 Concentration and Effect of NO and SO_2 on Mixed Clusters
	2	E(1000)	A(1000)	x	
	3	E(1000)	B(1000)	x	
	4	E(1000)	C(1000)	x	
	5	E(1000)	D(1000)	x	
VI	1	F(1000)	A(1000)	-	Determine Variation of CO SO_2 $(H_2O)_n$ with SO_2 Concentration and Effect of CO and SO_2 on Mixed Clusters
	2	F(1000)	A(1000)	x	
	3	F(1000)	B(1000)	x	
	4	F(1000)	C(1000)	x	
	5	F(1000)	D(1000)	x	
VII	1	G(1000)	A(1000)	-	Determine Variation of CO_2 SO_2 $(H_2O)_n$ with SO_2 Concentration and Effect of CO_2 and SO_2
	2	G(1000)	A(1000)	x	
	3	G(1000)	B(1000)	x	
	4	G(1000)	C(1000)	x	
	5	G(1000)	D(1000)	x	
VIII	1	E(1000)	F(1000)	-	Determine Variation of NO CO $(H_2O)_n$ with NO and CO Concentrations
	2	E(1000)	F(1000)	x	
	3	E(1250)	F(750)	x	
	4	E(1500)	F(500)	x	
	5	E(1750)	F(250)	x	
IX	1	E(1000)	G(1000)	-	Determine Variation of NO CO_2 $(H_2O)_n$ with NO and CO_2
	2	E(1000)	G(1000)	x	
	3	E(1250)	G(750)	x	
	4	E(1500)	G(500)	x	
	5	E(1750)	G(250)	x	
X	1	F(1000)	G(1000)	-	Determine Variation of CO CO_2 $(H_2O)_n$ with CO and CO_2
	2	F(1000)	G(1000)	x	
	3	F(1250)	G(750)	x	
	4	F(1500)	G(500)	x	
	5	F(1750)	G(250)	x	
XI	1	D(20), E(20), F(50), G(400), N_2(1510)		-	Determine Effects of Entire Melange on Mixed Clusters at High Temperature
	2	D(20), E(20), F(50)		x	

Designation	Gas
A	0.5 percent SO_2 in N_2
B	0.25 percent SO_2 in N_2
C	0.17 percent SO_2 in N_2
D	235 ppm SO_2 in N_2
E	1 percent NO in N_2
F	1 percent CO in N_2
G	5 percent CO_2 in N_2
N_2	Pure N_2

- Denotes That the Mixture Is NOT To Be Diverted Through the Water

x Denotes That the Mixture WILL Be Diverted Through the Water

* Formulated by AFCRL

Attempts were made to determine whether Ar^+ and N_2^+ ion beams could be formed. In the first attempts to make these measurements, the ion source filament was deactivated, leaving the focus and extractor settings unchanged. No evidence of the existence of Ar^+ or N_2^+ ion beams was obtained. The mass spectrometer was then replaced by a 17-stage Cu-Be electron multiplier mounted so that the molecular beam impinged directly on the surface of the first dynode. Again, no evidence of the existence of an ion beam was obtained.

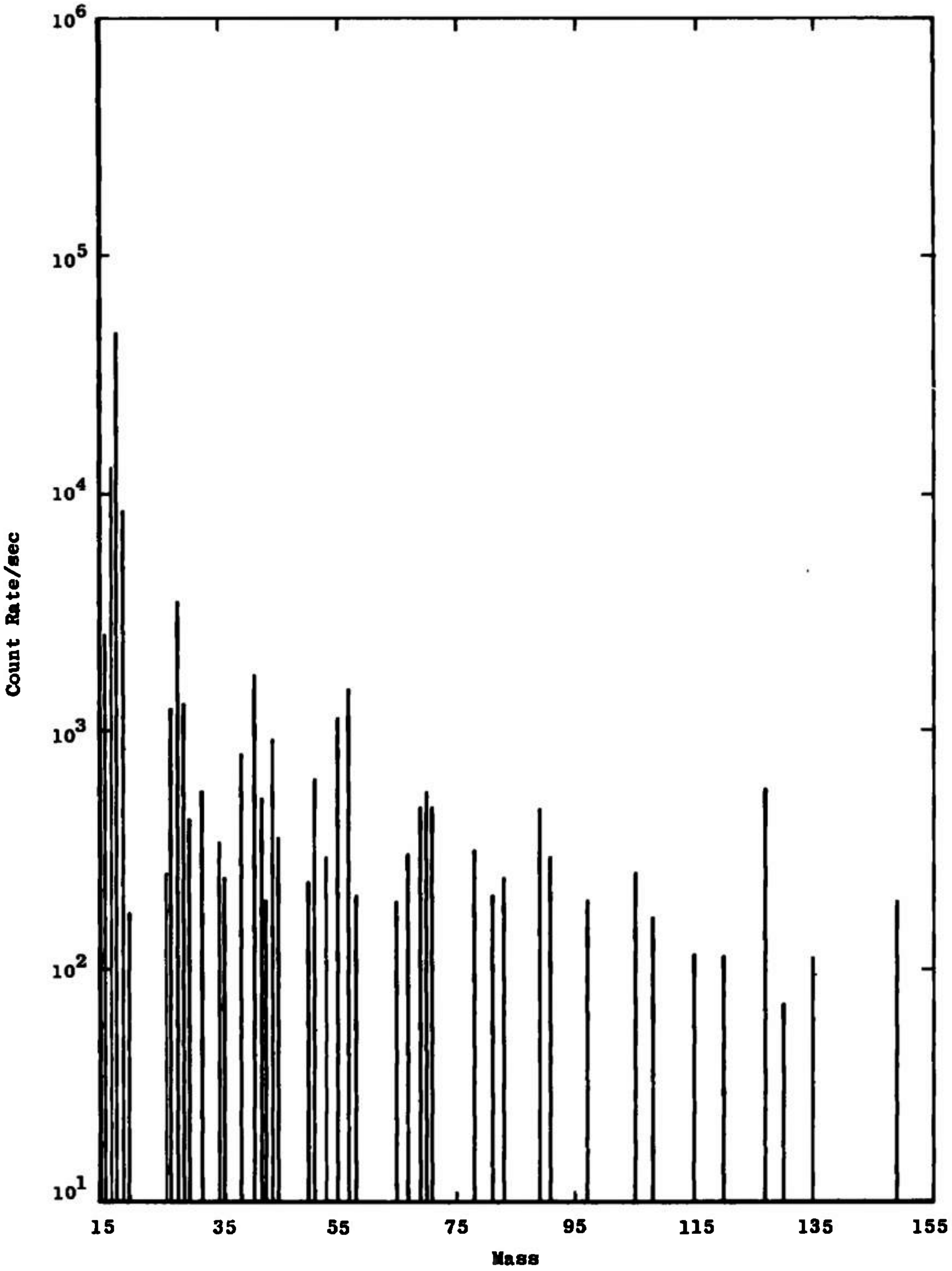
The failure to produce a satisfactory ion beam has resulted in an inability to attempt several portions of the test program outlined in the Introduction.

3.2 AN EVALUATION OF THE PULSE-COUNTING TECHNIQUE FOR OBTAINING MASS SPECTRA

A mass scan of the residual gas in the test chamber and a scan for a pure nitrogen molecular beam are compared in Fig. 3. To obtain these spectra, the mass range from 15. 2 to 159. 6 was scanned at mass increments of 0. 1. To obtain the mass spectra for the nitrogen beam, it was necessary to correct for the background gas signal. Two methods of correcting for the background gas signal were considered: (1) obtaining a background gas spectrum with the molecular beam off and (2) moving the mass spectrometer out of the beam and obtaining a background gas spectrum. Different background gas signals were obtained using these techniques. Associated with the uncertainty as to the correct background gas signal is the problem of the background signal resulting from the formation of metastables in the ionizer section of the mass spectrometer. This latter problem has been identified and discussed in another study (Ref. 3). Therefore, to simplify the interpretation of the spectra obtained in this study, it was decided to use the modulated beam technique since it eliminates any need for a correction for a background gas signal.

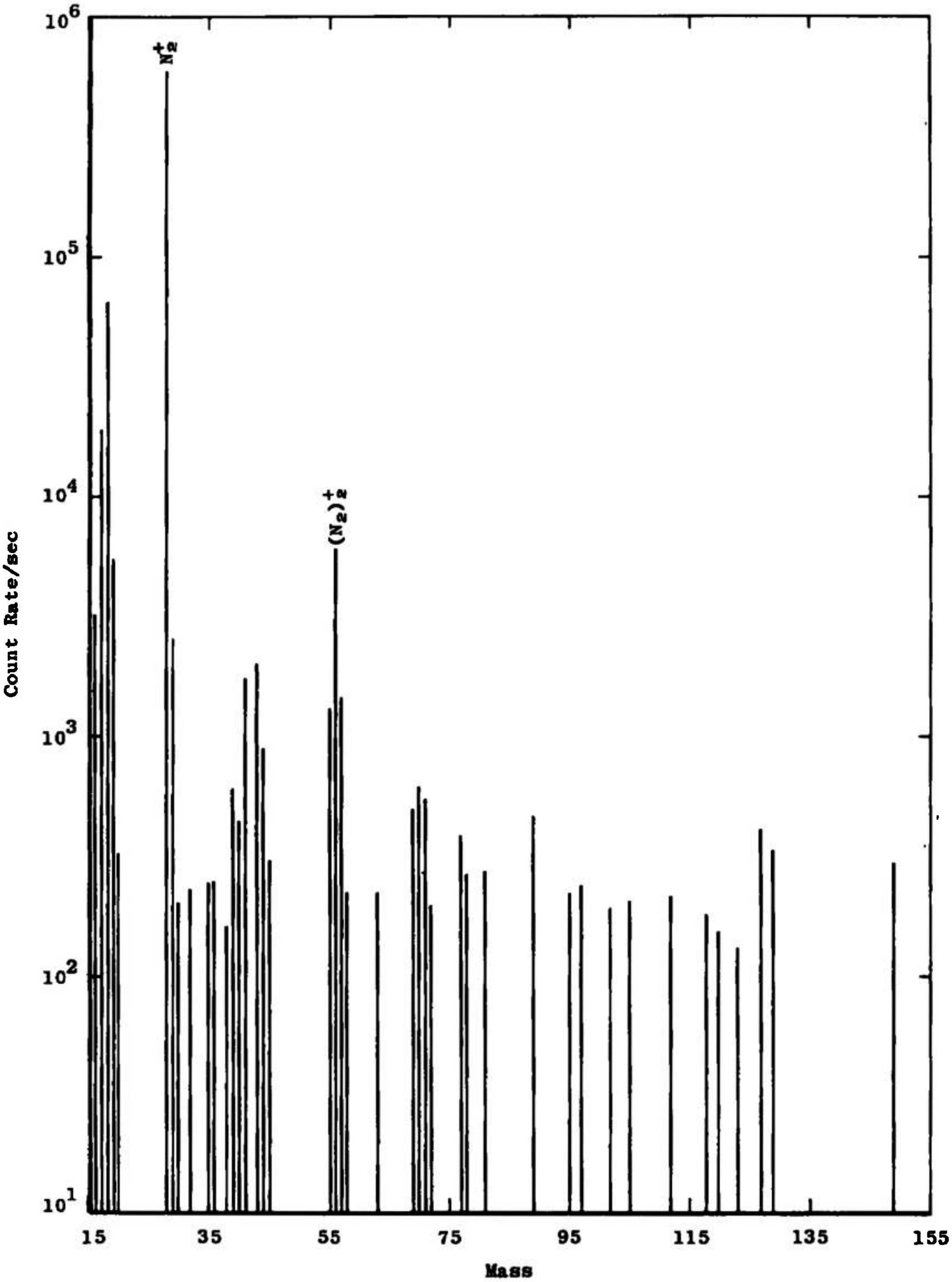
3.3 MASS SPECTRA OBSERVATIONS

The bulk of the mass spectra that will be discussed in this section were obtained using the modulated beam technique. However, regardless of the technique used to obtain the data, suitable corrections have been made for the background signals discussed in the previous section. It should not be assumed that the spectra presented herein contain all the mass peaks that occur over the range of the scan. The clusters of interest in each scan are identified in Table 1.



a. Background gas scan

Figure 3. Mass spectra obtained using the pulse-counting technique.



b. Mass scan for a nitrogen beam

Figure 3. Concluded.

In a similar investigation (Ref. 1), some problems were encountered with a lack of mass resolution at high mass numbers (i.e., greater than 80 AMU). In the present study, considerable increases in system sensitivity have been made. These increases in sensitivity have made it possible to increase the resolution of the mass spectrometer in the present study. A measure of the degree of mass resolution available with the present system is shown in Fig. 4. A mass scan in the region of the

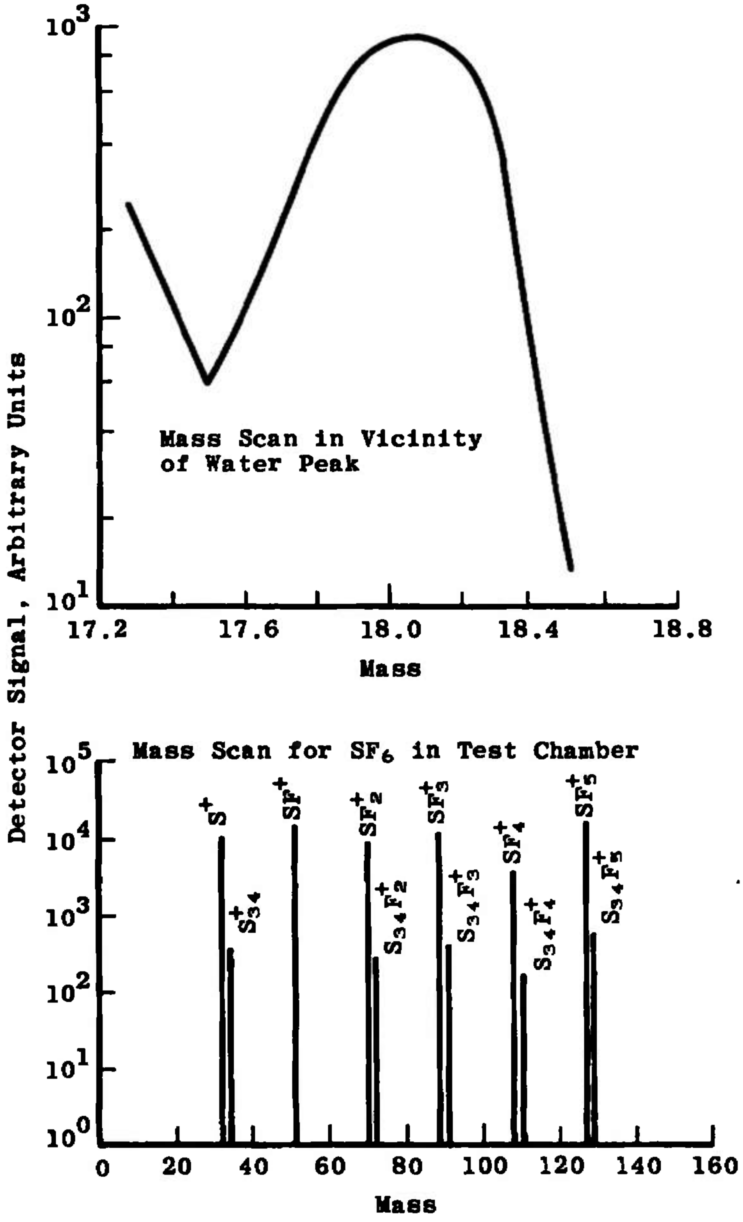


Figure 4. Resolution characteristics of the mass spectrometer.

water peak indicates that it is possible to distinguish between masses differing by 1 AMU at low mass numbers. Electron impact of the SF_6 molecule produces fragments containing the two major isotopes of sulphur having masses of 32 and 34 AMU. The ratio of the observed fragments $SF_5^+/S_{34}F_5^+ \ldots S^+/S_{34}^+$ is approximately equal to the ratio of the naturally occurring isotopes of sulphur. This indicates that the mass spectrometer in its present mode of operation can resolve between two masses at high mass numbers separated by 2 AMU.

In the course of the experimental investigation, it was considered necessary to determine the effect of carrier gas pressure upon the nucleation of water in the free-jet expansion in order to be able to interpret the spectra obtained for the conditions listed in Table 1. Accordingly, a series of nitrogen/water expansions was analyzed where the nitrogen carrier gas pressure varied from 0 to 2500 torr. The results of these measurements are summarized in Fig. 5. It is evident from these measurements that water cluster intensity is not a strong function of carrier gas pressure for $750 \lesssim p_{N_2} \lesssim 2500$ torr. For carrier gas pressures less than 750 torr, nucleation of the water appears to be a strong function of carrier gas pressure. On the basis of these measurements, no significant changes in the nucleation of water would be expected for the small changes in carrier gas pressure existing in the gas mixtures under investigation.

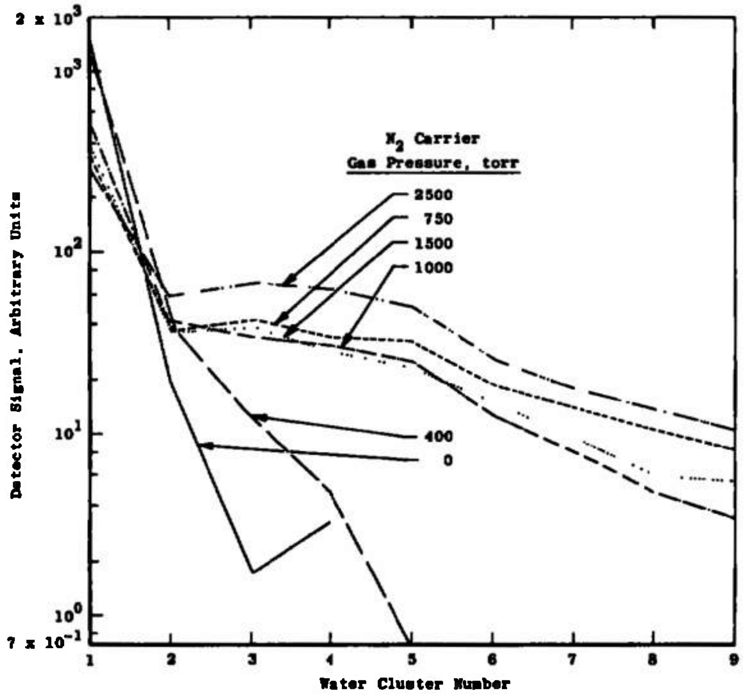


Figure 5. Effect of carrier gas pressure on nucleation of water.

The variation of water monomer intensity with carrier gas pressure is shown in Fig. 6. (A similar variation was observed for a water/argon expansion in Ref. 1). The increase in monomer intensity with increasing source pressure for $p_{N_2} > 1200$ torr may be indicative of an increasing contribution from fragmentation of larger clusters in the ionizer section of the mass spectrometer (cf. Ref. 7). Also shown in Fig. 6 are (1) the variation of the monomer, dimer, and trimer intensity with source pressure for dry nitrogen; and (2) the source pressure at which massive condensation in nitrogen occurs (cf. Ref. 3). In Ref. 3 the onset of massive condensation in pure dry gases has been associated with increasingly large contributions to the cluster signals from cluster fragmentation arising from electron impact. It has been shown (Ref. 1) that the nucleation of water vapor in an expansion process is enhanced

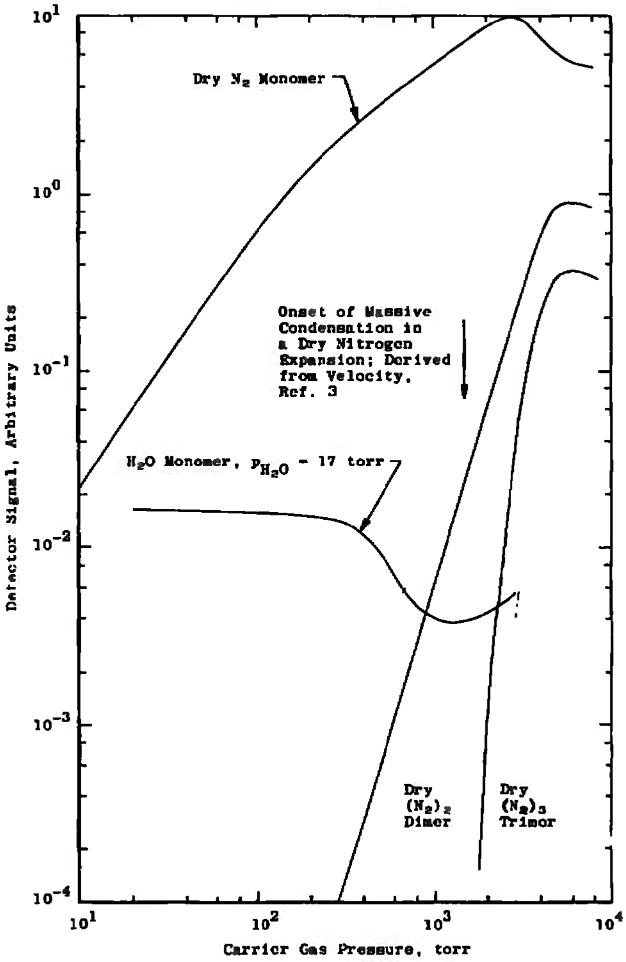
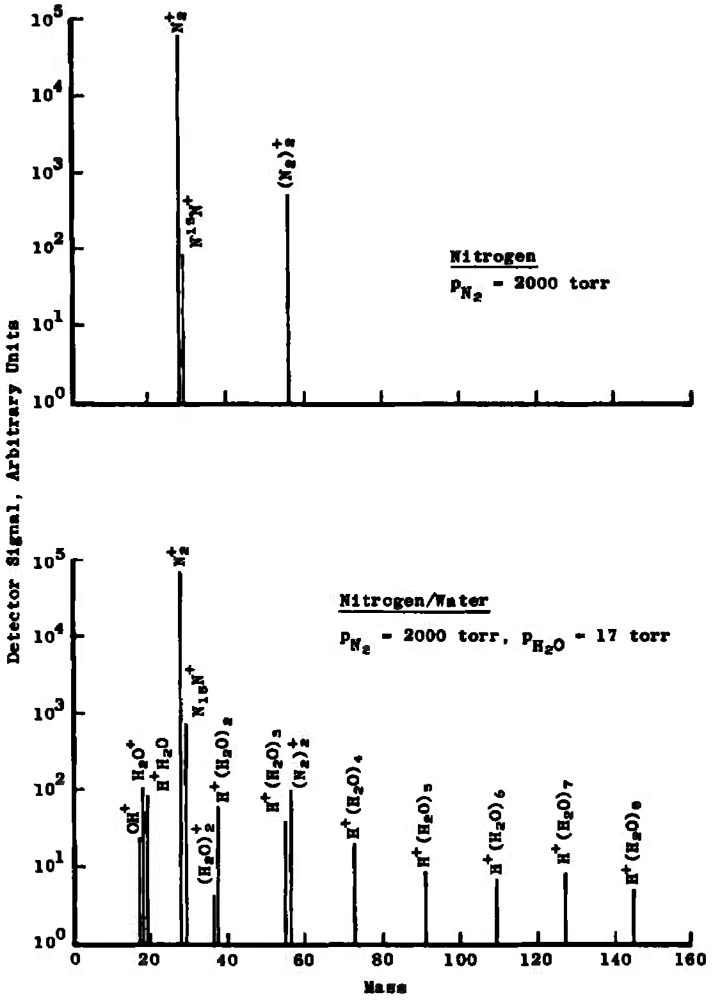


Figure 6. Effect of carrier gas pressure on water monomer intensity.

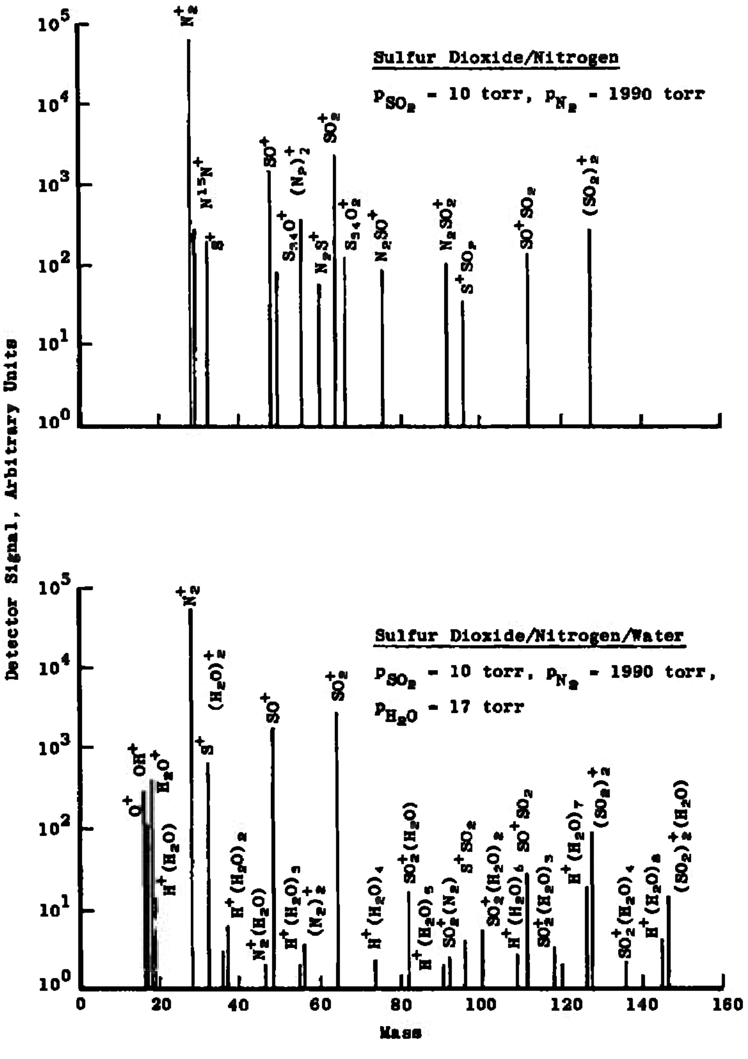
by mixing the water vapor with a high pressure carrier gas. When the source conditions are such that massive condensation (i.e., the formation of clusters containing approximately 100 molecules) has occurred in the carrier gas, it is reasonable to assume that very large clusters will have been formed in the water vapor expansion. It has been shown (i.e., in Fig. 5) that for $750 \lesssim p_{N_2} \lesssim 2500$ torr the cluster intensity signals are essentially independent of carrier gas pressure.

Mass spectra for the various gas mixtures listed in Table 1 are presented in Figs. 7a through l. To determine whether the nucleation of water has been affected by the presence of the trace gases, the water cluster intensities for these mixtures are compared in Fig. 8. In this comparison, the cluster intensities have been arbitrarily normalized to the trimer intensity. With the exception of the large water cluster intensity data obtained with the $H_2O/N_2/CO_2$ mixtures (Fig. 8c), all of these data (Figs. 8a through c) are in good agreement with that obtained for the N_2/H_2O expansion ($p_{N_2} = 2000$ torr, Fig. 6). It appears that the presence of trace amounts of CO_2 in an H_2O/N_2 expansion (Fig. 8c) may reduce the intensity of the larger cluster signals. In an attempt to determine whether CO_2 does have an effect upon the nucleation of water, a CO_2/H_2O expansion has been analyzed (Fig. 8c). The variation of water cluster intensity with the number of molecules per cluster for the CO_2/H_2O expansion is the same as that obtained for the N_2/H_2O expansion, which suggests that CO_2 does not have a significant effect upon the nucleation of water. However, further experimental studies covering a broader range of $CO_2/N_2/H_2O$ mixtures would be necessary to resolve the apparent discrepancy concerning the effect of CO_2 on water nucleation. Also, it is shown that the nucleation of water in $CH_4/N_2/H_2O$ and CO/H_2O expansions does not differ significantly from that observed for an N_2/H_2O expansion (Figs. 8a and b). Some of the spread in these data (i.e., Figs. 8a through c) may be attributable to the inherent scatter in measurements of this type. This observation is suggested by the data obtained for a number of N_2/H_2O expansions (Fig. 9). A further comparison of water cluster intensity measurements is made in Fig. 10, where it is shown that variations in water temperature (T_o), orifice size (d_o), carrier gas, and mass spectrometer do not affect the form of the water cluster intensity variation with the number of molecules per cluster.

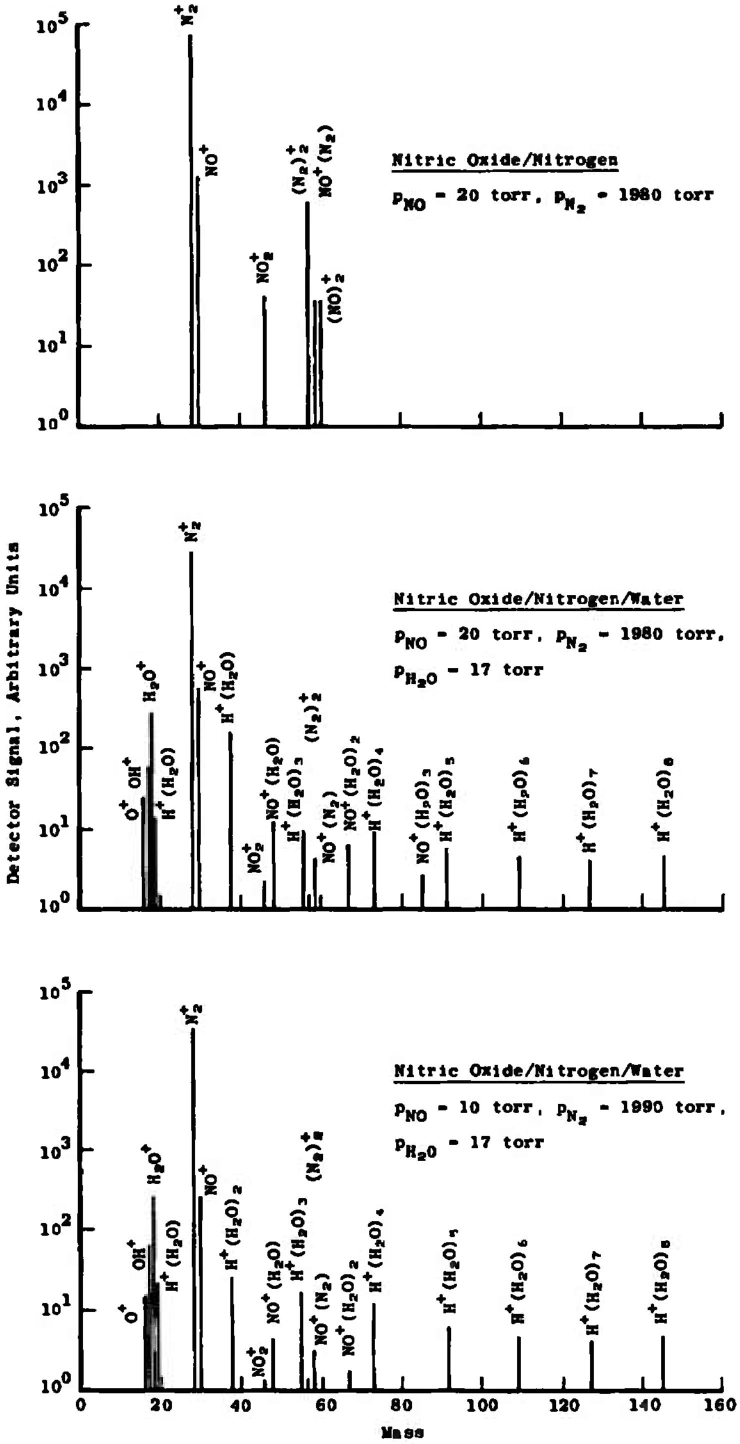


a. Nitrogen and nitrogen/water

Figure 7. Mass spectra obtained for various gas mixtures.

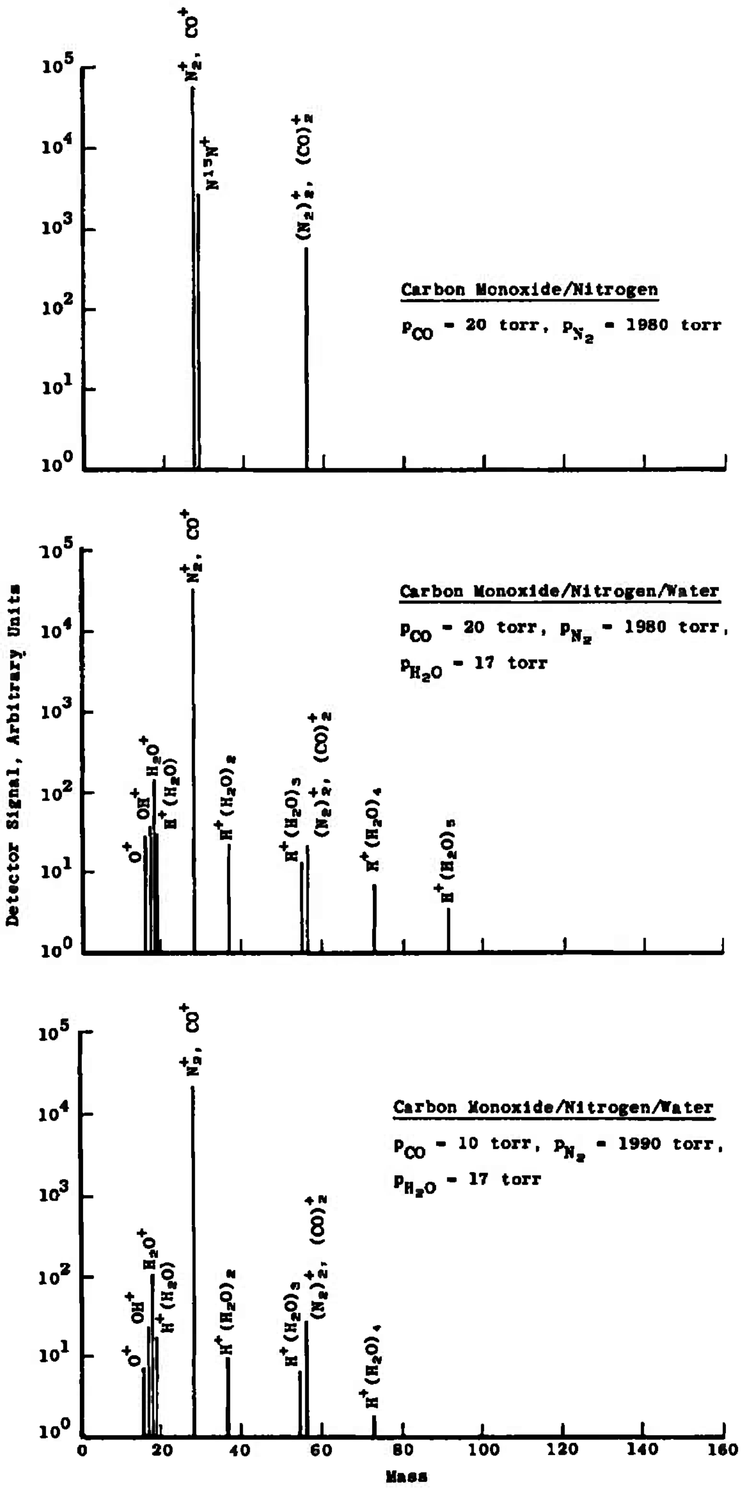


b. Sulfur dioxide/nitrogen and sulfur dioxide/nitrogen/water
Figure 7. Continued.



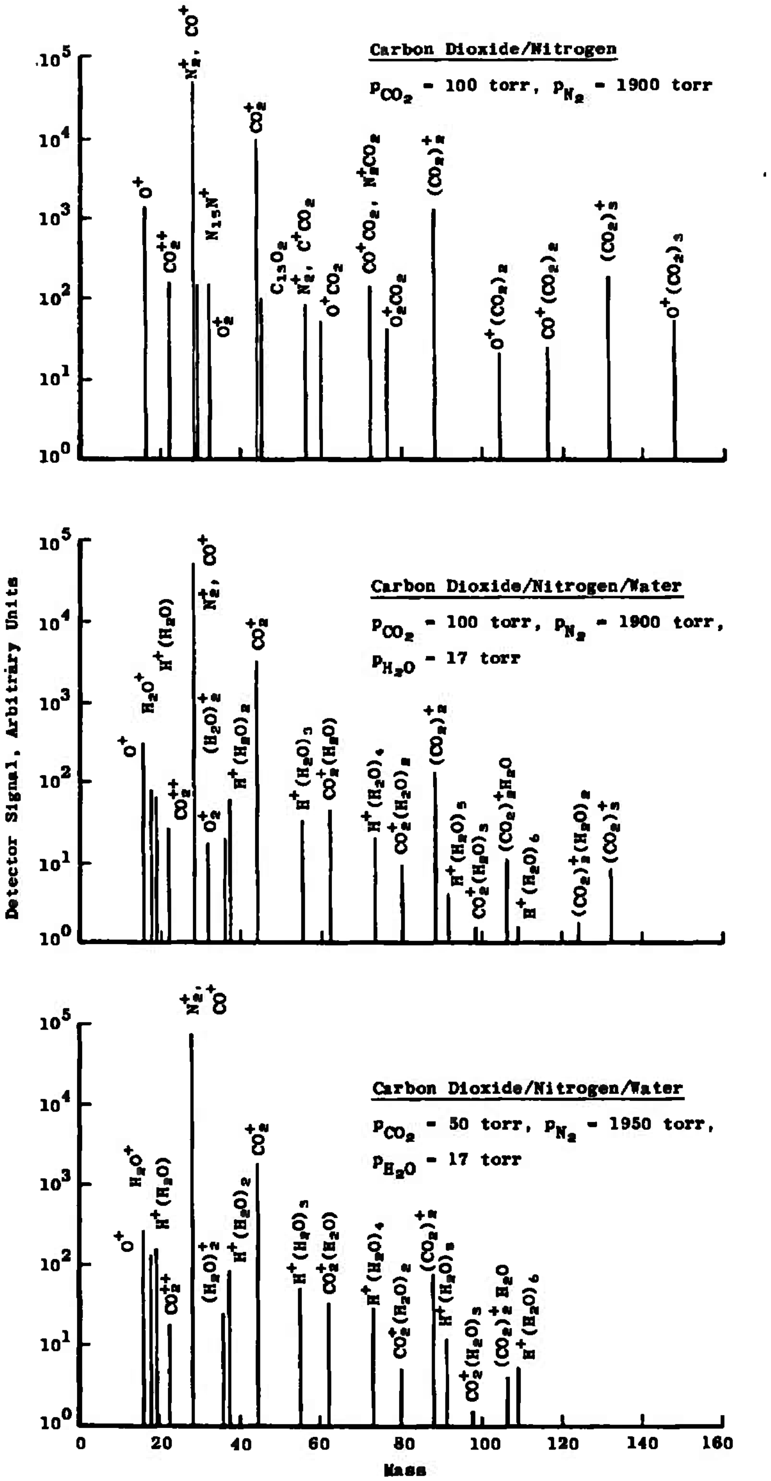
c. Nitric oxide/nitrogen and nitric oxide/nitrogen/water

Figure 7. Continued.

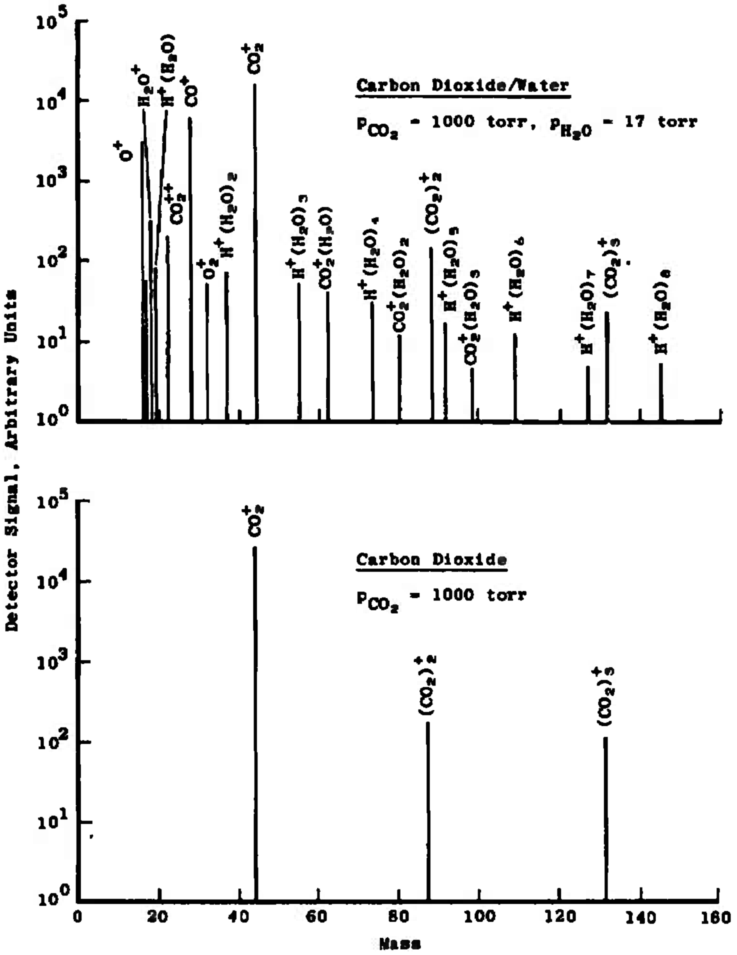


d. Carbon monoxide/nitrogen and carbon monoxide/nitrogen/water

Figure 7. Continued.

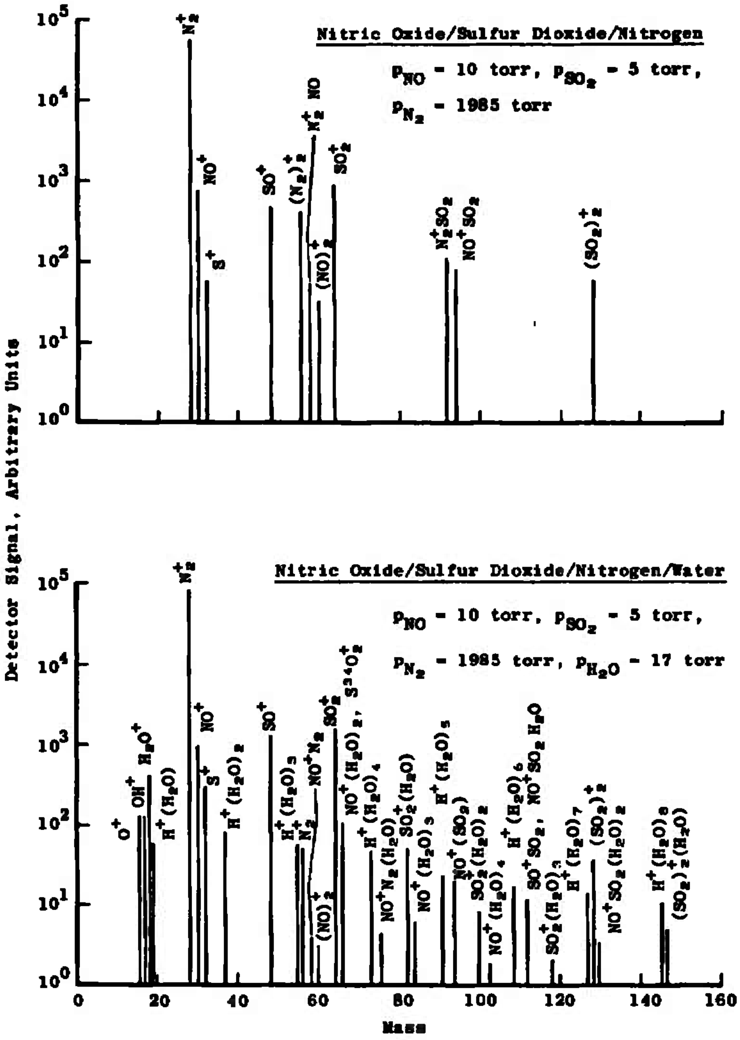


e. Carbon dioxide/nitrogen and carbon dioxide/nitrogen/water
Figure 7. Continued.



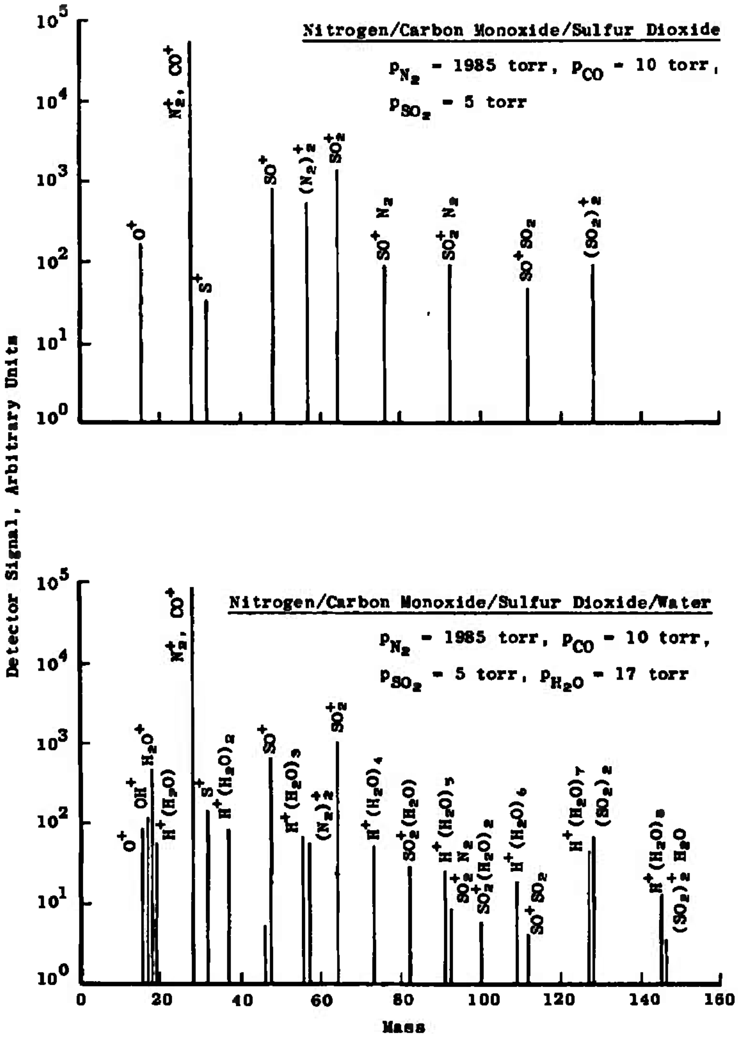
f. Carbon dioxide/water and carbon dioxide

Figure 7. Continued.



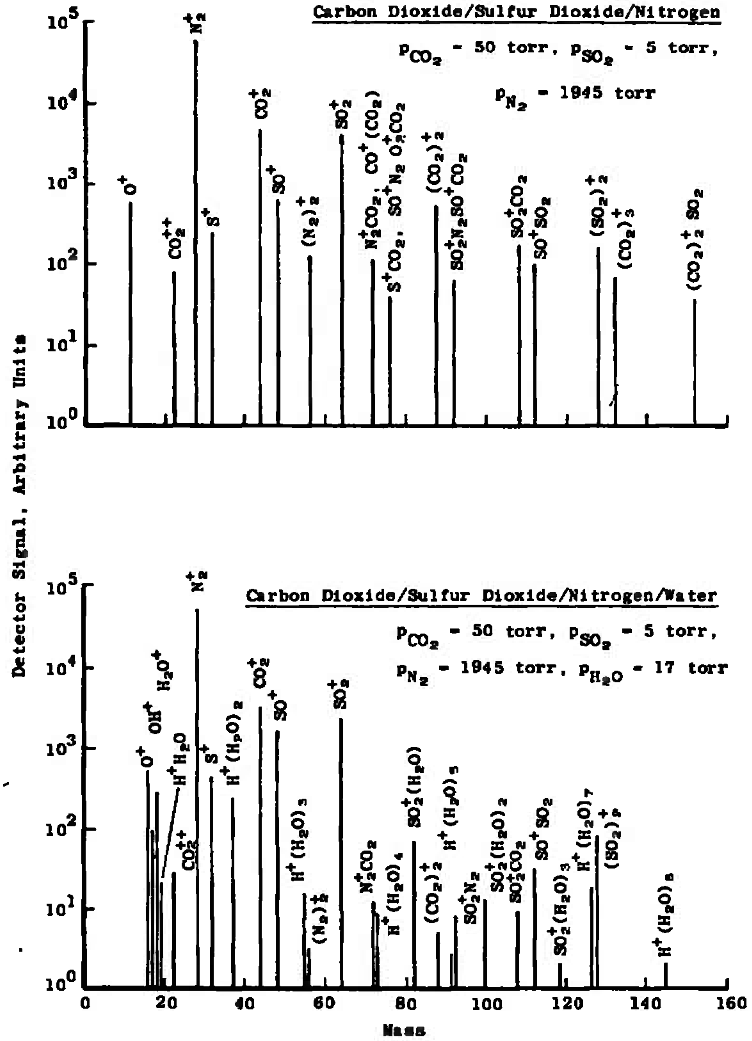
g. Nitric oxide/sulfur dioxide/nitrogen and nitric oxide/sulfur dioxide/nitrogen/water

Figure 7. Continued.



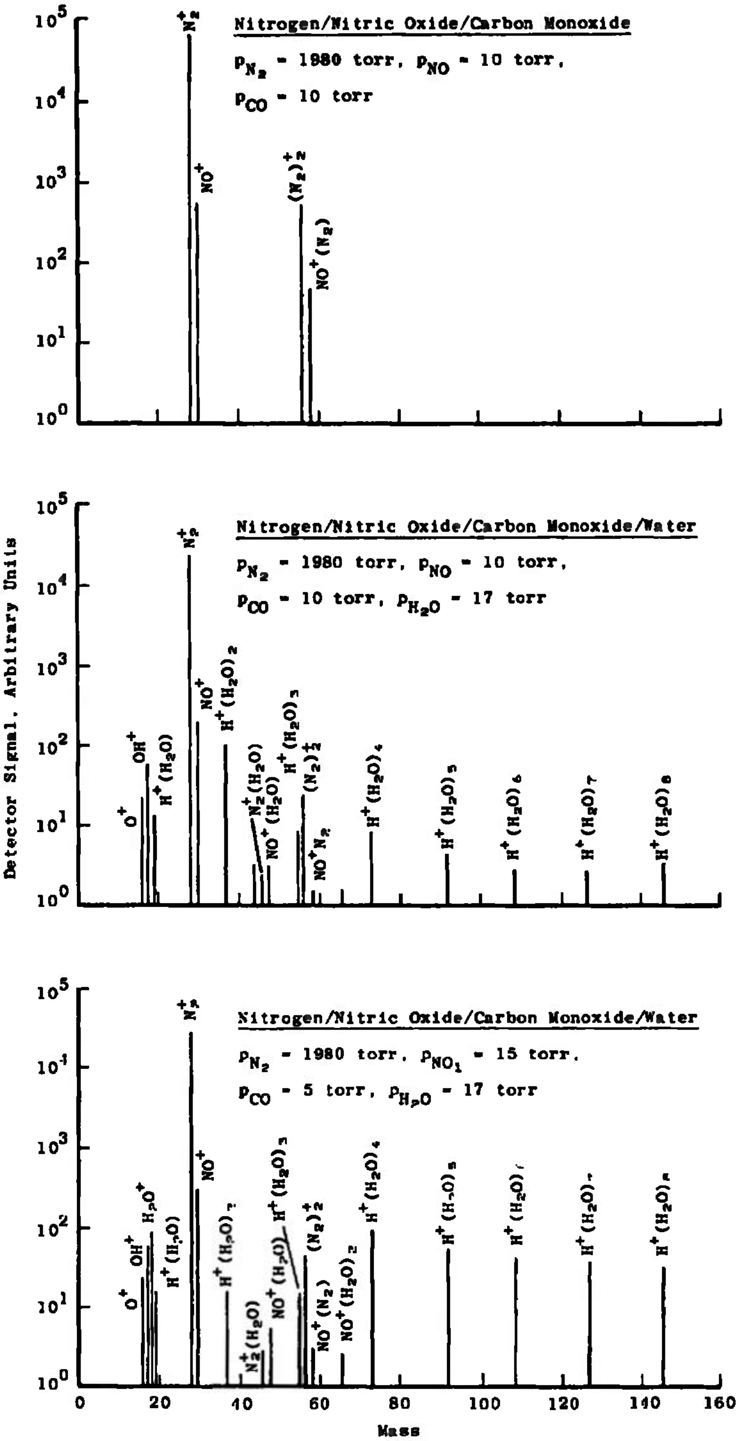
h. Nitrogen/carbon monoxide/sulfur dioxide and nitrogen/carbon monoxide/sulfur dioxide/water

Figure 7. Continued.



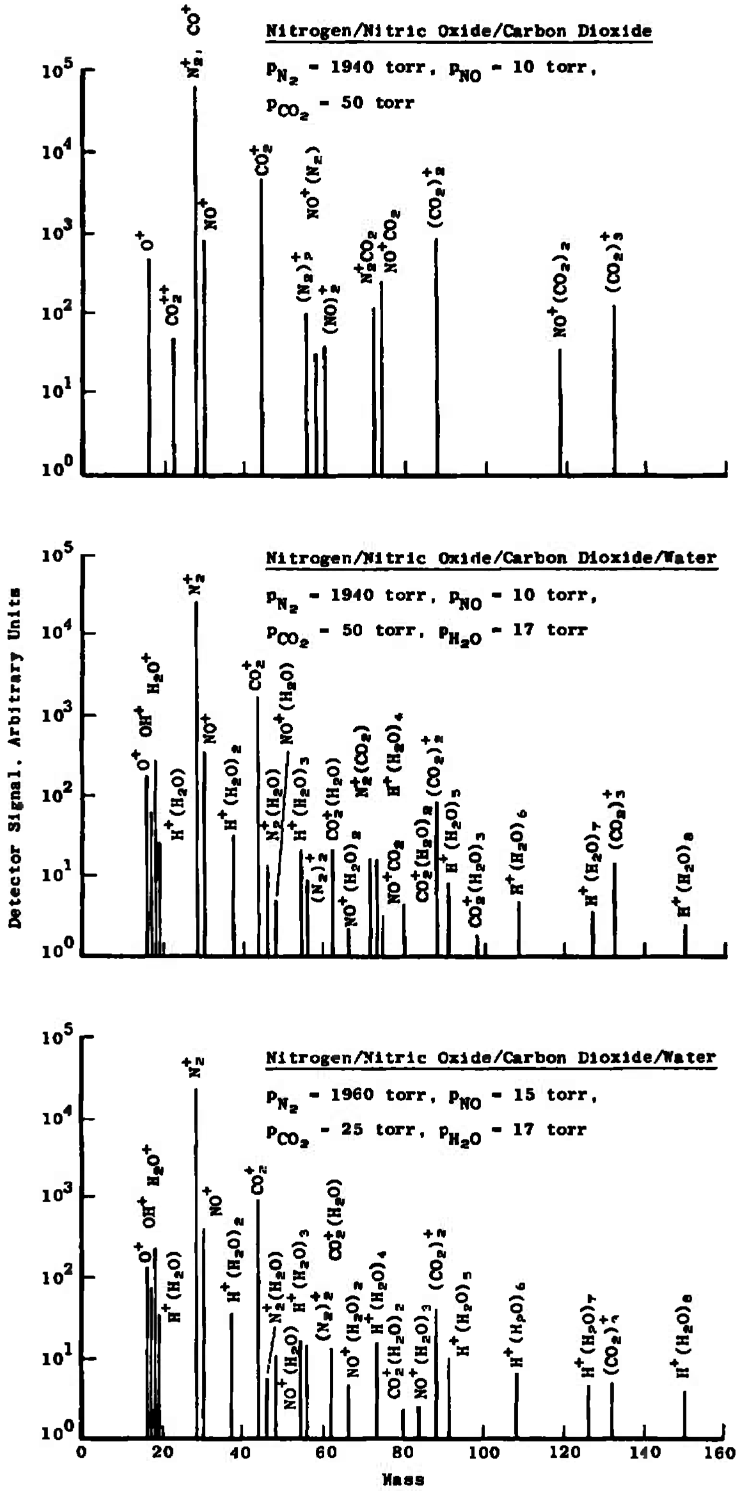
i. Carbon dioxide/sulfur dioxide/nitrogen and carbon dioxide/ sulfur dioxide/nitrogen/water

Figure 7. Continued.



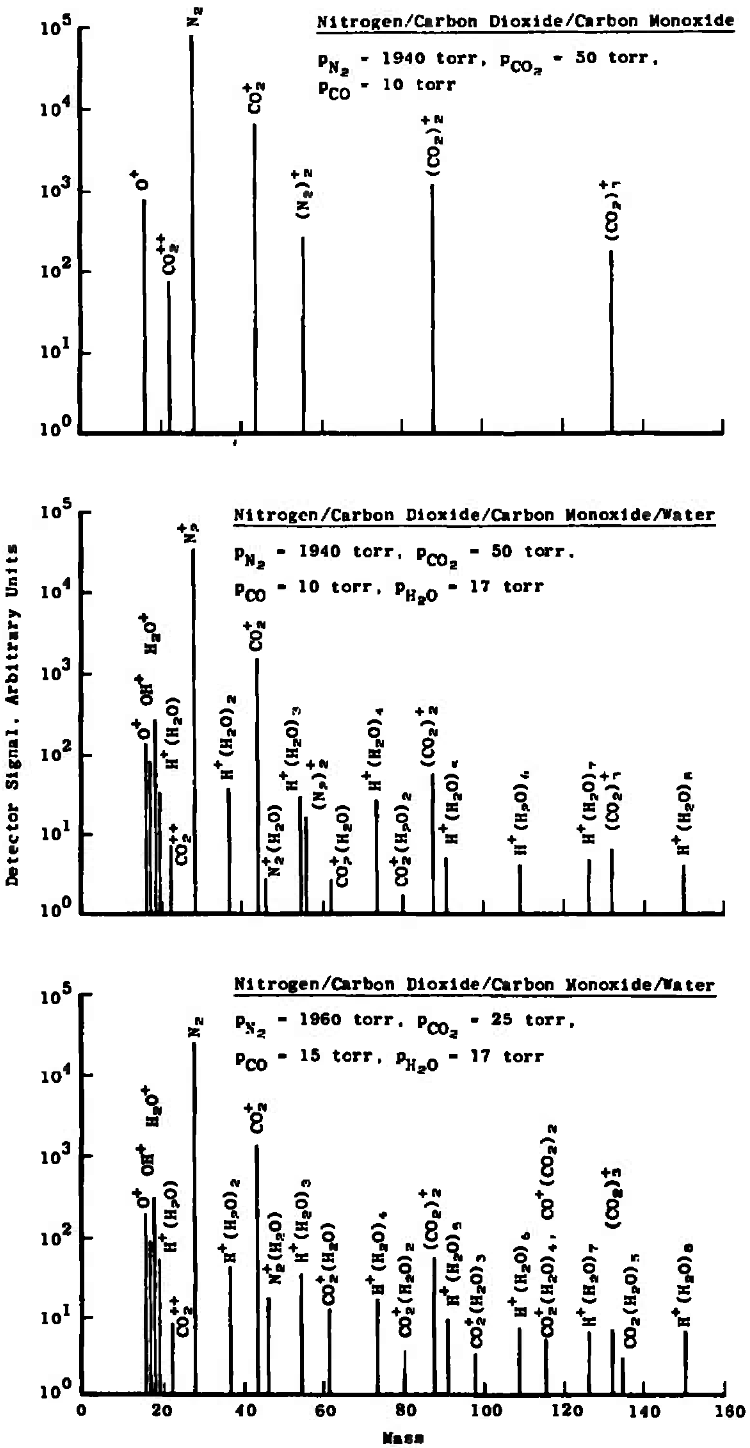
j. Nitrogen/nitric oxide/carbon monoxide and nitrogen/nitric oxide/carbon monoxide/water

Figure 7. Continued.



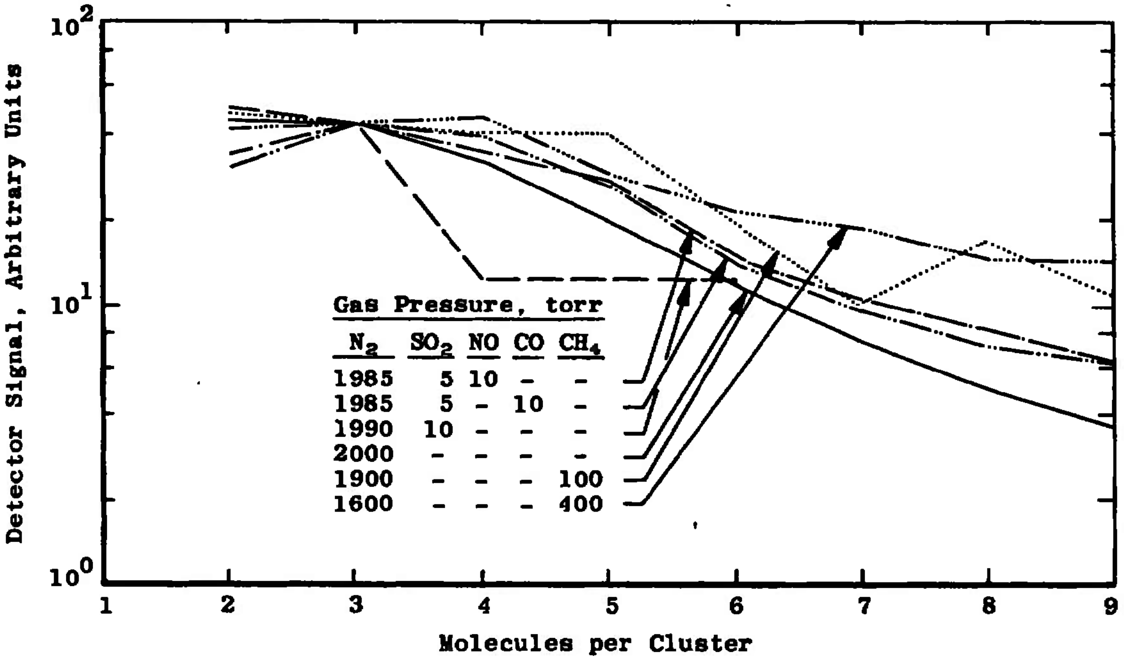
k. Nitrogen/nitric oxide/carbon dioxide and nitrogen/nitric oxide/carbon dioxide/water

Figure 7. Continued.

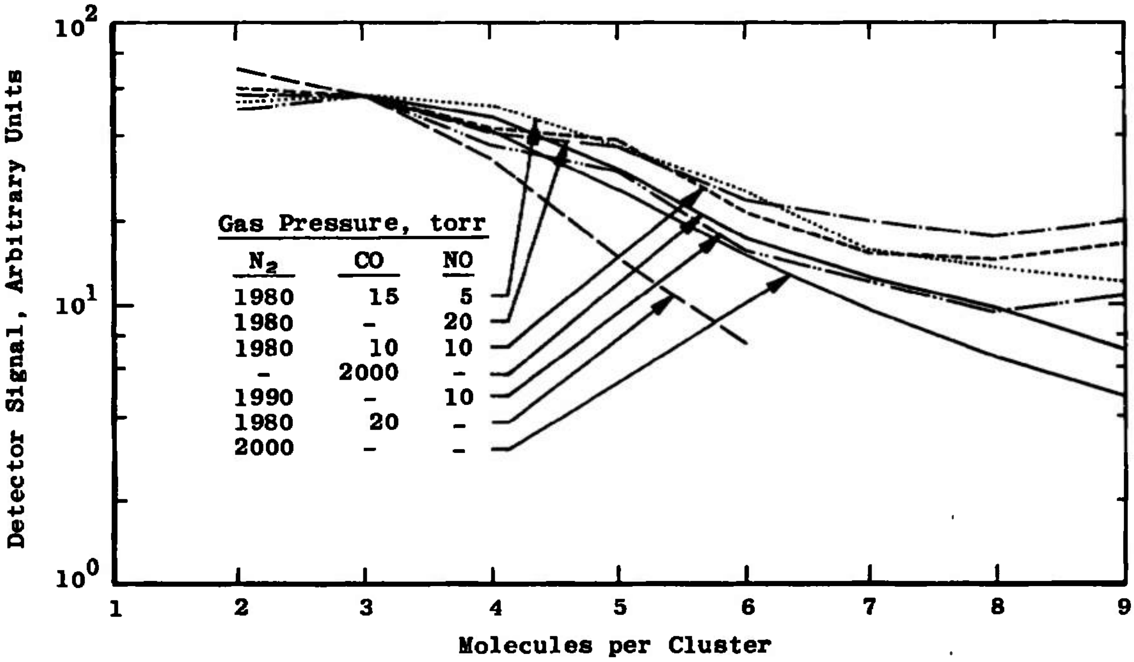


I. Nitrogen/carbon dioxide/carbon monoxide and nitrogen/carbon dioxide/carbon monoxide/water

Figure 7. Concluded.

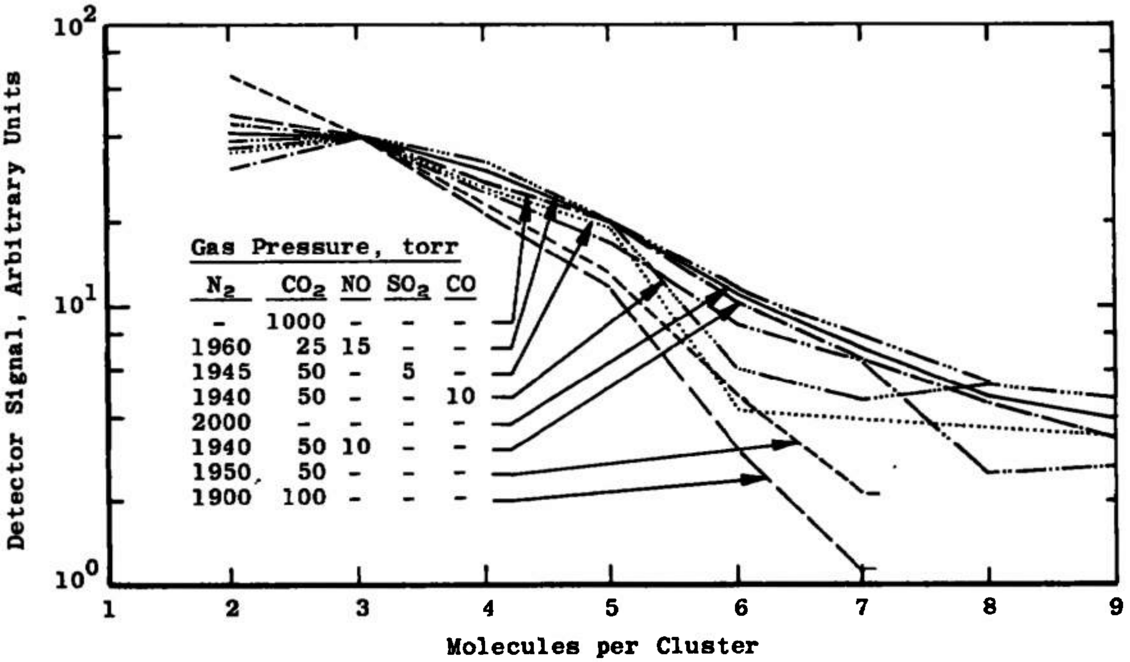


a. $H_2O/N_2/SO_2/NO/CO/CH_4$ mixtures



b. $H_2O/N_2/CO/NO$ mixtures

Figure 8. Effect of trace gases on the nucleation of water in a water/nitrogen expansion.



c. $H_2O/N_2/CO_2/NO/SO_2/CO$ mixtures

Figure 8. Concluded.

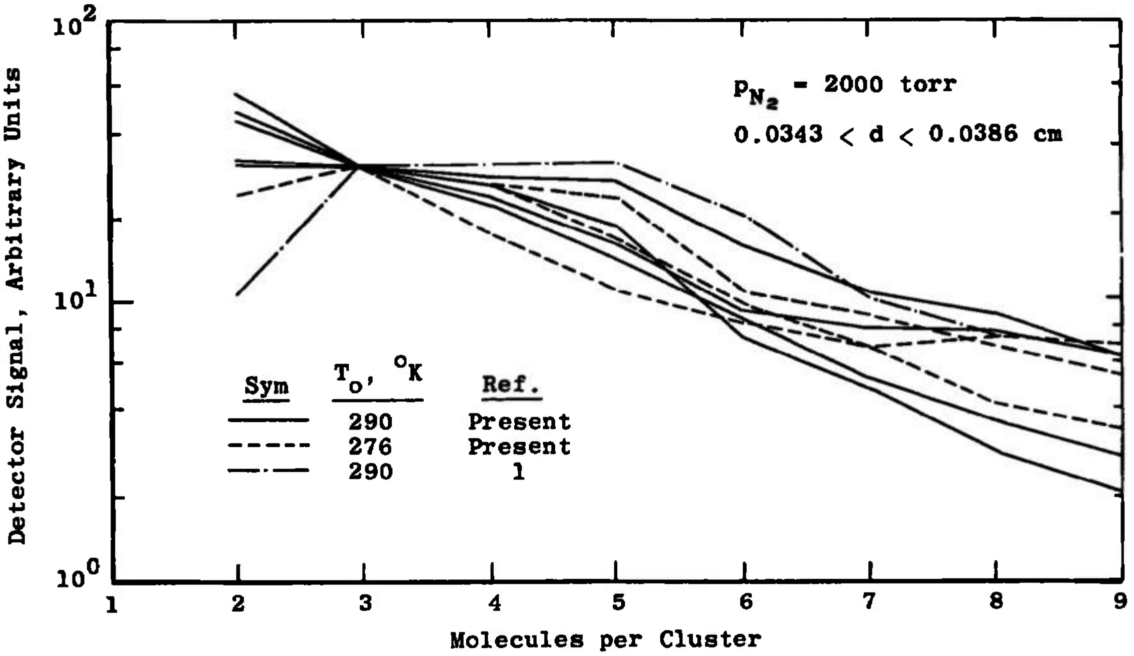


Figure 9. Comparison of water cluster intensity measurements at approximately the same source conditions.

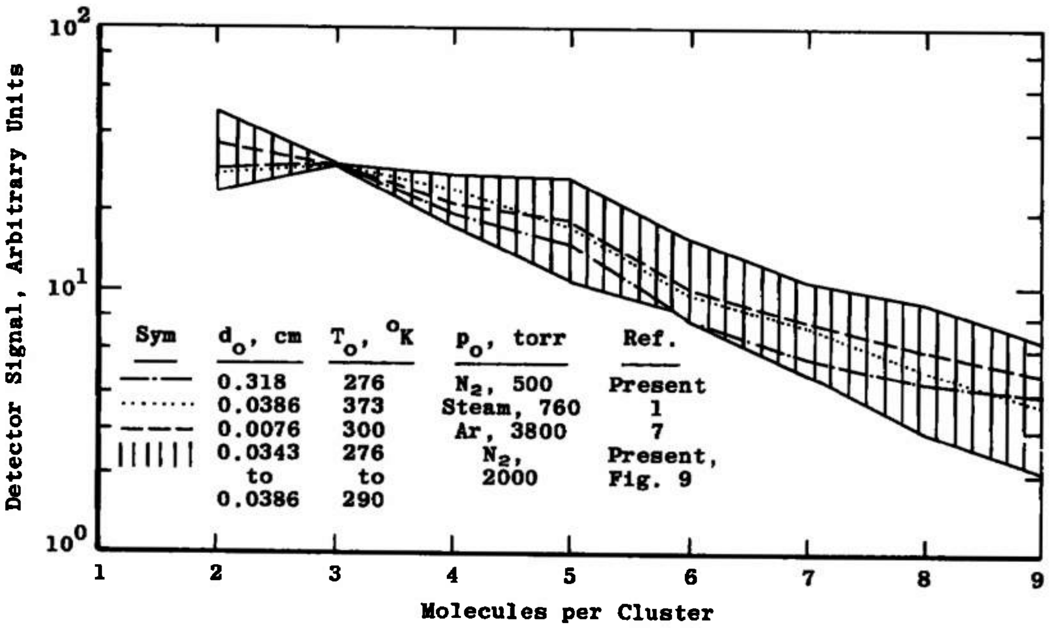


Figure 10. Effect of different source conditions on water cluster intensity.

Milne et al. (Ref. 7, cf. Fig. 10) made their measurements (1) in a molecular beam formed by a nonpumping conical skimmer, (2) with a time-of-flight mass spectrometer, (3) with a different carrier gas, (4) with a smaller orifice, (5) under conditions of massive condensation in the carrier gas (inferred from the source conditions and the results of Ref. 4), and (6) at a lower electron energy level. The source conditions for these expansions (see Fig. 10) are such that extensive clustering has occurred in the carrier gas. This implies that the flow conditions in the expansion should also promote the formation of very large water clusters. Armstrong and Stein (Ref. 8), using electron diffraction techniques, have observed large water clusters consisting of approximately 3000 molecules and having a diamond cubic crystalline structure in the free-jet expansion of steam. This result suggests that a factor common to all the measurements presented in Figs. 9 and 10 is that in the ionizer region of the mass spectrometer a water-crystal beam is crossed with an electron beam, the resulting variation of water cluster intensity with the number of molecules per cluster being representative of the fragmentation of a water crystal on electron impact. Implicit in the foregoing explanation is the assumption that changes in electron energy will change the absolute value of the cluster intensity but not the form of the variation with molecules per cluster. It is suggested that this variation is analogous to the "cracking pattern" (or mass spectrum) that is obtained when a gas molecule is bombarded with electrons.

It has been shown that there is scatter in the measurements of water cluster intensity at the same source conditions (see Fig. 9). This lack of repeatability in mass spectrometric measurements was not observed in earlier measurements with dry gases either at AEDC (Refs. 2 and 3) or elsewhere (Ref. 9). The present lack of repeatability may be indicative of some changes in mass spectrometer sensitivity resulting from the presence of water and, in some instances, weak acidic solutions in the mass spectrometer.

A review of the mass spectra presented in Figs. 7a through l indicates the presence of clusters of the following types: $(N_2)_n^+$, $(SO_2)_n^+$, $(CO_2)_n^+$, $(CH_4)_n^+$, $N_2^+(H_2O)_n$, $SO_2^+(H_2O)_n$, $(SO_2)_2^+(H_2O)_n$, $CO_2^+(H_2O)_n$, $(CO_2)_2(H_2O)_n$, $NO^+(H_2O)_n$, $SO_2^+N_2$, NO^+N_2, NO^+SO_2, $NO^+N_2H_2O$, $NO^+SO_2H_2O$, $NO^+SO_2H_2O$, $(CO_2)_2^+SO_2$, $(CO_2)^+SO_2$, and NO^+CO_2. The intensities of these signals relative to that of the nitrogen monomer are summarized in Table 2.

It is of interest to ascertain the effect of various trace gases upon the nucleation of nitrogen in dry gas mixtures. Changes in the nitrogen nucleation process should be accompanied by changes in the monomer-dimer ratio. For expansions of N_2, N_2/SO_2, N_2/NO, N_2/CO, and N_2/CO_2, it has been found (see Table 2) that the corresponding values of the monomer-dimer ratio were 136, 166, 140, 90, and 634. These measurements indicate that nitrogen dimer formation is inhibited by SO_2 and CO_2, unaffected by NO, and enhanced by CO.

It is important to remember that the ratio of the two masses 28 and 56 are not representative of the $N_2^+/(N_2)_2^+$ ratio since there can be contributions to the mass 28 signal from the presence of CO and CO_2 in the molecular beam.

The effects of NO, SO_2, CO_2, and CO on the nucleation of nitrogen in three component gas mixtures are summarized in Table 3. It can be seen that the effect of the addition of NO, SO_2, and CO to an N_2/CO_2 beam has the same qualitative effect as that observed when these gases were added to nitrogen alone. Similar qualitative effects are observed when these trace gases are added to N_2/SO_2, N_2/NO, and N_2/CO mixtures. Also shown in Table 3 are values of the $N_2^+/(N_2)_2^+$ ratio for the one-, two-, and three-component gas mixtures with the addition of water. The addition of water to these gas mixtures results in a considerable decrease in nitrogen dimer formation.

Table 2. Data Summary

Gas Mixture	Pressure, torr						Signal Ratios																									
	N_2	H_2O	SO_2	NO	CO	CO_2	$N_2/(N_2)_2$	$N_2/H(H_2O)$	N_2/SO_2	N_2/H_2SO_2	$SO_2/(SO_2)_2$	N_2/N_2H_2O	N_2/SO_2H_2O	N_2/NO	$NO/(NO)_2$	$N_2/NO\,N_2$	$N_2/NO\,H_2O$	N_2/CO_2	$CO_2/(CO_2)_2$	N_2/N_2CO_2	N_2/CO_2H_2O	$N_2/(CO_2)_2H_2O$	$N_2/NO\,SO_2$	$N_2/NO\,SO_2H_2O$	N_2/CO_2SO_2	$N_2/NO\,CO_2$	$CO/(CO)_2$	$CO/CO\,H_2O$	$CO/CO\,H_2O$	$CO_2/(CO_2)_2$	$CO_2/CO_2(H_2O)$	$CO_2/H^+(H_2O)$
N_2	2,000						100																									
N_2	2,000						136																									
N_2/H_2O	2,000	17					780	1,100																								
N_2/SO_2	1,990		10				166		30	580	8																					
$N_2/SO_2/H_2O$	1,990	17	10				17,000	7,428	20	25,000	30	25,000	3,870																			
N_2/NO	1,980			20			140							54	40	2,060																
$N_2/NO/H_2O$	1,980	17		20			22,500	2,000				13,500		54	--	6,000	5,000															
$N_2/NO/H_2O$	1,990	17		10			30,000	1,400				>30,000		128	---	9,140	7,500															
N_2/CO	1,980				20		90																									
$N_2/CO/H_2O$	1,980	17			20		1,600	1,360																								
$N_2/CO/H_2O$	1,990	17			10		800	2,220																								
N_2/CO_2	1,900					100	634											5.1	6,6	330												
$N_2/CO_2/H_2O$	1,900	17				100		984										18	23	3,375	1,200	4,900										
$N_2/CO_2/H_2O$	1,950	17				50		761										39	23	---	2,000	17,000										
$N_2/NO/SO_2$	1,985		5	10			155	---	64	570	13.5			80	23	1,150							740									
$N_2/NO/SO_2/H_2O$	1,985	17	5	10			1,600	1,150	47		45	4,000	1,850	84	340	20,000	200						4,500	6,700								
$N_2/CO/SO_2$	1,985		5		10		100		50	600	12																					
$N_2/CO/SO_2/H_2O$	1,985	17	5		10		1,300	1,000	84	9,500	50	16,500	2,800																			
$N_2/CO_2/SO_2$	1,945		5			50	500		47	800	8,5							13	9.0	560					320							
$N_2/CO_2/SO_2/H_2O$	1,945	17	5			50	20,000	250	26	7,500	27	2,100	850					19	600	5,400					6,400							
$N_2/CO/NO$	1,980			10	10		115							120		1,400																
$N_2/CO/NO/H_2O$	1,980	17		15	5		700	2,100				12,000		115		11,500	6,000															
$N_2/CO/NO/H_2O$	1,980	17		10	10		980	2,000				9,700		110		18,000	6,700															
$N_2/NO/CO_2$	1,940			10		50	640							520	16	1,750		12	6.0	530						230						
$N_2/NO/CO_2/H_2O$	1,940	17		10		50	2,500	700				1,850		75			4,500	13	21	1,500	1,100					7,500						
$N_2/NO/CO_2/H_2O$	1,940	17		15		25	1,800	660				4,000		55				26	23		1,900											
$N_2/CO/CO_2$	1,940				10	50	280											11	5	100												
$N_2/CO/CO_2/H_2O$	1,940	17			10	50	2,200	930				13,000						22	29	2,600	13,000											
$N_2/CO/CO_2/H_2O$	1,960	17			15	25	---	730				2,000						21	26		2,700											
CO	2,000																										190					
CO/H_2O	2,000	17																									400	3,000	1,000			
CO_2	1,000																													10		
CO_2/H_2O	1,000	17																												110	380	220

Table 3. Effect of Trace Gases on the Nucleation of Nitrogen

Gas	$N_2/(N_2)_2$	Gas	$N_2/(N_2)_2$	Gas	$N_2/(N_2)_2$	Gas	$N_2/(N_2)_2$
Pure Nitrogen Expansion, $N_2/(N_2)_2$ = 136							
N_2/CO_2	634	N_2/SO_2	166	N_2/NO	140	N_2/CO	80
$N_2/CO_2/NO$	640	$N_2/SO_2/NO$	155	$N_2/NO/SO_2$	155	$N_2/CO/NO$	115
$N_2/CO_2/SO_2$	500	$N_2/SO_2/CO$	100	$N_2/NO/CO$	115	$N_2/CO/SO_2$	100
$N_2/CO_2/CO$	280	$N_2/SO_2/CO_2$	530	$N_2/NO/CO_2$	640	$N_2/CO/CO_2$	280
Nitrogen/Water Expansion, $N_2/(N_2)_2$ = 780							
$N_2/CO_2/H_2O$	---	$N_2/SO_2/H_2O$	17,000	$N_2/NO/H_2O$	22,500	$N_2/CO/H_2O$	1,600
$N_2/CO_2/NO/H_2O$	2,500	$N_2/SO_2/NO/H_2O$	1,600	$N_2/NO/SO_2/H_2O$	1,600	$N_2/CO/NO/H_2O$	980
$N_2/CO_2/SO_2/H_2O$	20,000	$N_2/SO_2/CO/H_2O$	1,300	$N_2/NO/CO/H_2O$	980	$N_2/CO/SO_2/H_2O$	1,300
$N_2/CO_2/CO/H_2O$	2,200	$N_2/SO_2/CO_2/H_2O$	20,000	$N_2/NO/CO_2/H_2O$	2,500	$N_2/CO/CO_2/H_2O$	2,200

There are a number of possible explanations for this reduction in nitrogen dimer formation in mixed gas expansions. The presence of the additives changes the average molecular weight and specific heat ratio of the expanding mixture, resulting in a change in the flow conditions in the expansion. However, the concentrations of the additives are so small that the resultant changes in the pressure-temperature characteristics of the expansion would be expected to be minimal. It has been shown (Ref. 10) that when massive condensation occurs in a free-jet expansion there is a significant increase in the effective stagnation temperature of the gas through the addition of the heat of vaporization to the noncondensed gas. From a consideration of the expansion characteristics of pure nitrogen, it can be shown that the flow conditions are such that the trace gas becomes supersaturated early in the expansion. Recently, Lewis and Williams (Ref. 11) and Lewis et al. (Ref. 12) have made detailed studies of the condensation process in argon and nitrogen free-jet expansions. One of the conclusions drawn from these studies is that the onset of condensation in free-jet expansions occurs at low levels of supersaturation. The saturated vapor characteristics of the trace additives in the present study are such that they will condense earlier in the expansion than does nitrogen. Thus, the heat of vaporization of the trace additives is available to heat the noncondensed nitrogen and thus inhibit the formation of dimers in the nitrogen flow.

Some measurements have been made of the monomer-dimer ratio of CO_2, SO_2, and NO for both wet and dry expansions. (No data could be obtained for CO since it could not be distinguished from N_2.) These monomer-dimer ratios are summarized in Table 4. The values of these ratios for the trace gases in the dry mixtures correspond to the values observed in pure gas expansions where it is considered that massive condensation has occurred (see Refs. 1 and 3). If it is accepted that the value of the monomer-dimer ratio is related to the degree of condensation in the gas, then it can be assumed that massive condensation has occurred in the trace gases. Thus, the heat of vaporization of these gases is available to heat the nitrogen and, as has been stated earlier, inhibit the dimer formation in the nitrogen expansion.

Flow conditions in these expansions are such that water can freeze close to the sonic orifice. Thus, the heat of vaporization of water will be added to the flow upstream of the point in the expansion where any of the trace gases can condense. As was the case for the nucleation of nitrogen, the addition of this heat resulted in a decrease in trace gas nucleation (see Table 4).

Table 4. Nucleation of Trace Gases in Mixed Gas Expansions

Gas	$CO_2/(CO_2)_2$	Gas	$CO_2/(CO_2)_2$	Gas	$NO/(NO_2)_2$
N_2/CO_2	6.6	N_2/SO_2	8.0	N_2/NO	40
$N_2/CO_2/NO$	5.7	$N_2/SO_2/NO$	13.5	$N_2/NO/SO_2$	23
$N_2/CO_2/SO_2$	9.0	$N_2/SO_2/CO$	12.0	$N_2/NO/CO$	---
$N_2/CO_2/CO$	5.4	$N_2/SO_2/CO_2$	8.5	$N_2/NO/CO_2$	16
$N_2/CO_2/H_2O$	23	$N_2/SO_2/H_2O$	30	$N_2/NO/H_2O$	---
$N_2/CO_2/NO/H_2O$	21	$N_2/SO_2/NO/H_2O$	45	$N_2/NO/SO_2/H_2O$	340
$N_2/CO_2/SO_2/H_2O$	600(?)	$N_2/SO_2/CO/H_2O$	50	$N_2/NO/CO/H_2O$	---
$N_2/CO_2/CO/H_2O$	29	$N_2/SO_2/CO_2/H_2O$	27	$N_2/NO/CO_2/H_2O$	---

Wegener (Ref. 13) states that in expanding flows practically all the water vapor initially present in the gas condenses. Wegener observes that (1) the condensate formed in this process is comprised of ice crystals varying in diameter (depending upon source conditions) from 0.04 to 0.12 μ, (2) the crystals are formed in a very small region of the expansion, and (3) after these crystals have been formed in the flow, smaller clusters cannot exist. (This supports the suggestion made earlier that the observed water cluster signals result primarily from fragmentation of crystals in the ionizer section as a result of electron impact.) The above results have been obtained from experiments in nozzles where the typical time of flight of a sample volume from the location of saturation to the onset of measurable condensation ranges from 10 to 50 μsec. Wegener considers that this is too short a time for there to be any buildup of appreciable amounts of condensate by heterogeneous nucleation, even though there may be large concentrations of foreign nuclei. Buckle and Pouring (Ref. 14) confirmed this hypothesis when they found that the addition of significant quantities of silver iodide particles (ranging in size from 0.1 to 1.0 μ) had no discernible effect upon the condensation process.

A characteristic of expansions from sonic orifices is that the time of flight of a sample volume from saturation to the onset of measurable condensation is considerably less than that for expansions from the nozzles discussed by Wegener (Ref. 13). Thus, heterogeneous condensation on foreign nuclei in a free-jet expansion is not likely to be significant. Daum and Gyarmathy (Ref. 15) have also shown that heterogeneous condensation is not detectable in flows with high rates of expansion. It is for this reason that the water, CO_2, SO_2, CO, and NO clusters present in a nitrogen expansion do not increase the degree of nucleation of nitrogen.

Fricke et al. (Ref. 16) have made measurements of ion phase signals in a series of water vapor free-jet expansions. In a modulated molecular beam, it can be shown that the phase of the ion signal consists of two parts because of the flight of the neutral particles from the beam modulator to the ionizing region of the mass spectrometer, and the flight of the ionized particle in the mass spectrometer filter section. The phase of the ion signals was obtained for a series of water vapor pressures ranging from 20 to 370 torr. Fricke et al. (Ref. 16) found that with increasing source pressure the ion signals contained increasingly large contributions from the dissociative ionization of larger clusters and that the phase lag of these signals increased. This indicates that the speed of these large clusters decreases with increasing source pressure. Fricke et al. (Ref. 16) have taken this continuing change in phase with increasing source pressure to indicate that "the free-jet expansion is far from being fully developed." It is suggested that these results can be taken to support earlier suggestions that large crystals are formed in the expansion. There is experimental evidence (Refs. 3 and 10) which indicates that large clusters formed in free-jet expansions of argon and nitrogen travel at significantly slower speeds than the noncondensed portion of the flow.

In the formation of the mixed clusters $CO_2^+(H_2)$, $SO_2^+(H_2O)$, and $NO^+(H_2O)$ (see Table 5) the experimental data is too limited to draw any quantitative conclusions. However, the intensity of the $CO_2^+(H_2O)$ and $NO^+(H_2O)$ clusters appears to be independent of other trace gases, whereas the $SO_2^+ H_2O$ cluster intensity is dependent upon the presence of other trace gases.

Table 5. Effect of Additives on Mixed Cluster Formation

Gas	N_2/CO_2 H_2O	Gas	N_2/SO_2 H_2O	Gas	N_2/NO H_2O
$N_2/CO_2/H_2O$	2000	$N_2/SO_2/H_2O$	3870	$N_2/NO/H_2O$	7500
$N_2/CO_2/NO/H_2O$	1100	$N_2/SO_2/NO/H_2O$	1850	$N_2/NO/CO/H_2O$	6700
$N_2/CO_2/SO_2/H_2O$	---	$N_2/SO_2/CO/H_2O$	2800	$N_2/NO/CO_2/H_2O$	4500
$N_2/CO_2/CO/H_2O$	1300	$N_2/SO_2/CO_2/H_2O$	850	$N_2/NO/SO_2/H_2O$	---

Attempts have been made to measure the intensity of clusters of the following types: $NO^+ SO_2 (H_2O)_n$, $CO_2^+ SO_2 (H_2O)_n$, $CO^+ SO_2 (H_2O)_n$, $NO^+ CO (H_2O)_n$, $NO^+ CO_2 (H_2O)_n$, and $CO^+ CO_2 (H_2O)_n$. A trace of one of these clusters, $NO^+ SO_2 (H_2O)$, was observed. It has been shown that the formation of nitrogen dimers in a free-jet expansion is considerably reduced by the presence of small quantities of water in that expansion. It is considered that clustering of the trace additives will be affected in a like manner. This factor, together with the small quantities of additives present in the mixture, has evidently resulted in either the non-formation of hydrated mixed clusters or signal levels so low that they are beyond the range of the present system. The fact that one such mixed cluster (i.e., $NO^+ SO_2 (H_2O)$) has been observed suggests that the second possibility mentioned above may be correct.

On the basis of the present experimental study, there is evidence to suggest that massive condensation occurs in the carrier gas, the water vapor, and the trace gases. However, under these test conditions, the formation of mixed gas/water clusters has been insufficient to make studies of the nucleation characteristics of such clusters. On the basis of the present results and those obtained elsewhere (Refs. 6, 7, 8, 13, and 16), it can be assumed with some certainty that ice crystals are formed in these expansions. These crystals are of such a size (see Refs. 8, 13, and 16) that they travel at the speed and temperature at which they were formed. Prior to any condensation in the trace or carrier gases, the individual gas molecules reflect the temperature existing at each point in the expanding flow. In the mixed gas expansions, cold gas molecules will impinge on relatively warm ice crystals. Under these conditions, it is unlikely that the cold molecule will be absorbed by the warm surface and form a mixed cluster. It is suggested that in expansions of this kind there are very few noncondensed water monomers available for the formation of mixed clusters. This fact is illustrated by the fact that the ratios N_2/CO_2 H_2O and N_2/NO SO_2 H_2O are approximately 10^3 and 7×10^3, respectively. As noted earlier (i.e., in Ref. 3), the dynamic range of the present mass spectrometer system is limited to approximately 10^4 as a result of metastables formed in the ionizer section impinging on the first dynode of the multiplier. Thus, this lack of dynamic range, coupled with very low signal levels for the mixed clusters, has resulted in an inability to obtain sufficient mixed cluster data from which cluster kinetics data may be derived.

An attempt was made to determine whether ionization of the gas mixtures before expansion affected the degree of condensation in the subsequent expansion. It was found that a satisfactory corona discharge could be maintained in an N_2/H_2O expansion from a 0.318-cm-diam orifice. The water cluster spectra obtained with no ionization is shown in Fig. 10. The effect of ionization was to reduce the intensity of monomer signal by approximately 50 percent; there was no discernible effect upon the intensity of the larger clusters. On the basis of these measurements, it appears that for these source flow conditions, ionization does not have a significant effect upon condensation. This is not an unexpected result if it can be assumed that in the nonionized expansion the bulk of the water vapor is condensed (see Ref. 13). It is possible that ionization can affect the rate at which condensation takes place, but it is unlikely that it can have a significant effect upon the total quantity condensed.

Three sulfuric acid expansions were mass analyzed: (1) air at 730 torr bubbled through a 2-percent solution by volume of H_2SO_4, (2) air at 730 torr bubbled through a 10-percent solution of H_2SO_4, and (3) nitrogen at 700 torr bubbled through a 10-percent solution of H_2SO_4. A considerable effort was directed toward detecting the presence of sulfate ions and their fragments. If such ions or ion fragments are present in these expansions, they exist at levels beyond the range of detectability of the mass spectrometer.

4.0 CONCLUSIONS AND RECOMMENDATIONS

In the free-jet expansions of various gas mixtures, clusters of the following types have been observed: $(N_2)_n^+$, $(NO)_n^+$, $(CO_2)_n^+$, $(SO_2)_n^+$, $(CH_4)_n^+$, $N_2^+(H_2O)_n$, $NO^+(H_2O)_n$, $SO_2^+(H_2O)_n$, $(SO_2)_2^+(H_2O)_n$, $CO_2^+(H_2O)_n$, $(CO_2)_2^+(H_2O)_n$, $SO_2^+N_2$, NO^+N_2, NO^+SO_2, $NO^+N_2H_2O$, $NO^+SO_2H_2O$, $CO_2^+SO^2$, $(CO_2)_2^+SO^2$, and NO^+CO^2. These measurements demonstrated that it was possible to form the mixed clusters of interest in a free-jet expansion.

The existing mass spectrometer configuration is such that a modulated background signal derived from metastables formed in the ionizer section effectively restricts the dynamic range of the system to 10^4.

A corona discharge initiated upstream of the sonic orifice introduced into the flow a copious supply of ions which had little or no effect upon the nucleation of water in an N_2/H_2O expansion. Presumably, the reason for this is that the bulk of the water vapor was already being condensed in the absence of the ions.

Expansions of $N_2/H_2 SO_4$ and $Ar/H_2 SO_4$ were analyzed, and no sulfates were detected. Either sulfates were not formed, or the signals were too small to be detected.

When the objective of an investigation is to obtain information concerning the kinetics of cluster formation, it is necessary to determine whether a particular ion signal derives from a singly ionized particle of that mass number or is an ionized fragment of a larger cluster. In order to determine the relative magnitudes of the primary and fragment ions, it is necessary to measure the velocity and intensity of these ion signals.

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