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MASS SPECTROMETRIC SAMPLING OF THE FREE-JET EXPANSIONS OF GAS MIXTURES

A. B. Bailey

ARO, Inc.

June 1973

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FOREWORD

The research reported herein was conducted by the Arnold Engineering Development Center (AEDC) under sponsorship of 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. This work was conducted from February 3, 1971, to May 5, 1972, under ARO Project Nos. VW5224 and VF224. The manuscript was submitted for publication on March 19, 1973.

This technical report has been reviewed and is approved.

EULES L. HIVELY Research & Development Division Directorate of Technology	ROBERT O. DIETZ Director of Technology

ABSTRACT

To achieve a better understanding of the composition of the upper atmosphere, it is necessary to obtain more information on the reaction kinetics of cluster ions. The purpose of the present investigation has been to determine the feasibility of producing mixed molecular clusters in the free-jet expansions of a variety of gas mixtures. Mass spectra have been obtained from cluster beams formed by the expansions of water vapor, steam, sulfur dioxide, nitric oxide, water/sulfur dioxide, water/nitric oxide, water/sulfur dioxide/nitrogen, water/sulfur dioxide/Argon, and water/sulfur dioxide/nitric oxide. Cluster ions of the following types have been 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 $AR(SO_2)n$.

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SECTION I
INTRODUCTION

Data obtained from upper atmospheric sampling probes suggest that clusters of water and sulfur dioxide may be quite stable and long-lived. It is possible that such clusters detected in the stratosphere may have had their origin at ground level, arising from the combustion of automobile emissions and fuels of high sulfur content. To further the understanding of the composition of the upper atmosphere, additional information concerning the reaction kinetics of mixed clusters of this type is required. It has been suggested that it may be possible to obtain this information by studying the kinetics of mixed clusters formed in the expansion of various gas mixtures.

Aerodynamic molecular beams have been used to study condensation phenomena in free-jet expansions (e.g., Ref. 1). In the present investigation, free-jet expansions of water vapor (H_2O) with the addition of nitrogen (N_2), argon (Ar), nitric oxide (NO), and sulfur dioxide (SO_2) will be mass-analyzed with an Electronics Associates, Inc. (EAI) quadrupole mass spectrometer. The basic purpose of this investigation is to determine whether mixed clusters can be formed in free-jet expansions. This particular research is planned as the initiation of a continuing research program at Air Force Cambridge Research Laboratories (AFCRL) to investigate the reaction kinetics of mixed clusters.

SECTION II
APPARATUS

A complete description of the Aerodynamic Molecular Beam Chamber (Fig. 1, Appendix) and the associated beam detection systems is given in Ref. 1.

A schematic of the molecular beam source is shown in Fig. 2. The test gas flows through the center tube, which vents into a settling chamber prior to passing through the orifice. The heating (or cooling) fluid is passed through two tubes concentric with the gas supply tube. The source tube is over 1 m long; this length, together with the settling chamber, should give the test gas sufficient time to accommodate to the temperature of the circulating fluid. Source gas temperature is measured with a copper-constantan thermocouple located at the upstream end of the settling chamber. Source gas temperatures can be controlled over the range from 280 to 500°K by passing gaseous nitrogen through a resistance-heated stainless steel tube and then through the annular passages indicated in Fig. 2. The source orifices have been cut in 0.0127-cm-thick stainless steel using an Elox® process. This study has utilized two orifices having diameters of 0.0386 and 0.1245 cm.

A schematic of the gas inlet system used to produce the mixtures of water and the gases of interest is shown in Fig. 3. The temperature of the water boiler was thermostatically controlled and could be maintained at any preselected temperature between 300 and 373°K. Care was taken to ensure that the temperature of the gas delivery line from the boiler was kept at the same temperature as that of the boiler to prevent any condensation of the supply mixture in this line.

A cryogenically cooled (cooled by gaseous helium at approximately 20°K) plate with a centrally located 0.6-cm-diam orifice skimmed the central core from the free-jet expansion from the sonic orifice. Collimation of this beam prior to its entry into the test chamber was achieved with a 0.4-cm-diam orifice in a similar cryogenically cooled plate. Extensive studies of the forming of molecular beams (see Ref. 2) have indicated that cryopumping skimmers and collimators are necessary in order to produce an undisturbed gas sample in the test chamber. Total beam intensity was measured with a miniature ionization gage positioned on the beam centerline. A description of the modulated beam detection system used to measure specie concentration in the molecular beam is given in Ref. 3. It consists of (1) a mechanical beam chopper, (2) an EAI quadrupole mass spectrometer (range from 2 to 600 atomic mass units, AMU), and (3) a lock-in (narrow bandpass) amplifier. The chopped molecular beam enters the ionization chamber of the mass spectrometer. Ionized molecules are drawn into the quadrupole section, which is tuned to a particular mass number. The resulting ion current is amplified by an electron multiplier, which sends a pulsed signal to the lock-in amplifier, which acts as a bandpass amplifier centered on the chopper frequency. A light and a photocell detector, mounted at the chopper wheel, provide the chopping frequency to the amplifier and keep it synchronized with the actual molecular beam modulation frequency. The lock-in amplifier increases the signal-to-noise ratio by amplifying only those signals having the proper frequency and phase with respect to the reference signal from the photocell. This amplified signal, recorded on a voltmeter, is a measure of the intensity of the mass number under investigation.

Two mass spectrometers were located in the test chamber in such a way that the quadrupole section of one was parallel to the molecular beam (end-on) and that of the other was normal to the molecular beam (side-on).

SECTION III
DISCUSSION OF EXPERIMENTAL RESULTS

3.1 BEAM INTENSITY MEASUREMENTS

Prior to condensation, a molecular beam formed by skimming from the free-jet expansion of a gas is essentially a monomer beam. With the onset of condensation, polymers, liquid droplets, and crystals are formed in the expanding flow. Mass spectrometric measurements of the polymer intensity for an argon beam have been compared with an electron diffraction analysis of a similar argon beam (Ref. 2). As a result of this comparison, it has been concluded that the characteristic maximum that occurs in the variation of dimer intensity with source pressure is indicative of massive condensation (i.e., presence of microdroplets or crystals in the beam).

In the present investigation mass spectra have been obtained from expansions of H_2O, N_2, Ar, NO, SO_2, and mixtures thereof. To determine the effect of water upon the condensation characteristics of a pure gas, pure argon and water/argon mixtures have been analyzed (Fig. 4). The presence of water in an argon expansion has a pronounced effect upon the argon monomer/dimer ratios at high source pressures. The argon monomer beam intensity is significantly reduced, whereas the dimer beam intensity is greater than that for the pure gas for source pressures (p_o) greater than approximately 1500 torr. This indicates that a small quantity of water can significantly affect the nucleation processes in an argon free-jet expansion. The ratio of the partial pressure of water/argon changes from 100 to 0.1 percent as the total pressure changes from 17 to 1.7×10^4 torr.

Also shown in Fig. 4 is the variation of the water monomer intensity as a function of source total pressure. For $p_o < 60$ torr the water monomer intensity is essentially constant. For $60 \lesssim p_o \lesssim 200$ torr, the monomer intensity decreases with increasing source pressure. Finally, for $p_o > 200$ torr the monomer intensity increases with increasing source pressure. The initial decrease in the water monomer intensity is an indication of the occurrence of condensation in the water expansion. A similar variation has been observed by Milne et al. (Ref. 4). They have suggested, on the basis of their time-of-flight mass spectrometric analyses, that the increasing intensity of the 18^+ signal results from the complex dissociative ionization of water clusters involving the loss of one or more water molecules. This factor should be borne in mind because in subsequent discussion of mass spectra the total pressure of the water/gas mixtures is of such a magnitude that the water monomer and cluster signals may contain significant contributions from dissociative ionization of heavier polymers. Fricke et al. (Ref. 5) have observed similar dissociative ionization effects in their mass and phase spectrometry observations of a pure water vapor jet.

To provide an indication of the degree of condensation existing in the gases under investigation, mass spectrometric measurements of the monomer and dimer beam intensity for sulfur dioxide and nitric oxide were made and are presented in Fig. 5. For an orifice diameter of 0.0386 cm and a gas temperature of approximately 290°K it is reasonable to assume that no significant nucleation occurs in sulfur dioxide and nitric oxide for source pressures less than 50 and 300 torr, respectively. Unfortunately, it was not possible in the present investigation to obtain data for SO_2/Ar and NO/Ar similar to those obtained for H_2O/Ar (cf. Fig. 4). Thus, the direct effect of a high-pressure carrier gas upon the nucleation characteristics of the gas under investigation is not available.

3.2 MODULATED BEAM MASS SPECTRA OBSERVATIONS

3.2.1 Sulfur Dioxide

These (and subsequently discussed) mass spectra have been obtained by manually scanning the mass range for each of the test conditions and recording the voltmeter signal at each mass number of interest. In this manner an accurate measure of the intensity at each mass was obtained. However, no attempt was made to determine the shape of the mass signal. In some of the data this lack of definition of the shape of the mass signal has resulted in some uncertainty as to the correct interpretation of the signal. However, since the primary purpose of the present investigation was exploratory, a more complete study should resolve problems of this type.

Sulfur dioxide mass spectra for source pressures of 20, 100, 300, and 800 torr are shown in Fig. 6. It has been stated in the previous section that for $p_o < 50$ torr no significant nucleation will have occurred in the sulfur dioxide beam. Thus, it is reasonable to assume that the mass spectra obtained for $p_o = 20$ torr (Fig. 6) represents the cracking pattern of SO_2 in the mass spectrometer. The ratios of the masses 32/34, 48/50, and 64/66 are in reasonable agreement with the ratio of S_{32} to S_{34}, the two major naturally occurring isotopes of sulfur. Thus, it is reasonable to assign S^+, SO^+, and SO_2^+ to mass numbers of 32, 48, and 64. A mass number of 16 has been assigned to O^+ and S^{++}, and 24 has been assigned to SO^{++}. Thus, the electron impact process results in the production of fragment ions as a result of the removal of one or both of the oxygen atoms. At 100 torr some nucleation would be expected in the beam. The mass spectra obtained at this pressure demonstrate the presence of the cluster ion $(SO_2)_2^+$ and the cluster fragment $SO^+(SO_2)$. At 300 torr considerable nucleation will have occurred in the flow, and cluster and cluster fragment ions of the forms $(SO_2)_n^+$, $(S_nO_{2n-1})^+$, and $(S_nO_{2n-2})^+$ are present in significant concentrations. At 800 torr the cluster and cluster fragment ion intensity has decreased relative to SO_2 concentrations. Presumably, at higher source pressures the cluster and cluster fragment ion intensities may increase again as a result of the dissociative ionization process that Milne et al. (Ref. 4) have observed in water expansions.

Cuthbert et al. (Ref. 6) have obtained mass spectra for an SO_2 expansion from a 0.00254-cm-diam orifice at room temperature and a pressure of 2320 torr. They observed the cluster and cluster fragment ions $(SO_2)_n^+$ and $(S_nO_{2n-1})^+$. They also observed a weak signal for a mass of 96 (Ref. 6) and erroneously identified it as SO_3^+ instead of $S^+(SO_2)$. Furthermore, they observed cluster ions of the type $[(SO_3)(SO_2)_{n-1}]^+$ formed from SO_3, which was apparently present in their gas sample. This SO_3 series was a factor of 10^3 less than the SO_2 signal. At 300 torr in the present investigation the smallest detectable signal was a factor of 10^4 less than the SO_2 signal. If SO_3 was present in the present series of tests, it was at much lower concentration than was evidently the case for Cuthbert et al. (Ref. 6).

The present investigation utilized commercial-grade sulfur dioxide of the following composition:

Component	Specification, by Weight
Sulfur dioxide	99.9 percent, minimum
Moisture	100 ppm, maximum
Nonvolatiles	50 ppm, maximum
Acidity (as H_2SO_4)	10 ppm, maximum

The maximum water content is a factor of 10^4 less than that of sulfur dioxide. This represents the smallest concentration that could be observed with the present system (based on the 300-torr data of Fig. 6). The fact that no water was observed suggests that for this gas sample the water content may be less than 100 ppm.

The maximum sulfuric acid content is a factor of 10^5 less than that of sulfur dioxide. The ion SO_4^+ formed by electron impact from H_2SO_4 would be expected to be on the order of 10^5 less than the intensity of the ion SO_2^+ and as such could not be detected with the existing instrumentation. Therefore, it seems more reasonable to conclude that a mass of 96 represents the fragment $S^+(SO_2)$ rather than SO_4^+.

The spectra obtained with the quadrupole section of the mass spectrometer normal and parallel to the beam (side-on and end-on, respectively) are compared in Fig. 7. The test conditions for this comparison were such that microdroplets or crystals were present in the molecular beam. For the end-on mode of operation it is possible that these large neutral clusters could become fragmented when they impinge on the fine wire grid at the entrance to the ionizer section of the mass spectrometer and could affect the observed spectra. It appears from this comparison (Fig. 7) that the mode of operation of the mass spectrometer has no significant effect upon the observed spectra. Other spectra obtained for significantly different test conditions also support this conclusion for sulfur dioxide.

3.2.2 Nitric Oxide

The nitric oxide used in the present investigation has the following typical analysis:

Component	Mole, percentage
Nitric Oxide (NO)	99.2
Carbon Dioxide (CO_2)	0.2
Nitrogen (N_2)	0.5
Nitrous Oxide (N_2O)	0.05
Nitrogen Dioxide (NO_2)	0.05

Mass spectra for nitric oxide expansions have been obtained for several beam and mass spectrometer configurations. The spectra obtained for conditions where there is a small degree of clustering in the expansion are shown in Fig. 8a. For a source pressure of 200 torr the ratios of N_2/NO and CO_2/NO are in reasonable agreement with the above analysis. No mass of 46 (possible NO_2) was observed at this pressure, whereas at 800 torr it was detected. The density ratio of mass 44/mass 46 molecules was approximately 10, whereas the above analysis indicates that this ratio should be less than a factor of 5 if the mass 46 is that attributable to NO_2. A possible alternative designation for the mass of 46 is $O^+(NO)$, which represents a fragment of the observed dimer $[(NO)_2^+]$ ion. Mass spectra are compared for the end-on and side-on modes of mass spectrometer operation (Fig. 8b) for conditions where significant clustering occurs in the beam. As has been observed earlier in the sulfur dioxide analysis, the observed mass spectra do not seem to be significantly affected by the mode of operation of the mass spectrometer. These spectra were obtained with the mass spectrometer set on the medium mass range scale (i.e., amu $\lesssim$ 150).

At these source conditions the largest detectable mass is 106. On the basis of the above fragmentation hypothesis this mass would be considered a fragment of the tetramer (i.e., $O^+(NO)_3$). Since for two independent analyses of this expansion no tetramers were observed, it seems reasonable to conclude that fragment ions of the type $(N_{n-1}O_n)^+$ do not occur at detectable levels. Therefore, mass numbers of 46, 76, 106, etc. indicate the presence of the mixed cluster series $NO_2^+(NO)$. Thus, the mass of 46 observed at 800 torr (Fig. 8a) probably results from the naturally occurring NO_2 in the nitric oxide sample. Mass spectra (obtained with a different skimmer and chopper configuration) shown in Fig. 8c indicate the presence of the cluster series $(NO)_n$ and $NO_2(NO)_{n-1}$. A peculiarity of this data is the fact that no signals were observed at masses of 270 and 300, $(NO)_9^+$ and $(NO)_{10}^+$, respectively. The fact that clusters $NO_2^+(NO)_8$, $NO_2^+(NO)_9$, and NO_{11} were observed suggests that in the manual scan of the mass range, signals at masses of 270 and 300 were overlooked.

3.2.3 Water and Water/Nitrogen Expansions

Mass spectra for water vapor expansions have been obtained for a variety of test conditions. The mass spectra for a water vapor expansion from a 0.0386-cm-diam orifice at a temperature and pressure of 290°K and 17 torr, respectively, is shown in Fig. 9a. Ionization by electron impact of a single water molecule produces the ions O^+, OH^+, H_2O^+, and $H_2O^{18^+}$. The ion $H^+(H_2O)$ has been formed by the removal of OH from the neutral water dimer $(H_2O)_2$. The dimer concentration in this expansion is approximately 10^{-1}, as compared to a value of 2×10^{-5} obtained by Leckenby et al. (Ref. 7) in expanding water vapor through a 0.002-cm-diam orifice. Changes in the diameter of the sonic orifice result in different rates of flow expansion, which in turn affect the nucleation process in a free-jet expansion (i.e., the smaller the orifice, the more rapid the expansion,which results in a lesser degree of nucleation). This seems to be a reasonable explanation for the difference in dimer concentration observed in the present investigation and that of Leckenby et al. (Ref. 7). Mass spectra (Fig. 9b) obtained for a 0.1245-cm-diam orifice provide additional support for this explanation in that, as a result of an increase of orifice diameter from 0.0386 to 0.1245 cm, the largest observable cluster has increased from a dimer to a pentamer. Milne et al. (Ref. 4) have shown that nucleation of water vapor can be considerably enhanced by passing a high-pressure gas through liquid water (Fig. 10). A similar enhancement (Figs. 9a and b) has been observed in the present investigation. For small water clusters (i.e., dimer, trimer, and tetramer), the present measurements of cluster intensity as a function of mass (Fig. 11) show a significantly different form from that of Milne et al (Ref. 4). In the present investigation the molecular beam was formed with a 20°K cryopumping skimmer and collimator whereas the Milne et al. beam (Ref. 4) was formed with a 300°K conical skimmer and collimator. It has been shown (Ref. 2) that when large condensed clusters strike a warm conical skimmer the resulting debris (predominantly monomers) acts as an effective scatterer of the lighter molecules in the incident beam. However, the Milne et al. results (Ref. 4) indicate that the light specie $H^+(H_2O)$ is relatively more abundant than is indicated by the present investigation. A possible contribution to the signals at a mass of 19 could derive from doubly ionized argon, Ar^{++}. Studies at the Arnold Engineering Development Center (AEDC) have indicated that for some modes of mass spectrometer operation the ratio Ar^{++}/Ar^+ can approach 0.1. Thus, for source flow conditions where the ratio $H^+(H_2O)/Ar^+ << 0.1$ it is possible that a mass 19 signal could contain a contribution from Ar^{++}. Furthermore, low level signals of $H^+(H_2O)_2$ could be affected by contributions from the naturally occurring isotope of argon, since the ratio of $Ar_{36}{}^+/Ar_{40}$ is 3.4×10^{-3}.

The cluster intensity measurements presented in Fig. 11 have been plotted such that the trimer intensity is approximately the same for each of the spectra being considered. Curves 2, 3, and 4 have been derived from Figs. 9a and b and show directly the increased water clustering that occurs with the use of a carrier gas. Reviewing the data obtained with the carrier gases, it is apparent that it can be split into two categories, (1) cluster intensity approximately constant with increasing mass, curves 2 and 5, and (2) cluster intensity decreasing with increasing mass, curves 1, 4, and 6. Curves 5 and 6 were obtained with the mass spectrometer end-on and side-on, respectively. Thus, the mode of operation of the mass spectrometer does have an effect on the water-cluster intensity measurements. Mass spectra obtained for a free-jet expansion of steam for both modes of mass spectrometer operation are shown in Fig. 12. For the room-temperature water vapor expansion, the cluster intensity was essentially constant with increasing mass for the end-on mode (Fig. 11), whereas for steam this type of variation is observed for the side-on mode (Fig. 12). In light of these experimental data, caution should be exercised in attempts to interpret water-cluster intensity measurements.

Steam spectra obtained using the low and high ranges of the mass spectrometer are shown in Fig. 13a. These spectra indicate a rather sudden decrease in intensity for the $H^+(H_2O)_{13}$ cluster and subsequent larger clusters. At first it was thought that this decrease in cluster intensity resulted from a change in the electron multiplier sensitivity. These test conditions were repeated at a later time, and the spectra obtained are shown in Fig. 13b. It can be seen that the variation of cluster intensity with cluster size is almost identical to that obtained earlier (Fig. 13a), the only difference being that the decrease in cluster intensity occurs for the 14th rather than the 13th cluster ion.

Leckenby et al. (Ref. 8) have obtained mass spectra for superheated steam. Their values of cluster intensity are compared with those of the present investigation and those of Ref. 4 (see Fig. 14). In this comparison the data have been arbitrarily matched in such a way that the pentamer intensities are the same. As a result of this matching it can be seen that there is a similarity of variation of cluster intensity with increasing cluster size for the various test conditions. This is an interesting result since these data have been obtained with three different types of mass spectrometer, namely, magnetic sector, time-of-flight, and quadrupole. Steam expansions have been examined with high-energy electron diffraction techniques (Ref. 9). It has been determined that clusters containing approximately 3000 molecules are present in expansions of this type. It is possible that clusters of this type also exist in the lower-temperature water vapor expansions shown in Fig. 14. When a large cluster impinges on a warm surface, the resulting debris is almost entirely composed of monomers and small polymers (Ref. 1). Thus, the differences in cluster intensity for the small clusters in the steam expansions (Fig. 14) may result from the interaction of these large clusters with some components of the beam-forming and detection systems.

3.2.4 Water/Nitric Oxide/Sulfur Dioxide Mixtures

Sulfur dioxide at a pressure of 300 torr passed through room-temperature water and subsequently expanded through a 0.0386-cm-diam orifice produces the mass spectra shown in Fig. 15. As has been shown earlier (cf. Figs. 5a and 6), at this source pressure there is significant nucleation of the SO_2, and the observed mass spectra contain a large number of cluster fragments (e.g., SO^+, S^+, $S^+(SO_2)$, etc). A comparison of the water-cluster distribution for 25 torr $< p_{SO_2} <$ 300 torr indicates that increasing the SO_2 pressure does not significantly affect the degree of water nucleation. Weak signals indicating the presence of mixed water-sulfur dioxide clusters have been observed (i.e., $SO_2(H_2O)$ and $(SO_2)_2H_2O$). The mass 80 signal has been designated as SO_3^+. When SO_2 is passed through room-temperature water, a weak sulfurous acid solution (H_2SO_3 or SO_2H_2O) is formed which may give rise to the SO_3 signal since it is not present in a pure SO_2 expansion at 300 torr. Increasing the water temperature and pressure and reducing the SO_2 pressure results in the mass spectra shown in Fig. 15c. Considerable nucleation has occurred in the steam, and strong water-cluster signals are observed to a mass of 145 (i.e., $H^+(H_2O)_8$). However, SO_2 nucleation, if it exists at all, has been reduced to an undetectably low level. An SO_3^+ signal was observed, whereas an $SO_2^+(N_2O)$ signal was not observed. No particular significance should be attached to the lack of $SO_2^+(H_2O)$ signal since this may have been overlooked in the manual scan of the mass range.

It has been shown in Figs. 5a and b that for source pressures less than 20 torr there is no detectable nucleation in a pure SO_2 expansion. The mass spectra obtained for a water/nitrogen expansion are shown in Fig. 16a to provide a base line for comparison with the subsequently discussed mixed gas expansions. An expansion of a water/sulfur dioxide/nitrogen mixture produces the spectra shown in Figs. 16b and c. Of interest is the presence of signals at masses of 112, 127 and 145. The mass of 112 is of prime interest since it can be assigned to the cluster fragment $SO^+(SO_2)$, which derives from the dimer $(SO_2)_2$, which has a mass of 128. From a consideration of the pure sulfur dioxide mass spectra (cf. Fig. 6), the ratio of $SO^+(SO_2)/(SO_2)_2^+ \lesssim 0.1$. If it is assumed that this ratio applies to the present mixed-gas expansion, this implies that the $(SO_2)_2^+$ and $H^+(H_2O)_7$ signals would be of comparable magnitude, and as such it would be difficult to distinguish between them. A similar observation can be made with regard to the observed mass of 145, which can represent contributions from the $H^+(H_2O)_8$ and $(SO_2)_2^+(H_2O)$ ions having masses of 145 and 146, respectively.

Resolution problems of this type are common to most mass spectrometric studies where instrument performance compromises have to be made by trading mass resolution for sensitivity. For example, (1) the Bendix time-of-flight mass spectrometer used by Milne et al. (Ref. 4) to analyze a water/argon expansion was apparently unable to distinguish between $(Ar)_5^+$ and $H(H_2O)_{11}$ (masses of 200 and 199, respectively), and (2) some rocket-borne mass spectrometer studies (e.g., Ref. 10) have mass uncertainties of ±1 amu at mass numbers of approximately 100.

A nitric oxide/water mixture on expansion produces a mass spectra of the type shown in Fig. 16d. It can be seen that the mixed water/nitric oxide series $NO^+(H_2O)_n$ is readily identified.

The mass spectra obtained using argon instead of nitrogen is shown in Fig. 16e. Argon appears to form mixed clusters very readily, and the following were observed, i.e., $Ar^+(H_2O)_n$ and $Ar^+(SO_2)_n$. The mass spectra obtained with a nitric oxide/water/sulfur dioxide expansion is shown in Fig. 16f. The following mixed clusters can be identified: $NO^+(H_2O)_n$, $SO_2^+(H_2O)_n$, $(SO_2)^+(H_2O)_n$, $NO^+(SO_2)_n$, and $NO^+SO_2(H_2O)_n$. There are, as has been shown earlier, difficulties in resolving between two ion signals of comparable magnitude. Because spectra have been obtained for the individual components of the various mixtures tested, it is possible to make reasonably reliable estimates of the ions that are contributing to those signals which are thought to be averages of contributions from several mass numbers.

3.3 PROBLEMS ASSOCIATED WITH OBTAINING MASS SPECTRA FROM CLUSTER BEAMS

One of the stated objectives of the present work was to determine whether mixed clusters of water, sulfur dioxide, and nitric oxide could be formed. From the foregoing discussion it is evident that such clusters can be formed. As a result of further studies of this type, knowledge of the reaction kinetics of cluster ions could be obtained, which could in turn lead to an improved understanding of the composition of the upper atmosphere. In other words, attempts will be made to relate ground-based mass spectrometric measurements to those obtained from a rocket-borne instrument.

The skimmer used in the aerodynamic molecular beam chamber ideally introduces an undisturbed sample of the cluster beam into the mass spectrometer. In this case the clusters are moving and impinge on the skimmer, whereas for the rocket-borne case the skimmer is moving through a field of essentially statitonary clusters. The surface interaction phenomenon should be much the same for both cases. Molecular beam studies of the sampling process (in the near-continuum to free-molecular flow regime) from cluster beams of pure gases have shown that unless a cryopumping skimmer is used the mass spectra of the cluster beam is significantly affected by the sampling process (Ref. 2). It has been postulated (Ref. 2) that when large clusters strike a warm surface the resultant monomer debris forms a cloud in front of the sampling orifice and significantly attenuates the intensity of the lighter species in the incident beam. Most rocket-borne mass spectrometers do not use cryopumping skimmers and may therefore be producing cluster mass spectra which are not representative of that which exists in the upper atmosphere. Thus there may be some inconsistencies between the flight- and ground-based data resulting from these differences in skimmer configuration.

Because of the limitations of the present readout instrumentation, it was necessary to reduce the mass resolution to increase the sensitivity of the readout system in order to be able to detect weak signals. This resolution limit has been overcome in rocket-borne mass spectrometers through the use of standard pülse-counting techniques. It is planned to have this capability for future investigations of this type.

Considerable contamination of the whole molecular beam chamber was found at the conclusion of this series of tests. The weak acid solutions formed by these gas mixtures necessitated a complete stripdown and overhaul of all mechanical, diffusion, and cryo pumps. This resulted from the fact that the chamber was originally designed to purge toxic gases (i.e., SO_2 and NO) through the mechanical pumps. A positive purge system has been installed on the chamber to minimize contamination in future tests of this type.

SECTION IV
CONCLUSIONS AND RECOMMENDATIONS

The present investigation indicates that nucleation in a free-jet expansion can be enhanced by either (1) mixing the test gas with a high-pressure carrier gas, or (2) increasing the size of the source orifice. In the free-jet expansions of various gas mixtures, it has been found possible to produce mixed clusters of the following types: $SO_2^+(H_2O)_n$, $NO^+(H_2O)_n$, $(SO_2)_2^+(H_2O)_n$, $Ar^+(H_2O)_n$, $Ar(SO_2)_n$, $NO^+(SO_2)_n$, and $NO^+(SO_2)(H_2O)_n$. In these same gas mixture clusters, expansion clusters of the following pure gases have been observed: $(SO_2)_n^+$, $(S_{34}O_2)_n^+$, $(NO)_n^+$, $H^+(H_2O)_n$, and $(Ar)_n^+$. The fragmentation characteristics of many of these clusters in the EAI quadrupole mass spectrometer have been established. For example, it has been shown that electron impact of the sulfur dioxide dimer produces the following ion cluster fragments: $SO^+(SO_2)$, $S_{34}O^+(SO_2)$, and $S^+(SO_2)$. For test conditions where the primary objective is to determine the distribution of neutral clusters in an expansion, a knowledge of the cluster fragmentation characteristics is of great importance. For example, in a water/nitric oxide/sulfur dioxide expansion it is necessary to be able to distinguish between (1) $NO^+(H_2O)$ cluster and the fragment SO^+ and (2) $S_{34}O_2$ monomer $NO^+(H_2O)_2$ cluster and the fragment $SO^+(H_2O)$, in order to separate ion cluster fragments from the naturally occurring neutral species.

As a result of the present investigation it has become clear that in order to be able to distinguish between two species of approximately equal mass and intensity, greater mass resolution than is available with the existing system is necessary. An adaptation of pulse-counting techniques currently in use on rocket-borne quadrupole mass spectrometers should provide a satisfactory solution to this problem.

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APPENDIX
ILLUSTRATIONS

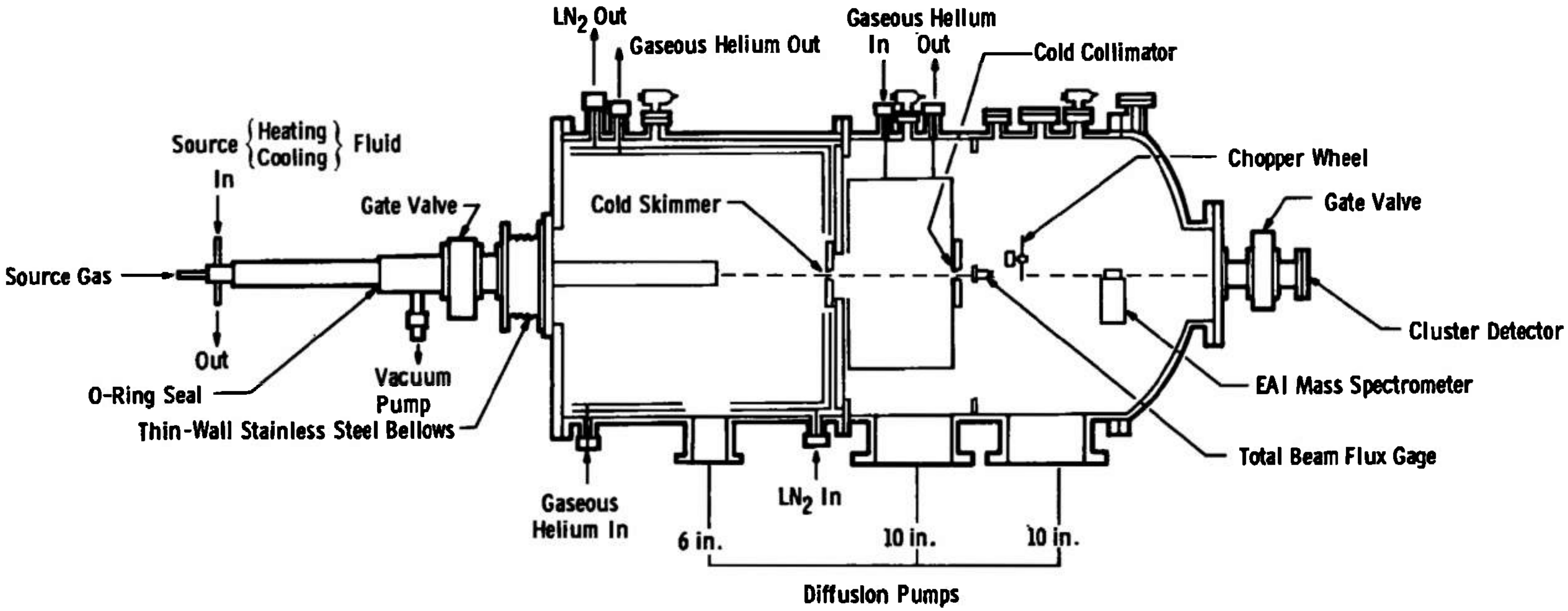


Fig. 1 Schematic of Molecular Beam Chamber

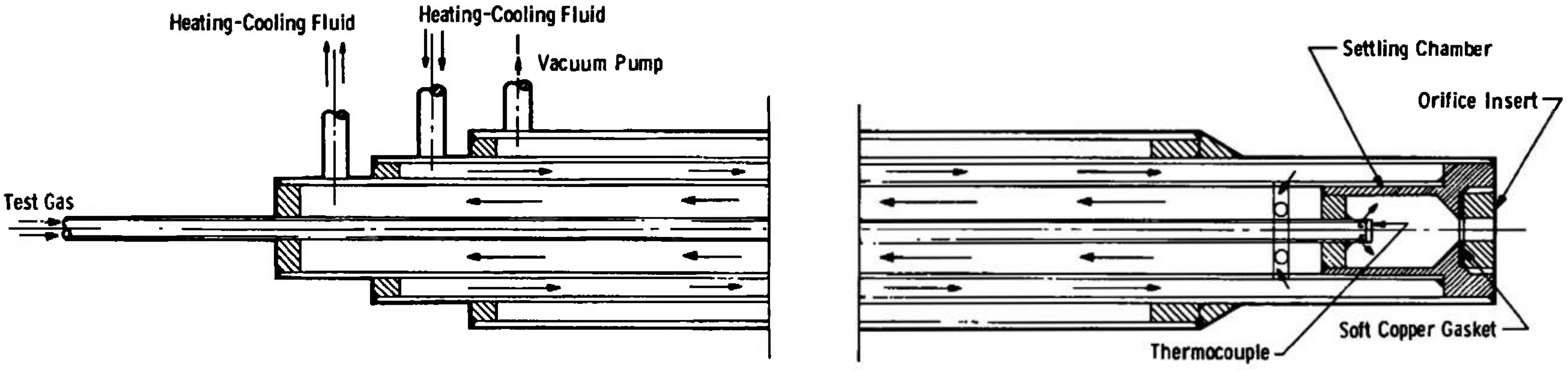


Fig. 2 Schematic of Temperature-Controlled Molecular Beam Source

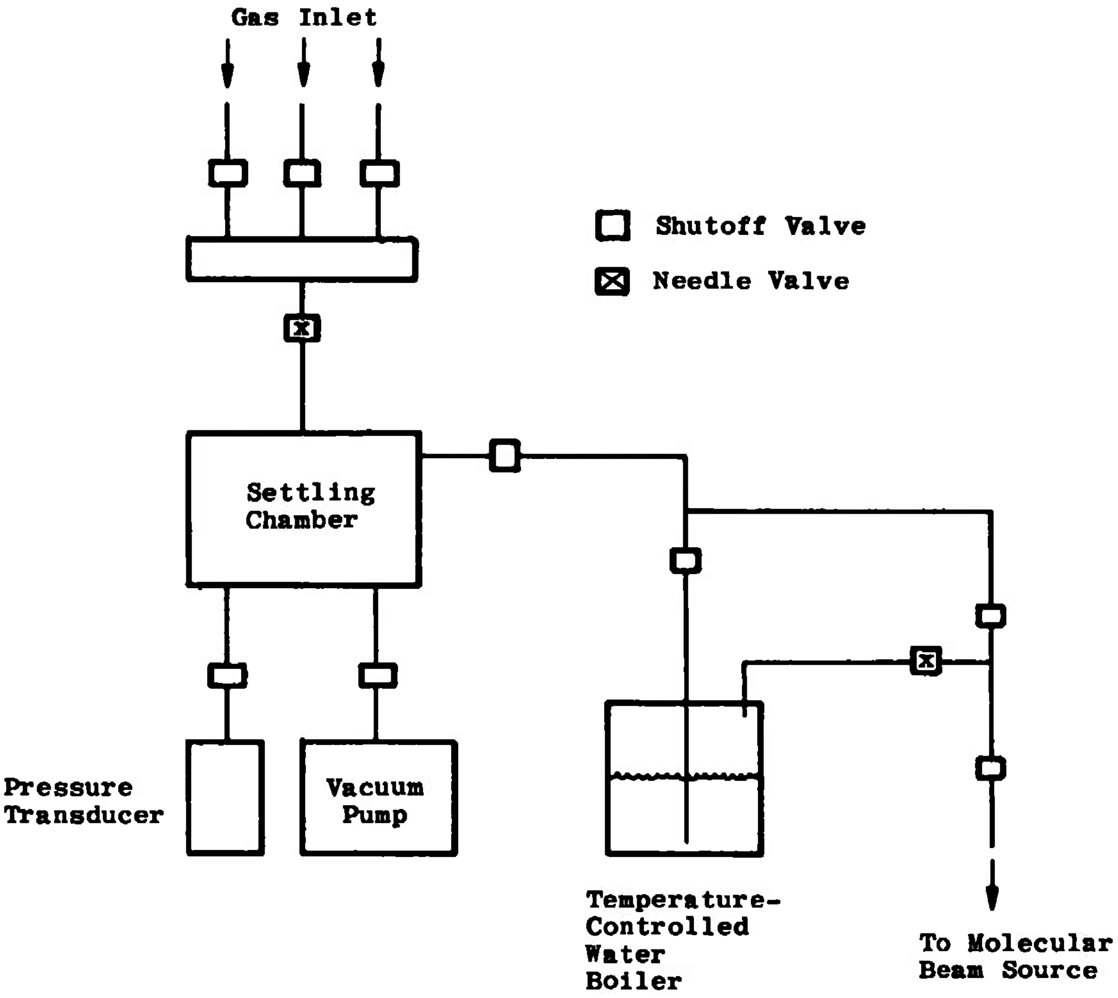


Fig. 3 Schematic of Water Addition System

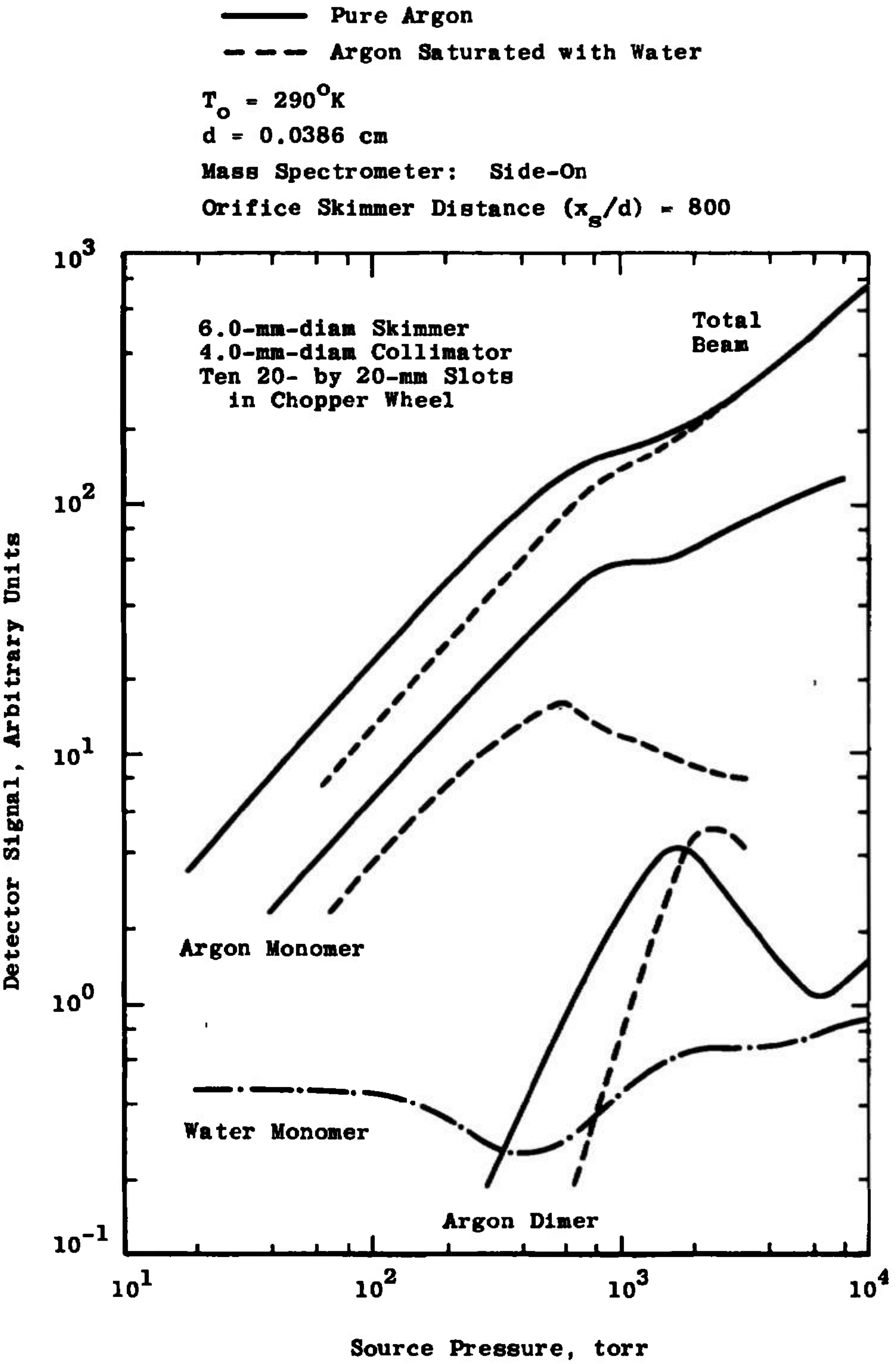
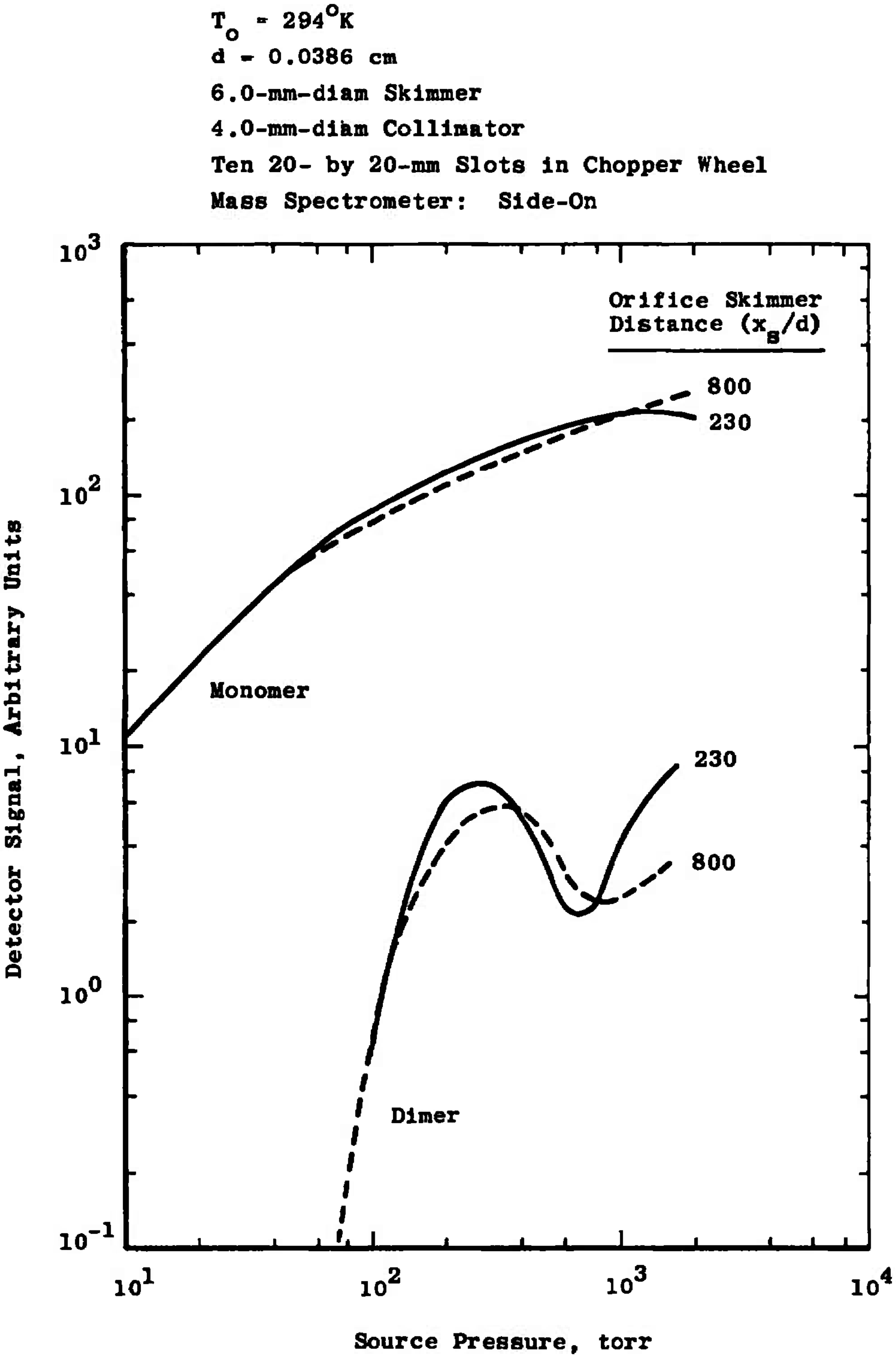
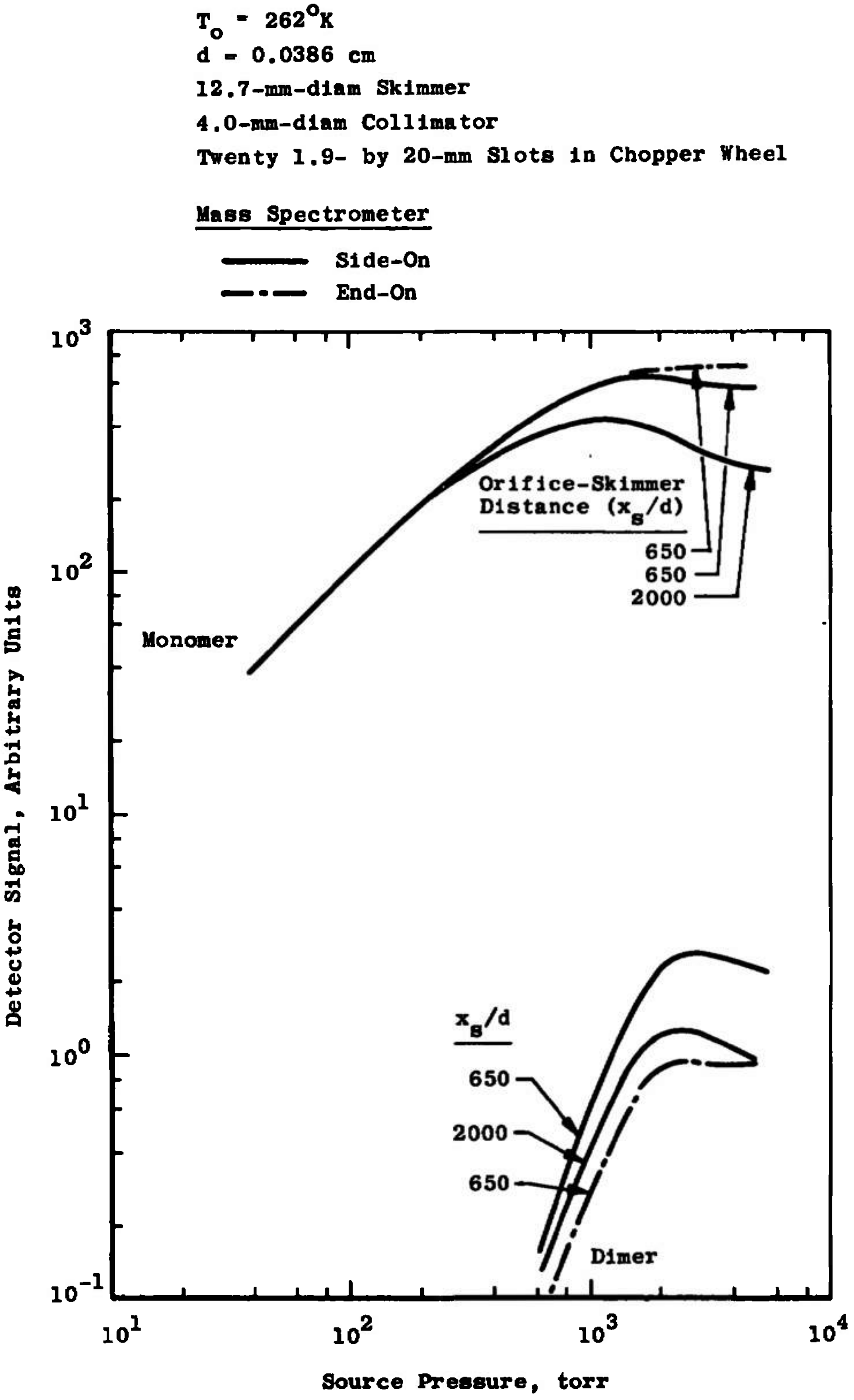


Fig. 4 Effect of Water on Condensation Characteristics of Argon



a. Sulfur Dioxide

Fig. 5 Monomer and Dimer Intensity Variation with Source Pressure



b. Nitric Oxide
Fig. 5 Concluded

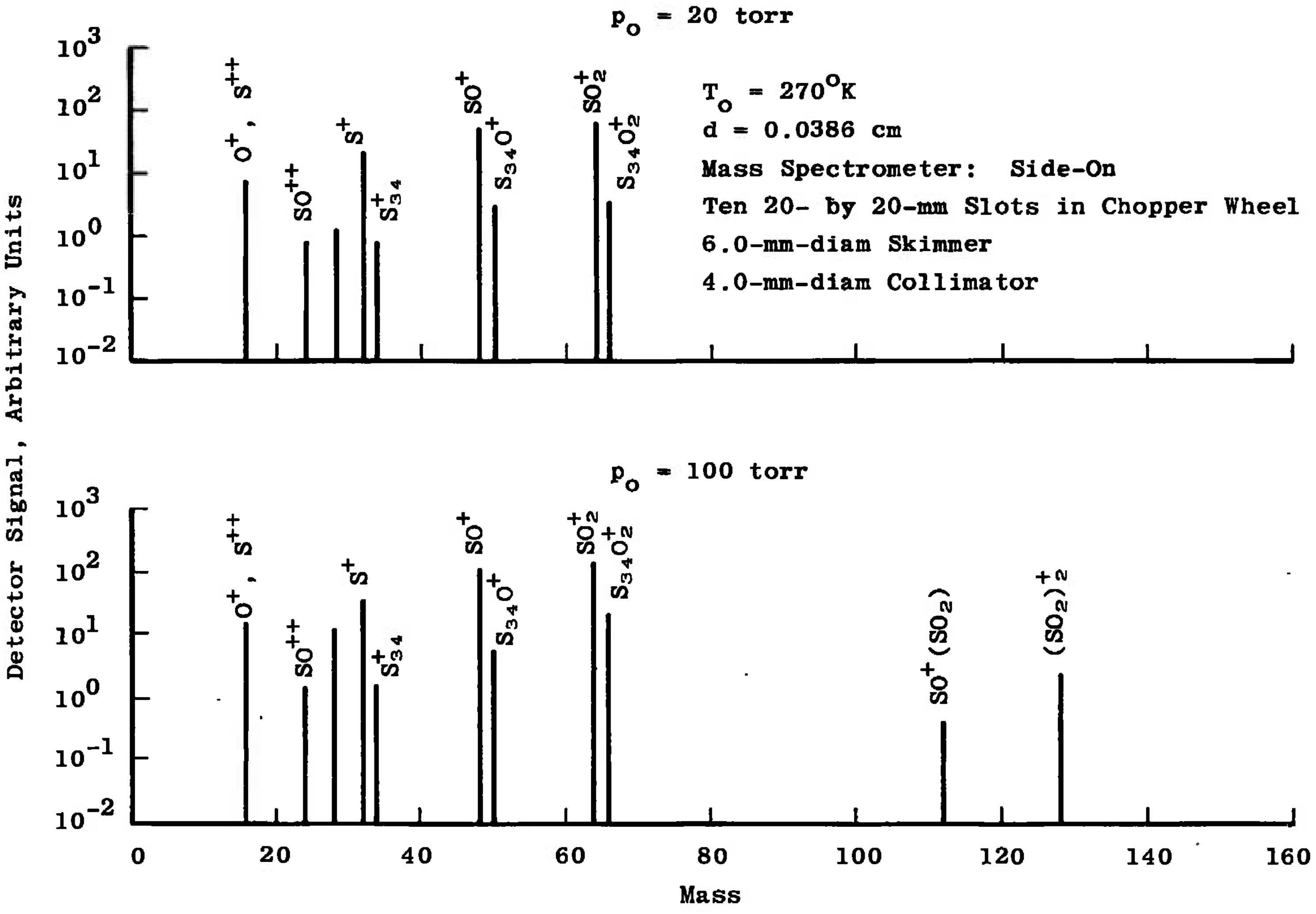


Fig. 6 Sulfur Dioxide Mass Spectra for a Range of Source Pressures

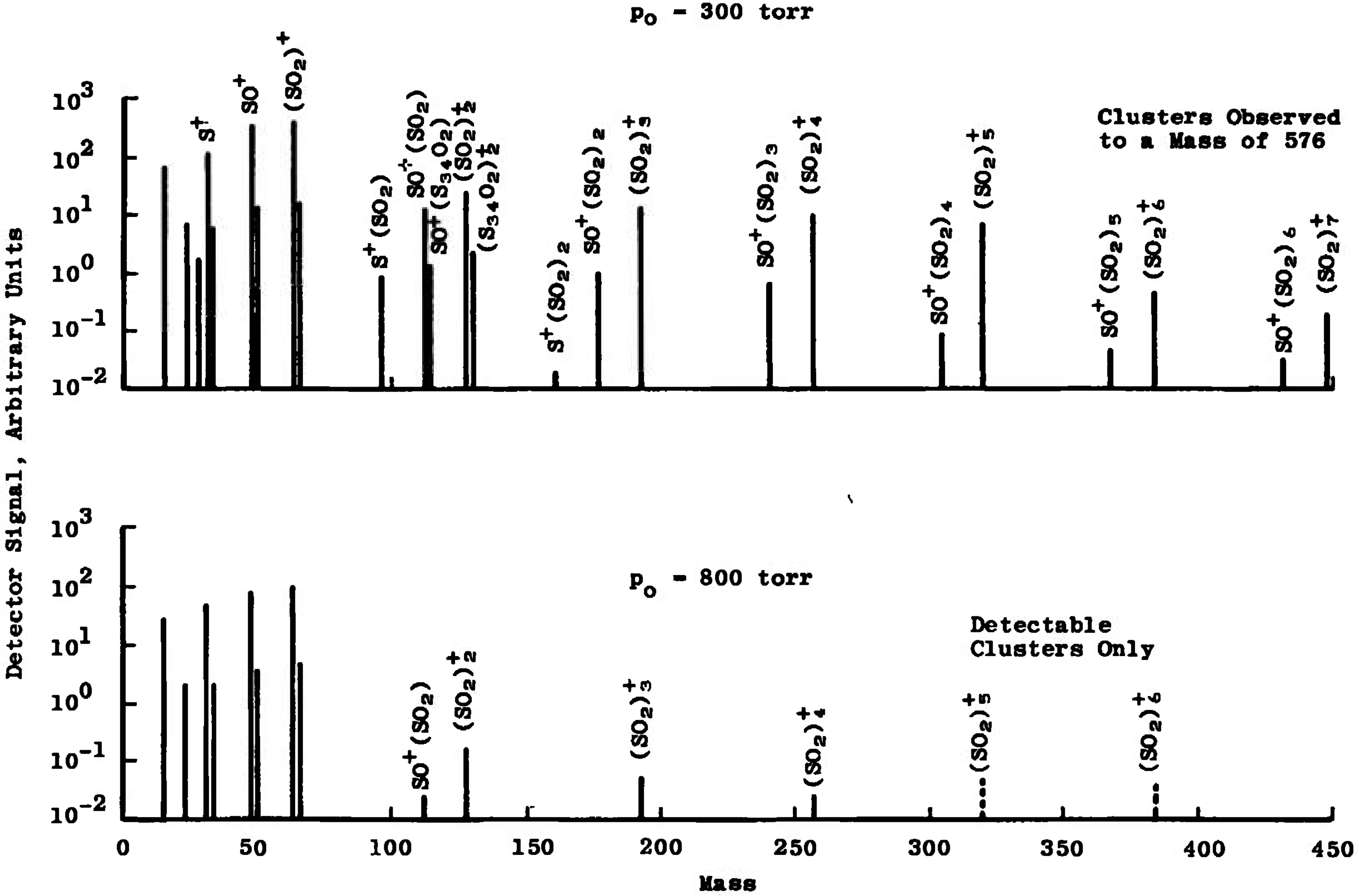


Fig. 6 Concluded

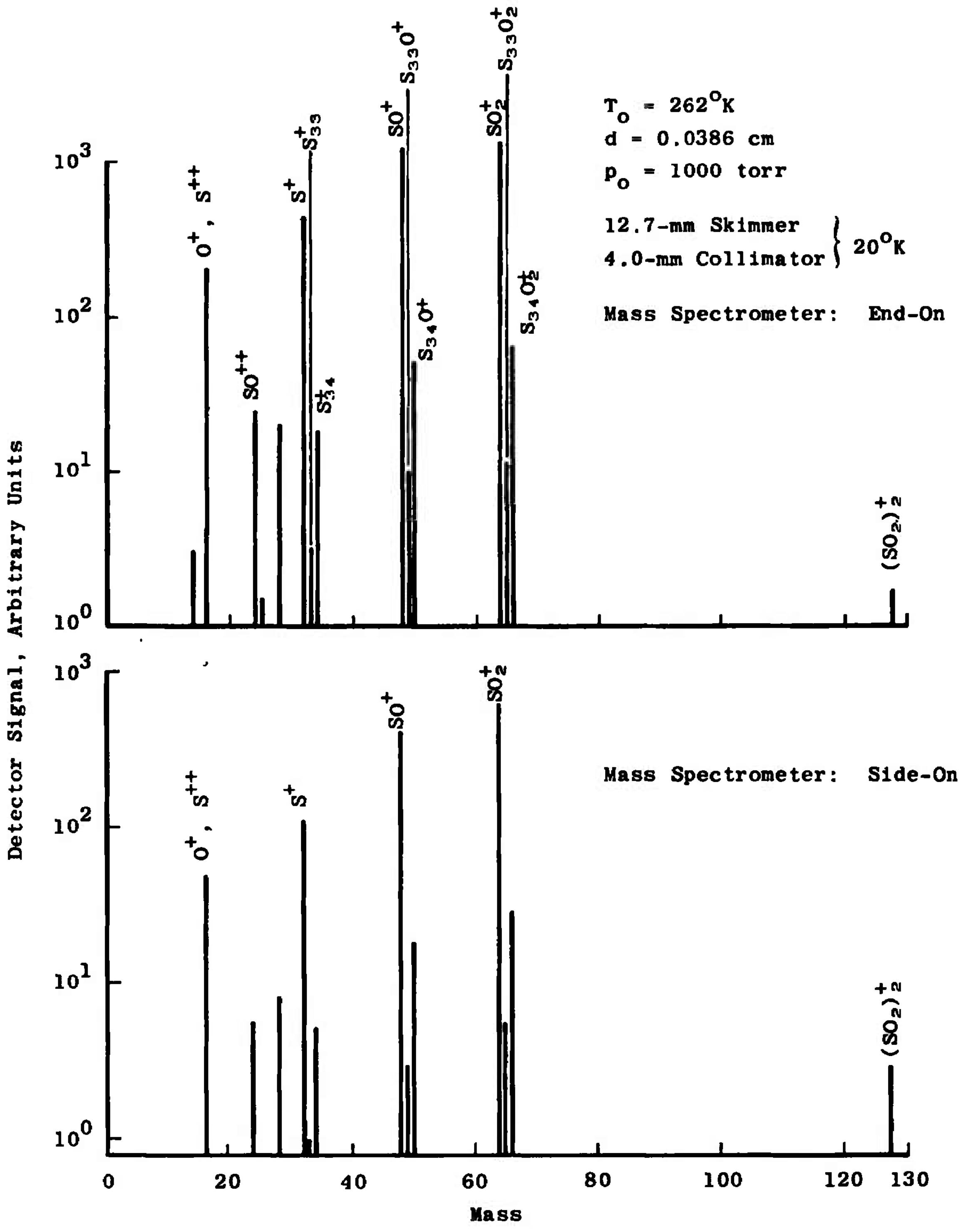
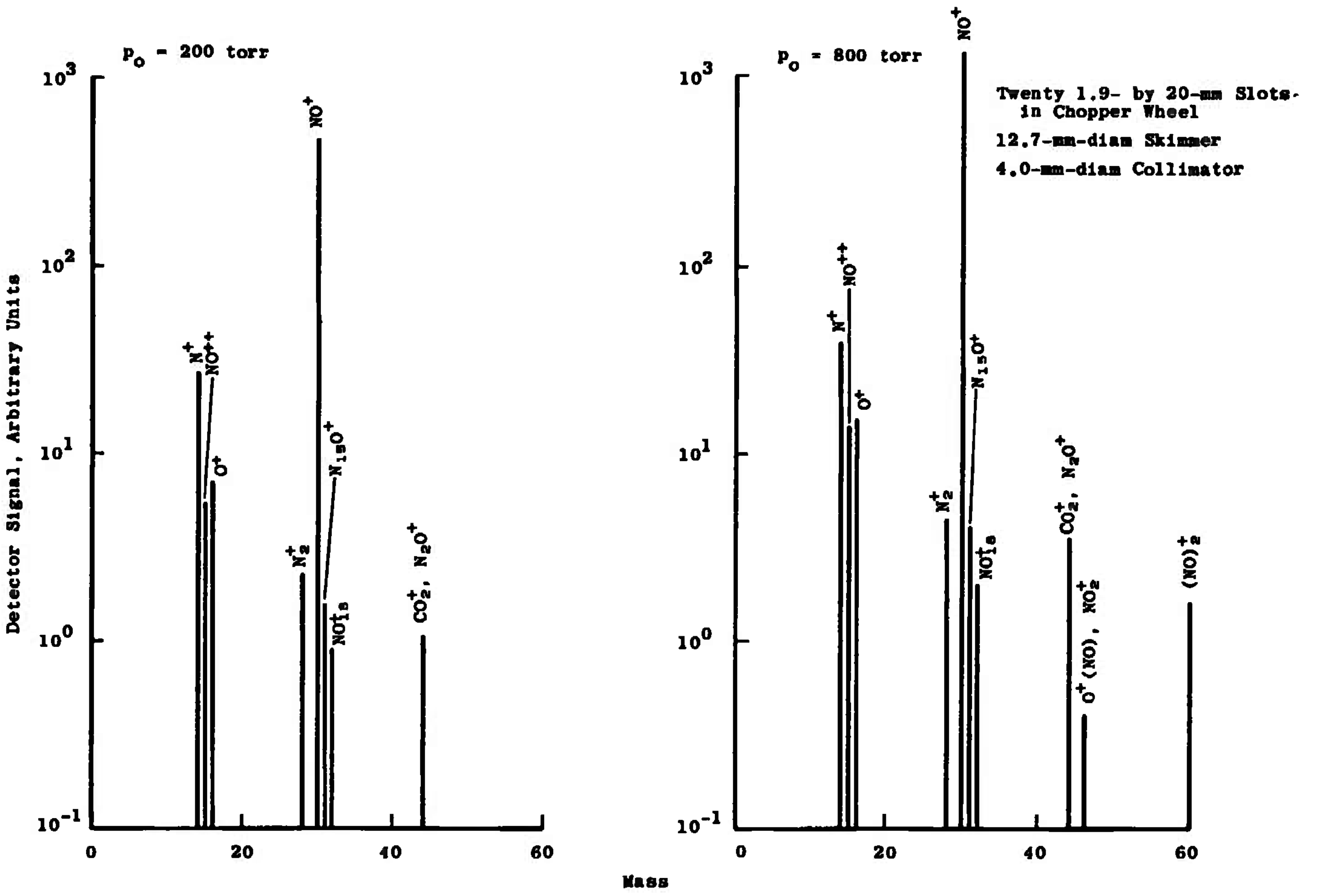
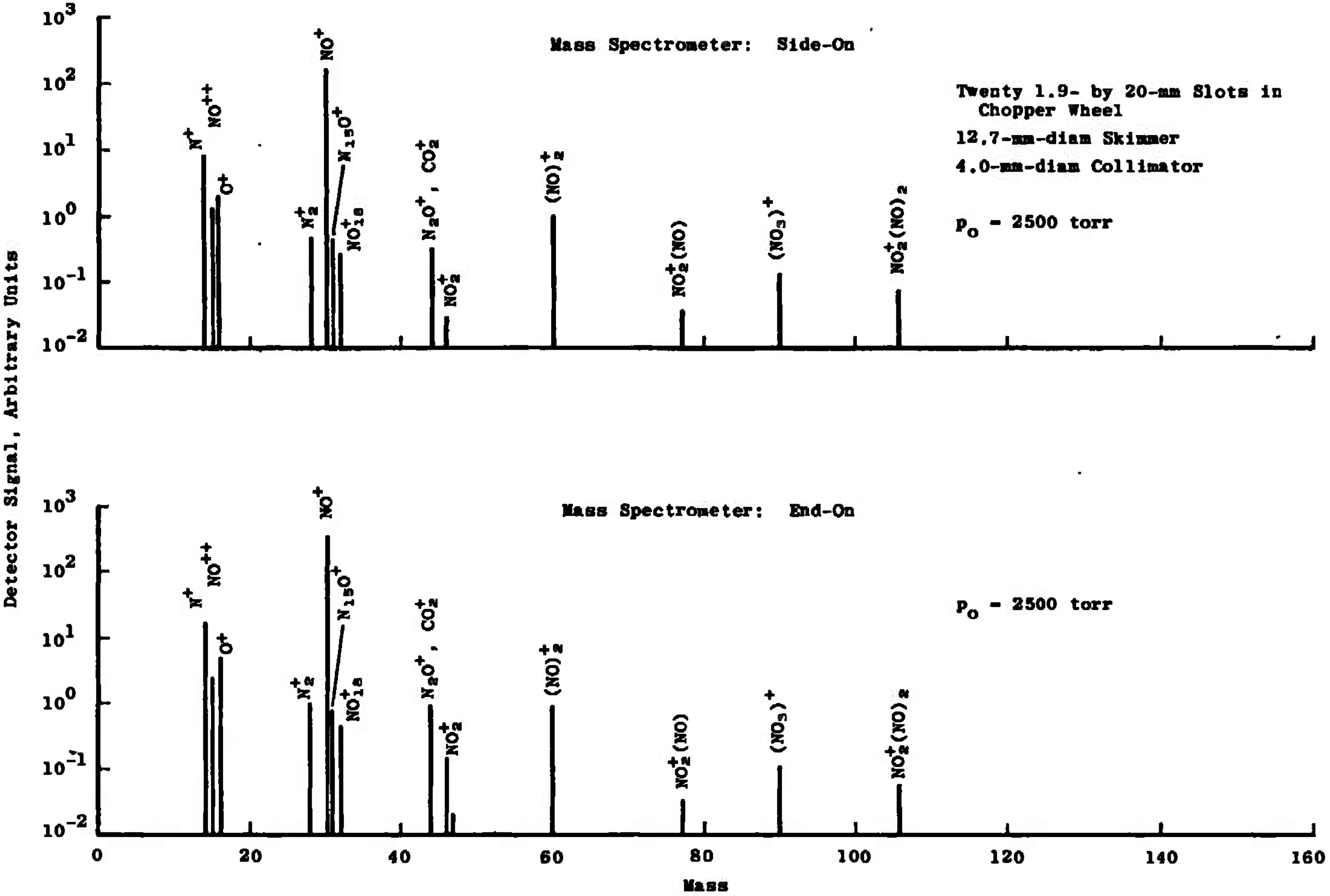


Fig. 7 Effect of Mass Spectrometer Mode of Operation on Observed Sulfur Dioxide Spectra

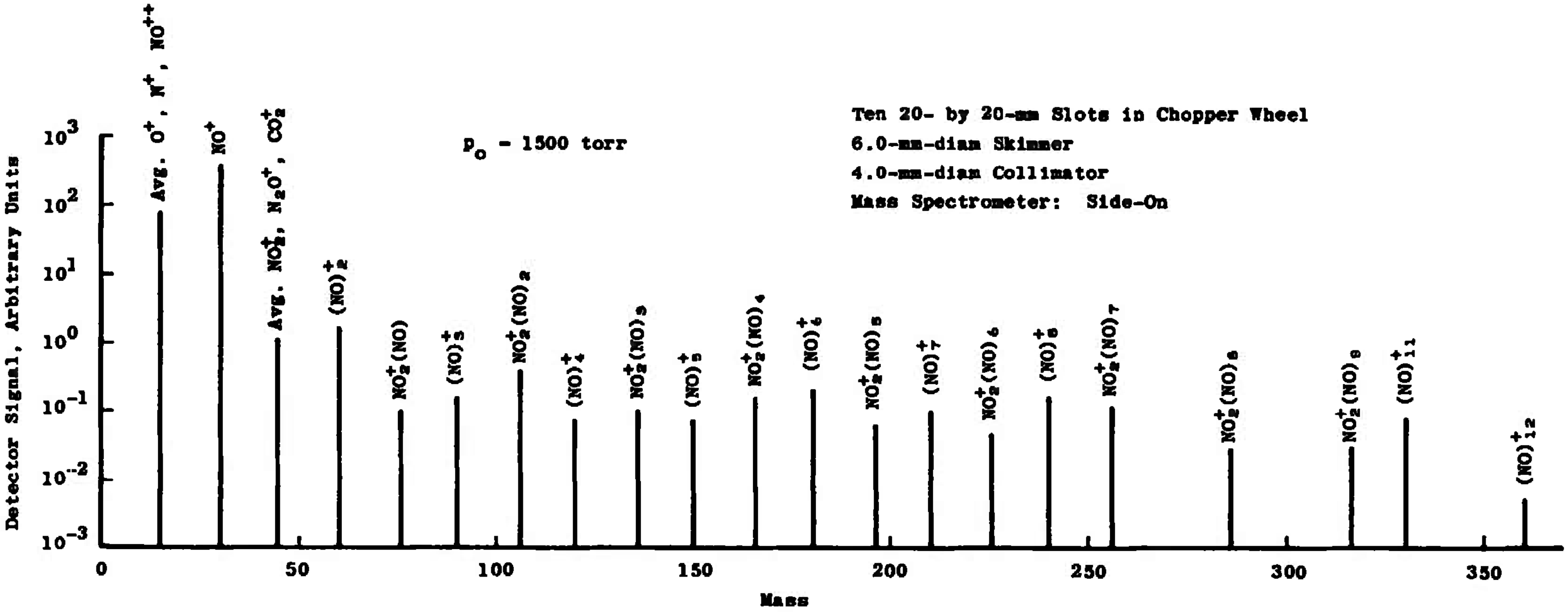


a. T_o = 260°K, d = 0.0386 cm

Fig. 8 Nitric Oxide Mass Spectra for Various Test Conditions

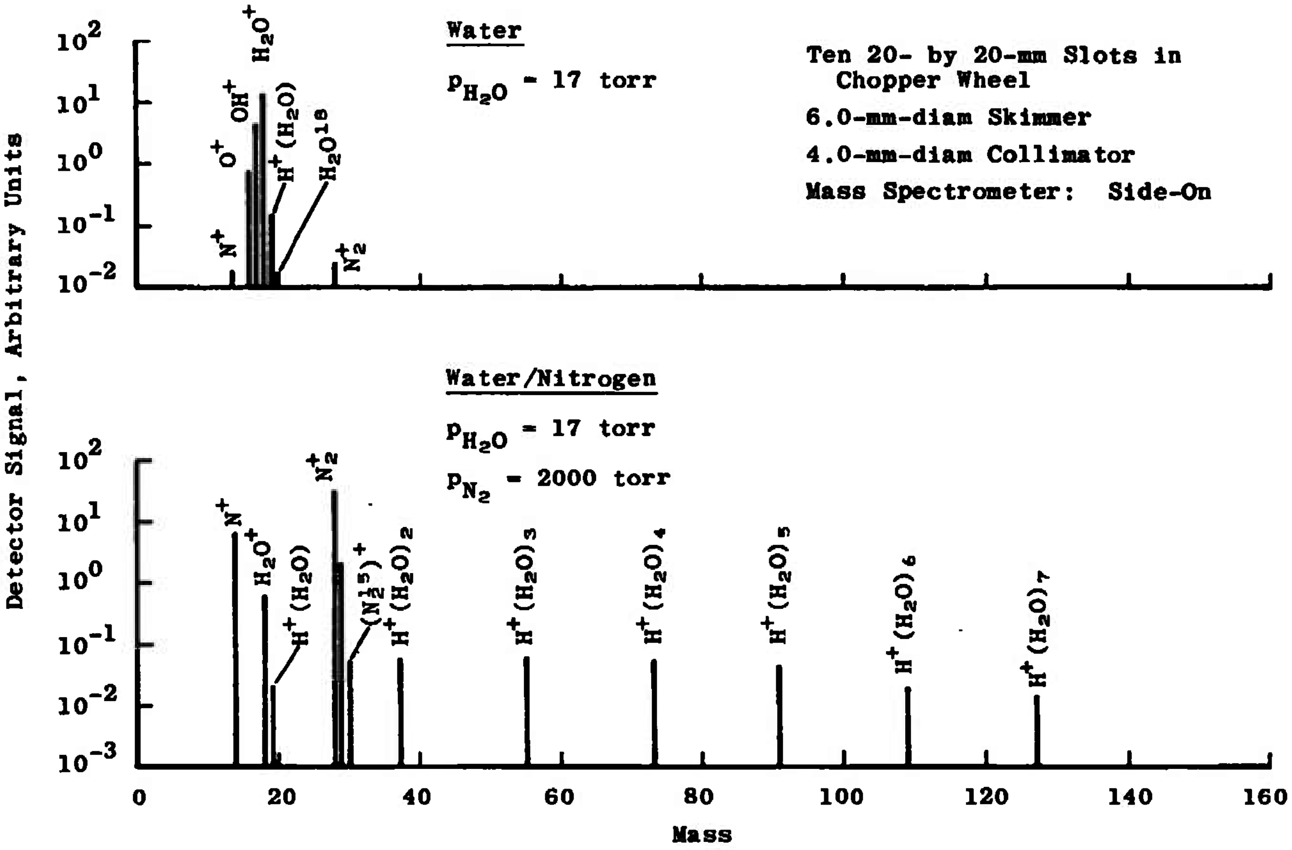


b. T_o = 262°K, d = 0.0386 cm
Fig. 8 Continued



c. T_o = 270°K, d = 0.0386 cm

Fig. 8 Concluded

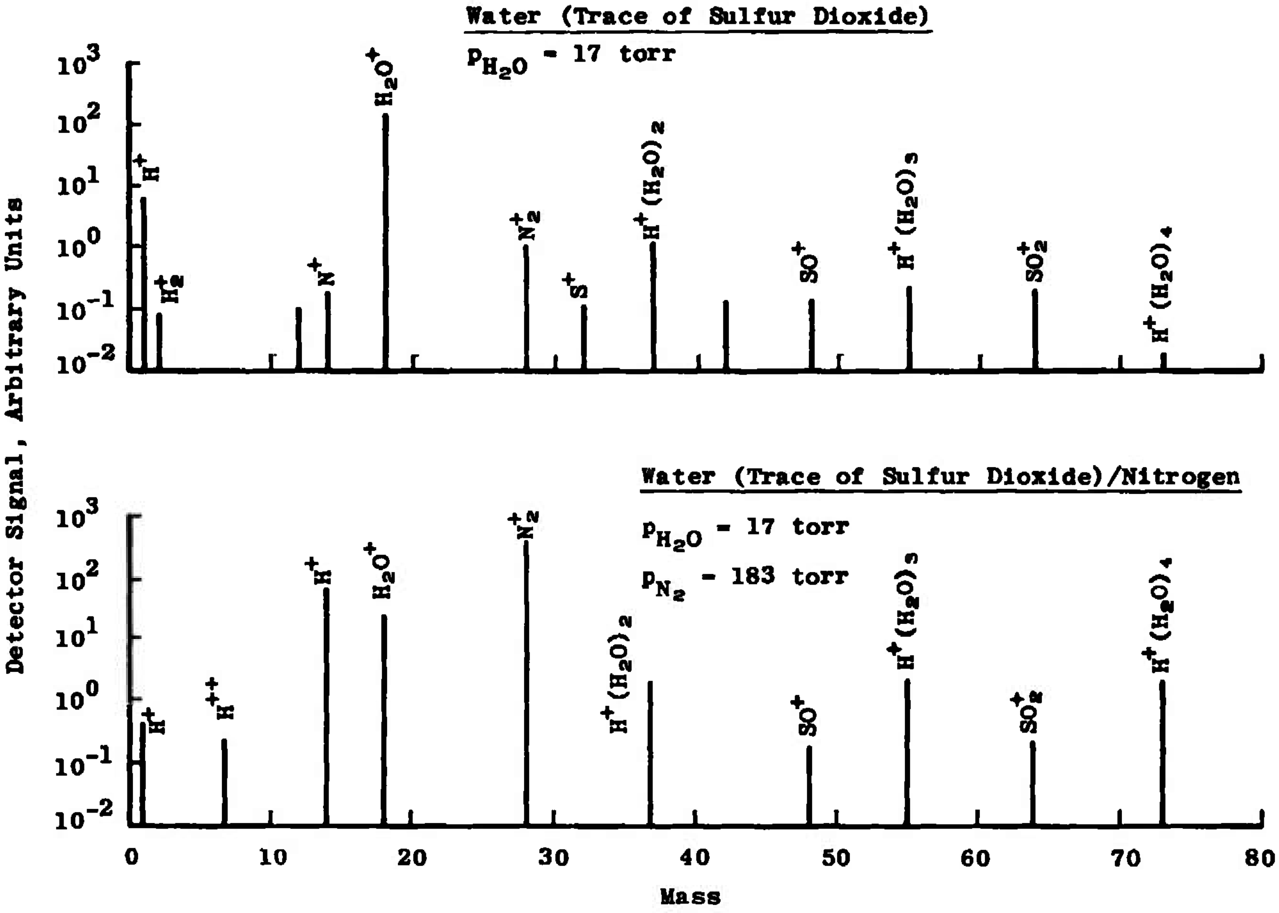


a. T_o = 290°K, d = 0.0386 cm

Fig. 9 Water Vapor Mass Spectra for Various Test Conditions

Ten 20- by 20-mm Slots in Chopper Wheel
6.0-mm-diam Skimmer

4.0-mm-diam Collimator
Mass Spectrometer: End-On



Water (Trace of Sulfur Dioxide)

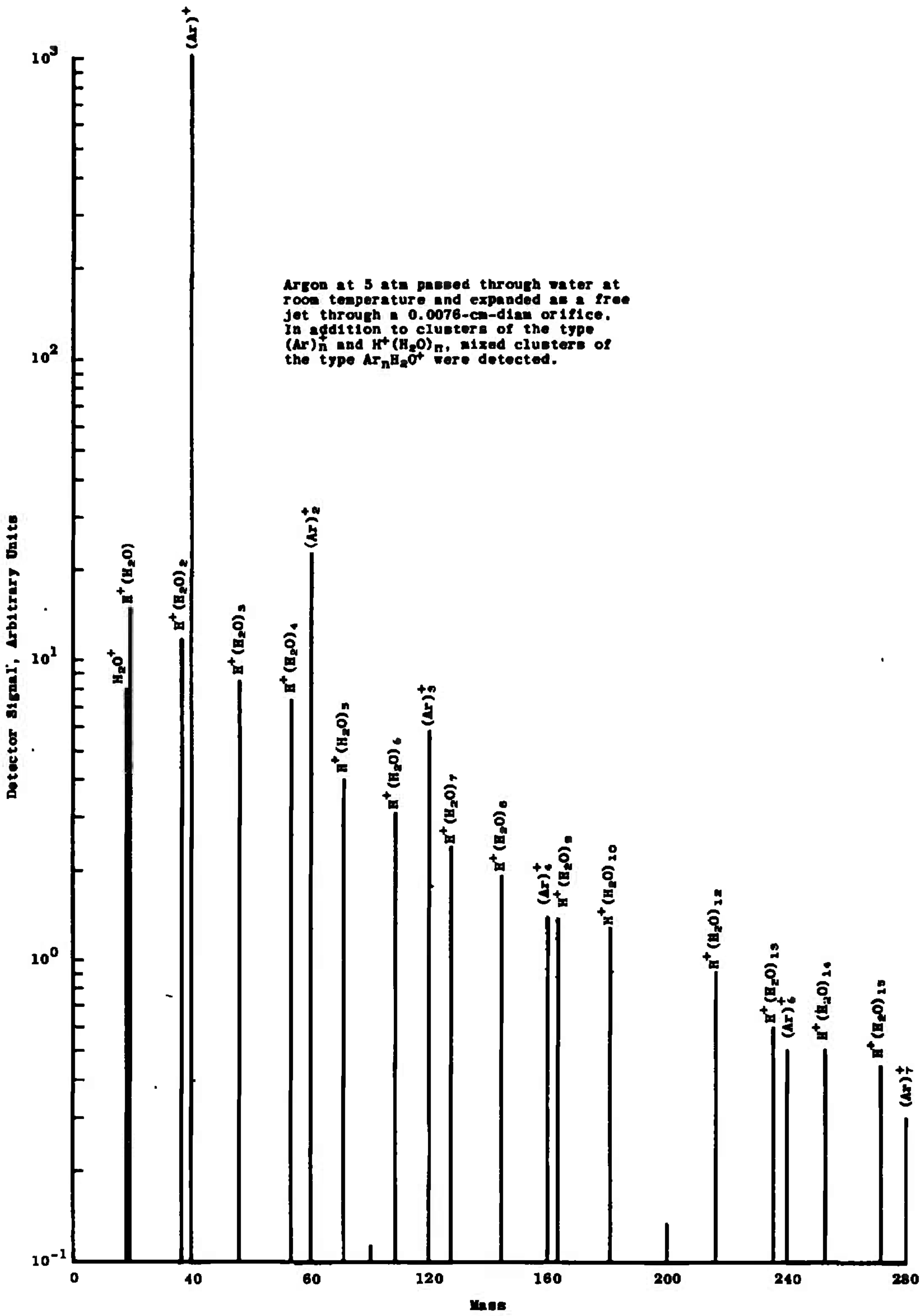
p_{H_2O} = 17 torr

Water (Trace of Sulfur Dioxide)/Nitrogen

p_{H_2O} = 17 torr

p_{N_2} = 183 torr

b. T_o = 295°K, d = 0.1245 cm
Fig. 9 Concluded



Argon at 5 atm passed through water at room temperature and expanded as a free jet through a 0.0076-cm-diam orifice. In addition to clusters of the type $(Ar)_n^+$ and $H^+(H_2O)_n$, mixed clusters of the type $Ar_nH_2O^+$ were detected.

Fig. 10 Mass Spectra Obtained with Argon/Water Mixture (Ref. 4)

Symbol	d, cm	T_o, °K	p_o, torr	Carrier Gas	Mass Spectrometer	Reference
① ———	0.0076	300	3800	Ar	Side-On	4
② — — —	0.1245	295	200	N_2	End-On	Present
③ —— - ——	0.1245	295	17	None	End-On	↓
④ —— - —	0.0386	290	2000	N_2	Side-On	
⑤ ···········	0.0386	290	1250	N_2	End-On	
⑥ —··—	0.0386	290	1250	N_2	Side-On	

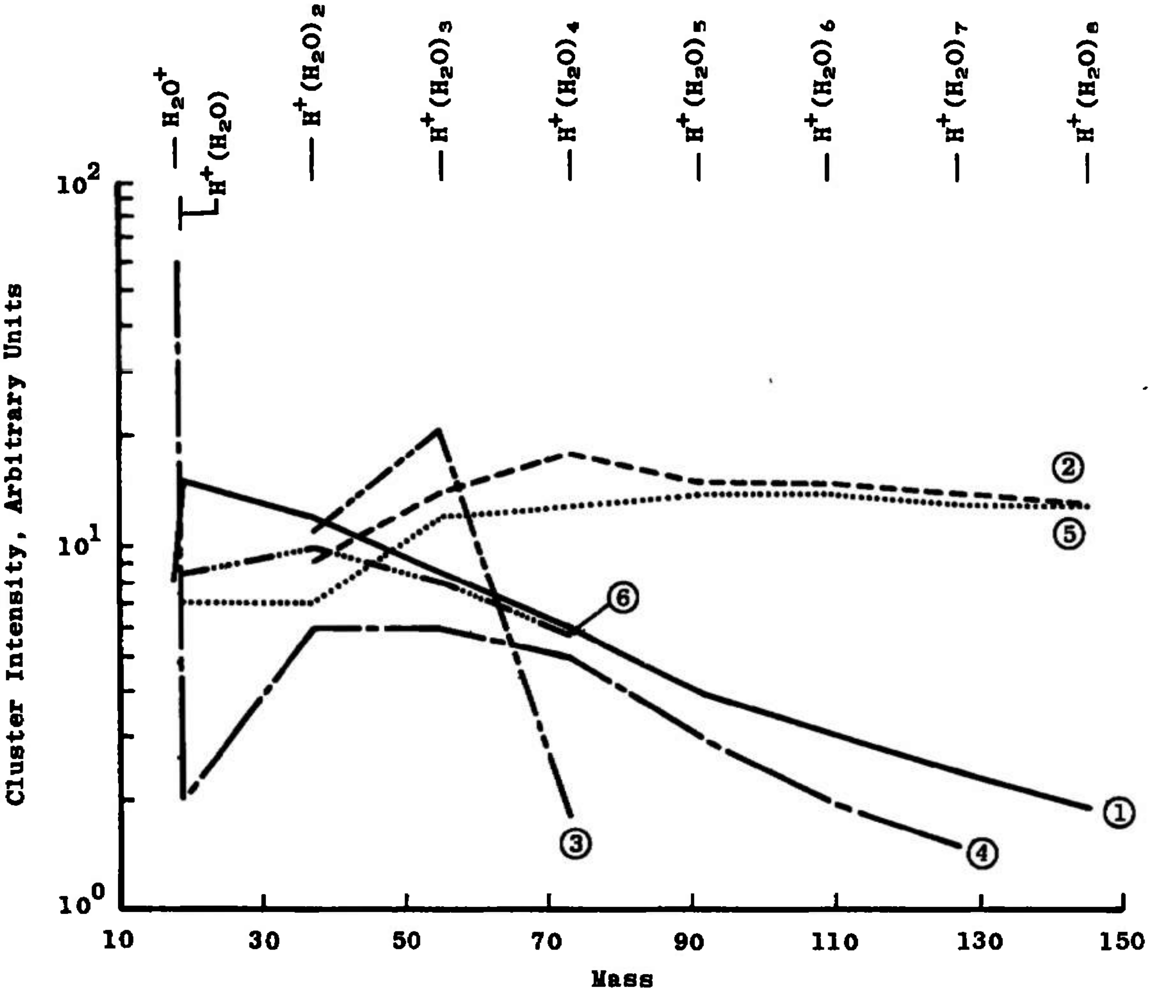


Fig. 11 Effect of Carrier Gas Pressure and Orifice Diameter on Water Cluster Intensity

T_o = 373°K, p_o = 760 torr, d = 0.0386 cm
Ten 20- by 20-mm Slots in Chopper Wheel
6-mm-diam Skimmer, 4.0-mm-diam Collimator
Medium Range

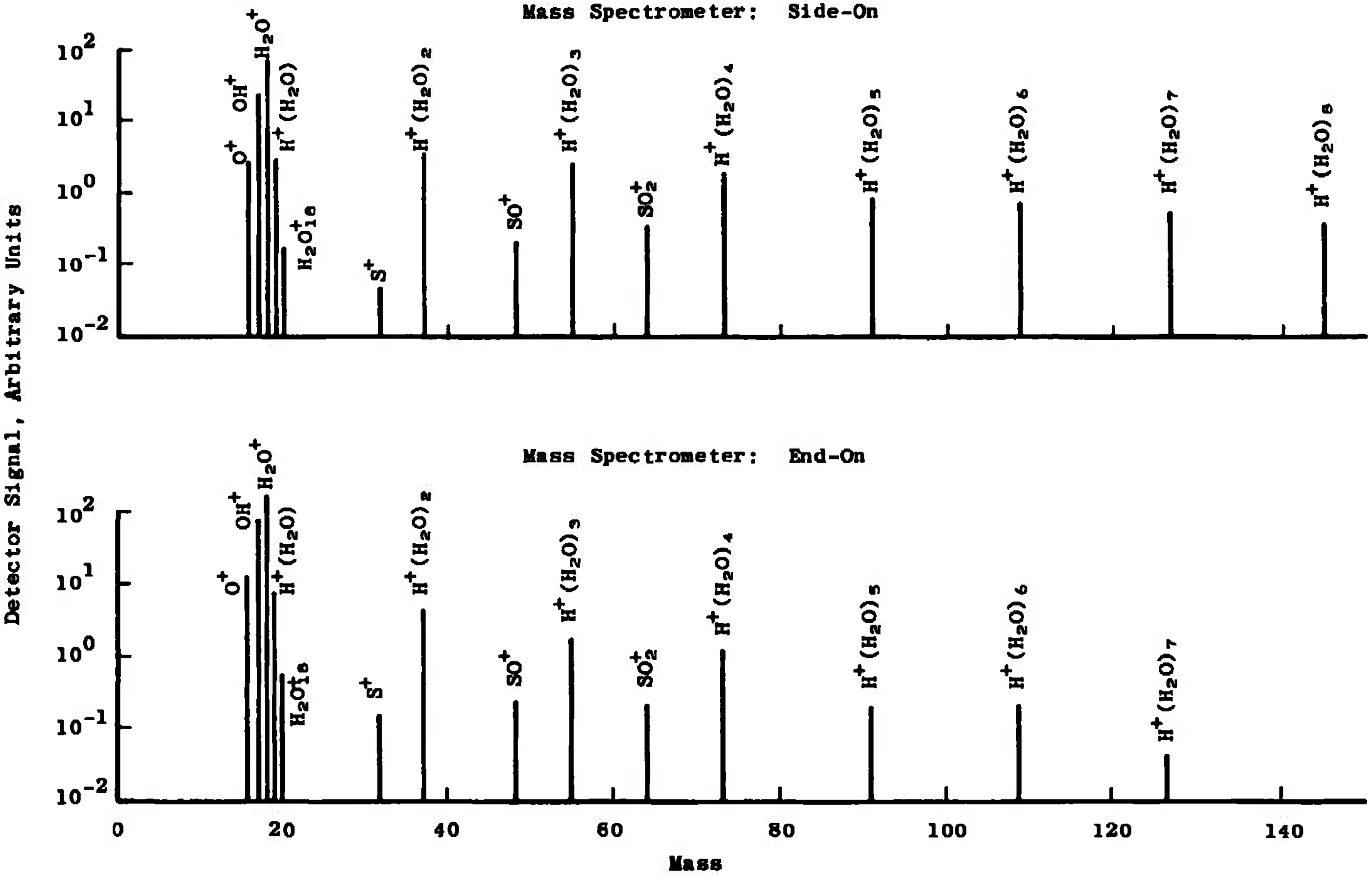
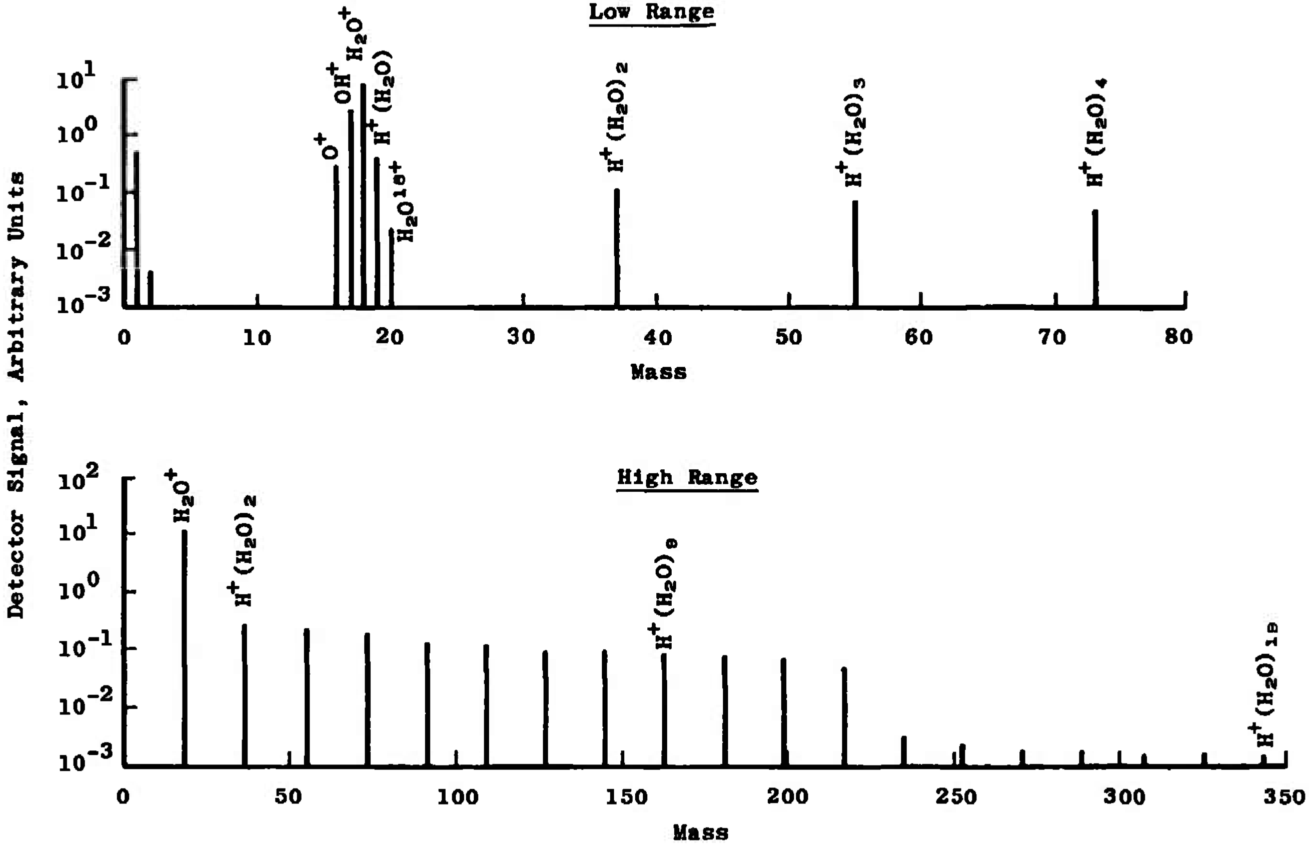


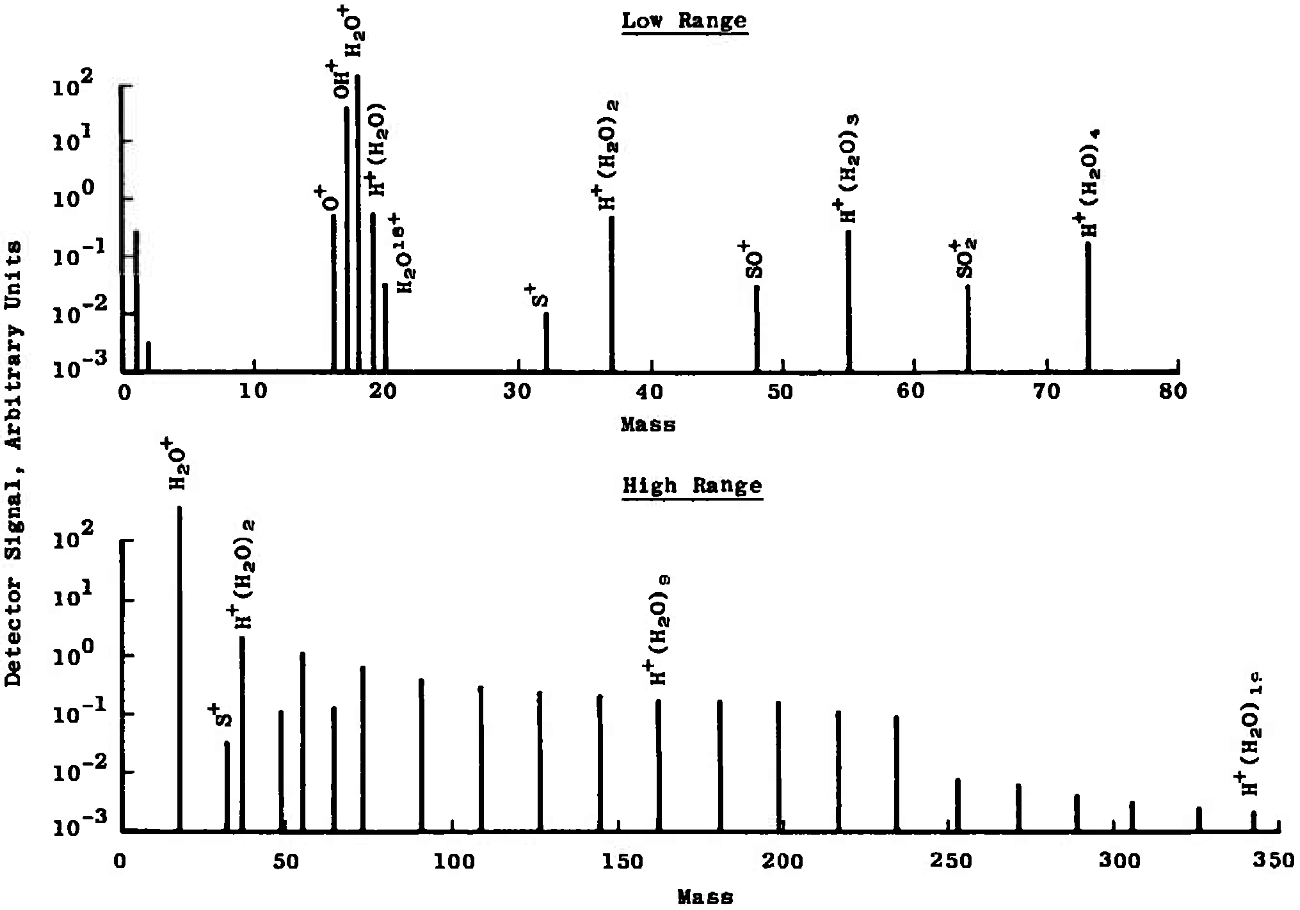
Fig. 12 Effect of Mass Spectrometer Mode of Operation on Steam Spectra

T_o = 373°K, p_o = 760 torr, d = 0.0386 cm
Mass Spectrometer: Side-On
Ten 20- by 20-mm Slots in Chopper Wheel
6.0-mm Skimmer, 4.0-mm Collimator



a. Water
Fig. 13 Mass Spectra for Steam

T_o = 373°K. p_o = 760 torr, d = 0.0386 cm
Mass Spectrometer: Side-On
Ten 20- by 20-mm Slots in Chopper Wheel
6.0-mm-diam Skimmer. 4.0-mm-diam Collimator



b. Water (Trace of Sulfur Dioxide)
Fig. 13 Concluded

Trace	Orifice Diameter, cm	T, °K	P_o, torr	Gas	Mass Spectrometer	Reference
①	0.0076	300	3800	H_2O/Ar	Time-of-Flight	4
②	0.0386	373	760	Steam	Quadrupole	Present
③	0.0386	290	2000	H_2O/N_2	Quadrupole	Present
④	0.001	463	6840	Steam	Magnetic Sector	8

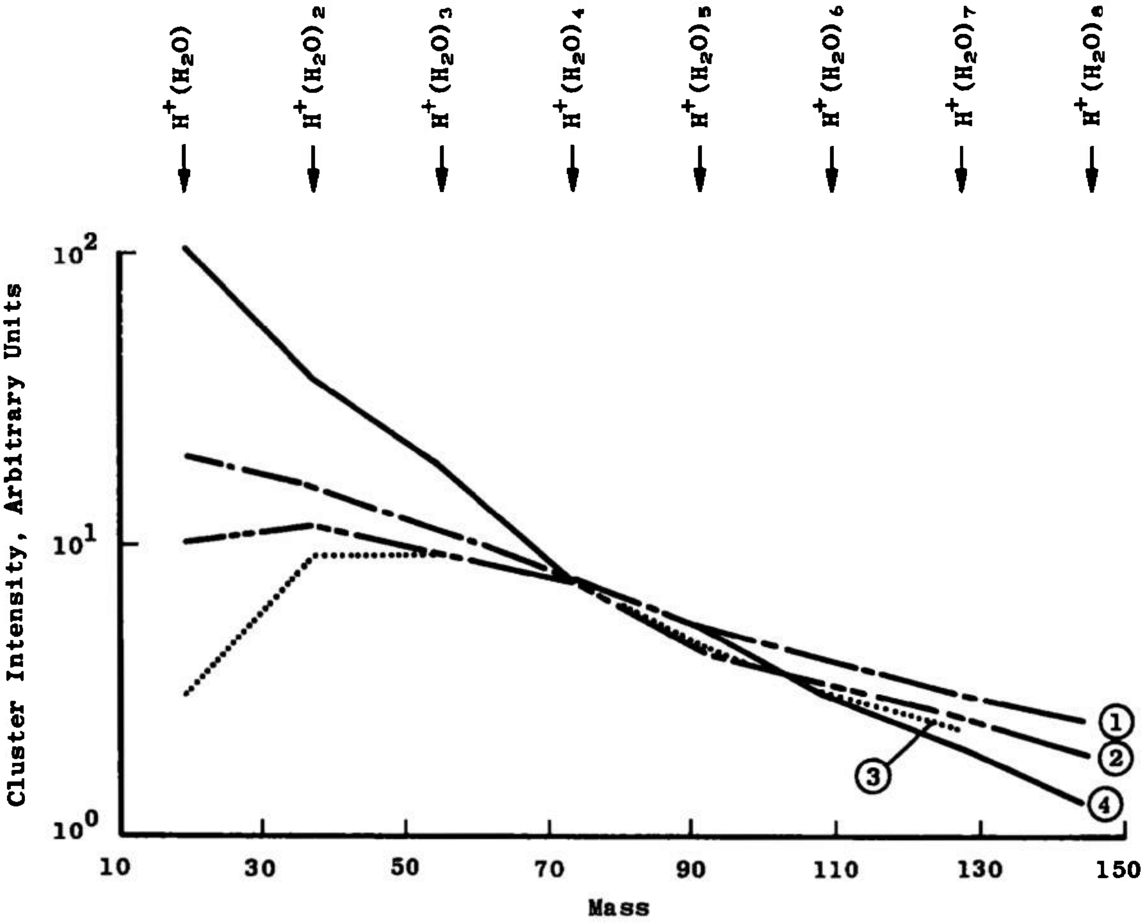
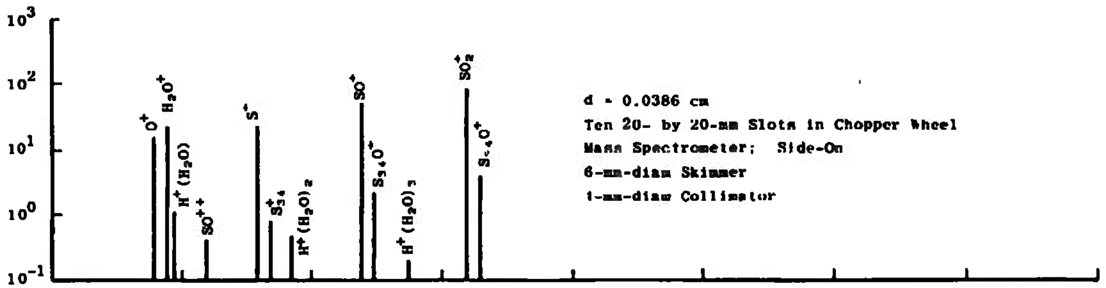
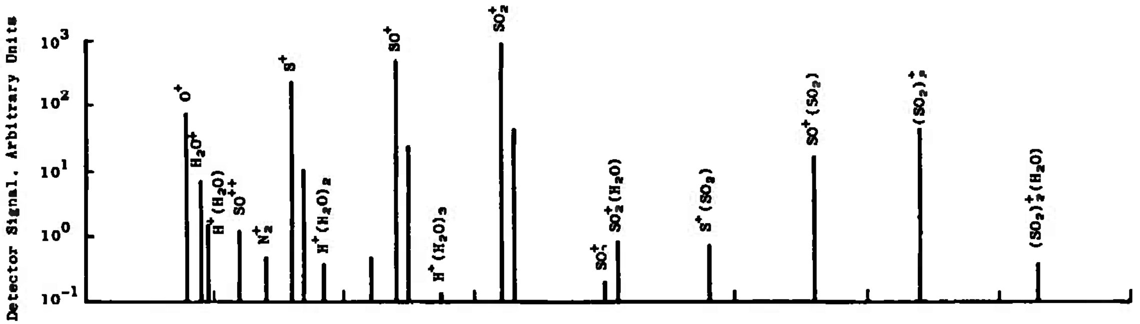


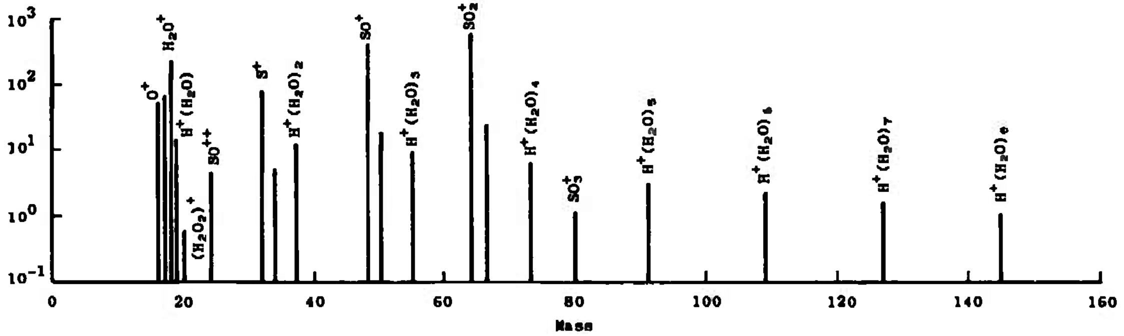
Fig. 14 Comparison of Water-Cluster Intensity Measurements



a. p_{SO_2} = 25 torr, p_{H_2O} = 17 torr, T_o = 290°K

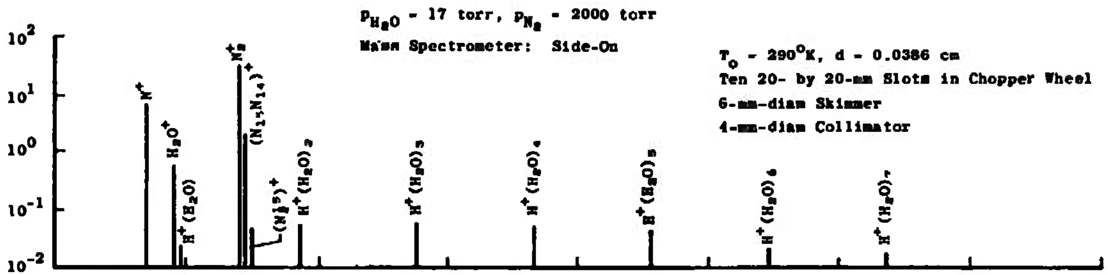


b. p_{SO_2} = 300 torr, p_{H_2O} = 17 torr, T_o = 290°K

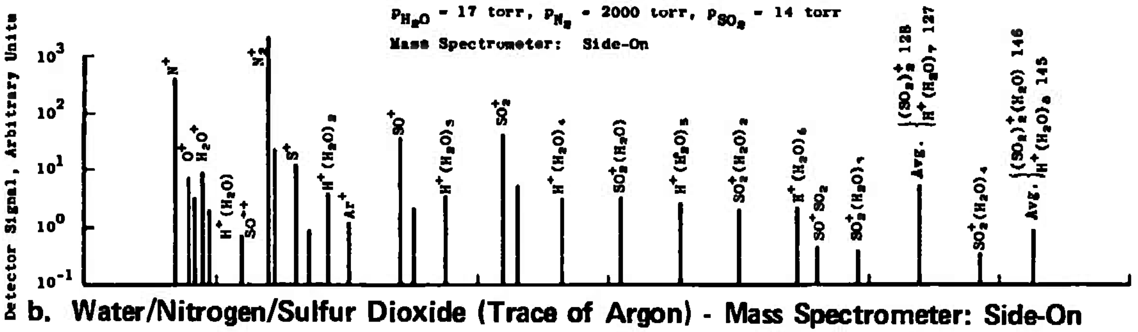


c. p_{SO_2} = 140 torr, p_{H_2O} = 760 torr, T_o = 373°K

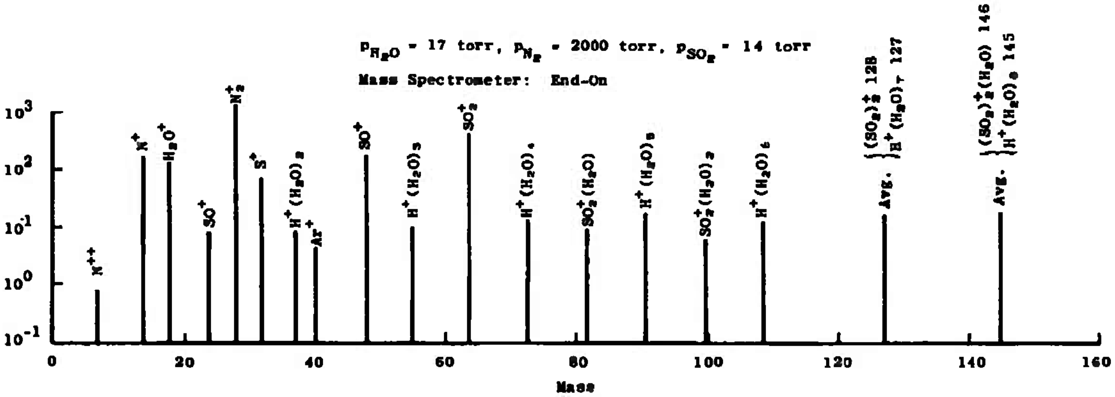
Fig. 15 Water/Sulfur Dioxide Mass Spectra



a. Water/Nitrogen - Mass Spectrometer: Side-On

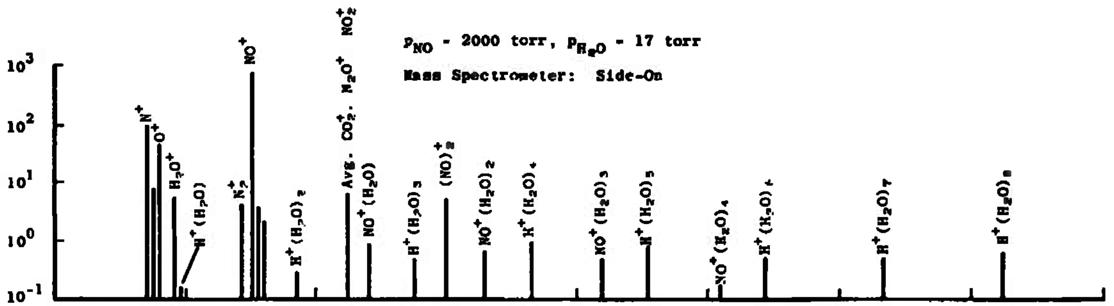


b. Water/Nitrogen/Sulfur Dioxide (Trace of Argon) - Mass Spectrometer: Side-On

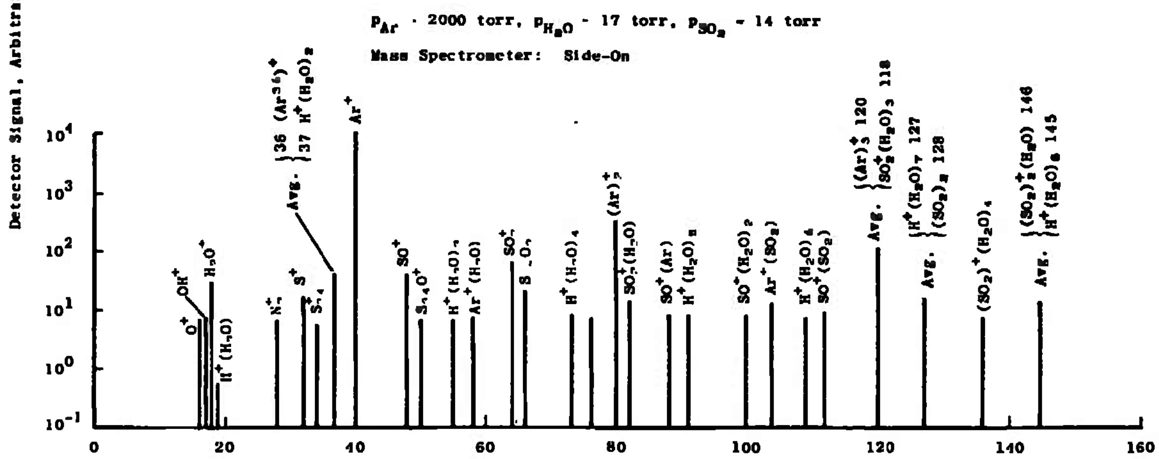


c. Water/Nitrogen/Sulfur Dioxide (Trace of Argon) - Mass Spectrometer: End-On

Fig. 16 Water/Sulfur Dioxide/Nitric Oxide/Carrier Gas Mixture Mass Spectra

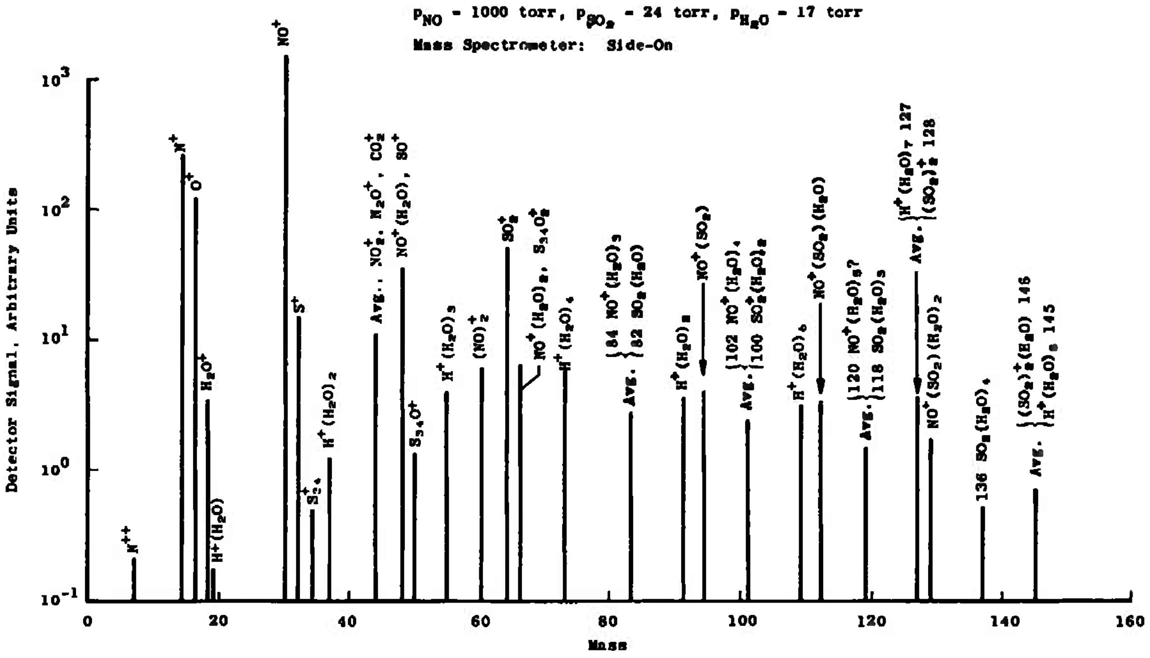


d. Nitric Oxide/Water - Mass Spectrometer: Side-On



e. Argon/Water/Sulfur Dioxide - Mass Spectrometer: Side-On

Fig. 16 Continued



f. Nitric Oxide/Sulfur Dioxide/Water - Mass Spectrometer: Side-On
Fig. 16 Concluded

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13 ABSTRACT

To achieve a better understanding of the composition of the upper atmosphere, it is necessary to obtain more information on the reaction kinetics of cluster ions. The purpose of the present investigation has been to determine the feasibility of producing mixed molecular clusters in the free-jet expansions of a variety of gas mixtures. Mass spectra have been obtained from cluster beams formed by the expansions of water vapor, steam, sulfur dioxide, nitric oxide, water/sulfur dioxide, water/nitric oxide, water/sulfur dioxide/nitrogen, water/sulfur dioxide/Argon, and water/sulfur dioxide/nitric oxide. Cluster ions of the following types have been 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 $AR(SO_2)n$.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
spectrometers						
molecular beams						
cryopumping						
skimmers						
condensation						
vacuum chambers						
background noise						
argon						
carbon dioxide						
nitrogen						
sulfur dioxide						

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