Thermochemical Generation of CS for CO Chemical Lasers

V. R. Buonadonna* and R. J. Richardson†
McDonnell Douglas Corporation, St. Louis, Mo.

The development of a thermochemical technique for generating large quantities of carbon monosulfide (CS) is reported. The CS is produced from the thermal dissociation of carbon disulfide (CS_2) in a cyanogen-oxygen-CS_2 combustor operating at 1 atm and temperatures in excess of 2500 K. The CS is extracted from the combustor through a Mach 4 supersonic nozzle. The supersonic flow stream was sampled and then analyzed with a quadrupole mass spectrometer, and the data were compared with the results of an equilibrium calculation. Ratios for CS/CS_2 greater than two were measured. Such ratios are sufficient to fuel a CO chemical laser directly with CS.

Introduction

RECENT advances[1,2] in the development of a carbon monosulfide (CS) fueled carbon monoxide (CO) chemical laser capable of high cw power output have created the need for an efficient, scalable method of generating large quantities of CS. In this CS-fueled laser, molecular oxygen (O_2) in combination with CS produces a chemical chain reaction which results in the production of vibrationally excited CO.* The CS molecule is stable in the gas phase; however, a heterogeneous loss reaction[3] precludes accumulation and storage of large quantities of CS. Any practical large-scale CS-fueled CO chemical laser will, therefore, require a CS generator as an integral component.

The most practical method of producing CS for this application is from the thermal dissociation of CS_2.[2,4,5] If the energy for the dissociation can be provided by a thermochemical combustion process, large quantities of CS can be produced from a combustor unrestricted in size, provided that the CS can be extracted from the combustor plenum. Additional chemical species generated by the thermochemical combustion must not interfere with either the chemistry of the laser or the optical gain of CO* produced in the laser.

These considerations have led us to develop a thermochemical combustor using cyanogen (C_2N_2), O_2, and CS_2 as reactants to generate CS. The energy for the dissociation of CS_2 is provided by the energy release from a C_2N_2-O_2 flame,[6,7] and the CS is extracted from the combustor by supersonic expansion through a nozzle.

Theory

Equilibrium calculations were performed on a CDC 6600 computer using a program based on the work of D. R. Cruise,[8] which is capable of calculating adiabatic flame temperatures and equilibrium species concentrations for a large variety of fuels and oxidizers. This program was used in our calculations with only one modification: the heat of formation for CS was changed from 55 to 65 kcal/mole to agree with recently reported values.[5,9]

The adiabatic flame temperatures and species concentrations were calculated for a variety of fuel-oxidizer-CS_2 gas mixtures at 1 atm. Only the results for a C_2N_2-O_2-CS_2 combustion will be presented, since this fuel-oxidizer combination was used for the experimental verification of the thermochemical CS generation technique. The C_2N_2-O_2 flame was chosen as a test case since it does not produce H_2O (a significant CO* deactivator), and it has an extremely high enthalpy.

Figure 1 depicts the calculated adiabatic flame temperature and major product species concentrations for reactant gas mixtures stoichiometric in C_2N_2 and O_2, with varying amounts of CS_2. Important factors to consider are the CS mole fraction and the CS/CS_2 ratio. Since CS_2 acts as a chain terminator in the chain reaction of the CO chemical laser, CS/CS_2 ratios greater than 2 are necessary for a practical device.[2] As indicated in Fig. 1, CS_2 mole fractions less than 0.33 produce CS/CS_2 ratios greater than 2.

Calculations also were performed for gas mixtures rich and lean in C_2N_2. The C_2N_2-lean results yielded unacceptably low CS concentrations. The C_2N_2-rich ($C_2N_2/O_2 \sim 1.2$) calculations are shown in Fig. 2. For the C_2N_2-rich flame, larger CS concentrations and higher CS/CS_2 ratios can be obtained at a lower temperature with less CS_2 reactant than for the stoichiometric case. Carbon from the excess C_2N_2 apparently combines with the sulfur obtained from the decomposition of CS_2 to produce CS. (Note the decrease in S_2 and S for the C_2N_2-rich vs the stoichiometric gas mixture.) From these calculations, the optimum CS/CS_2 ratio with reasonable CS production for the C_2N_2-O_2 combustor was determined to be $C_2N_2/O_2 = 1.2$, with about 0.2 mole fraction of CS_2 reactant. Calculations with mixtures much richer than $C_2N_2/O_2 = 1.2$ predicted the formation of large quantities of solid carbon.

Based on the known rate of the dissociation reaction for CS_2,[10,11] the average half-life of a CS_2 molecule is approximately 2×10^{-4} sec at 100 kPa (760 Torr) and 2500 K; the dwell time for the CS_2 in a practical device must be substantially greater than this to reach equilibrium.

Experiment

Apparatus

A C_2N_2-O_2-CS_2 combustor was constructed to verify experimentally the results of the computer calculations and to determine if CS could be extracted from the high-temperature combustor plenum. The combustor experimental apparatus is illustrated schematically in Fig. 3.

The combustor, fabricated from 304 stainless steel, consisted of a water-cooled plenum, supersonic nozzle, injector head, and injector head plug. The plenum dimensions were 1.0 cm i.d. by 1.5 cm long. The nozzle throat diameter was 0.13 cm with a 19 to 1 area expansion ratio to produce a Mach 4 supersonic exit flow. The supersonic expansion was used to

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Index categories: Combustion in Gases; Lasers; Thermochemistry and Chemical Kinetics.

*Research Scientist, Research Laboratories. Member AIAA; Presently Boeing Aerospace Co., Seattle, Wash.

†Scientist, Research Laboratories.

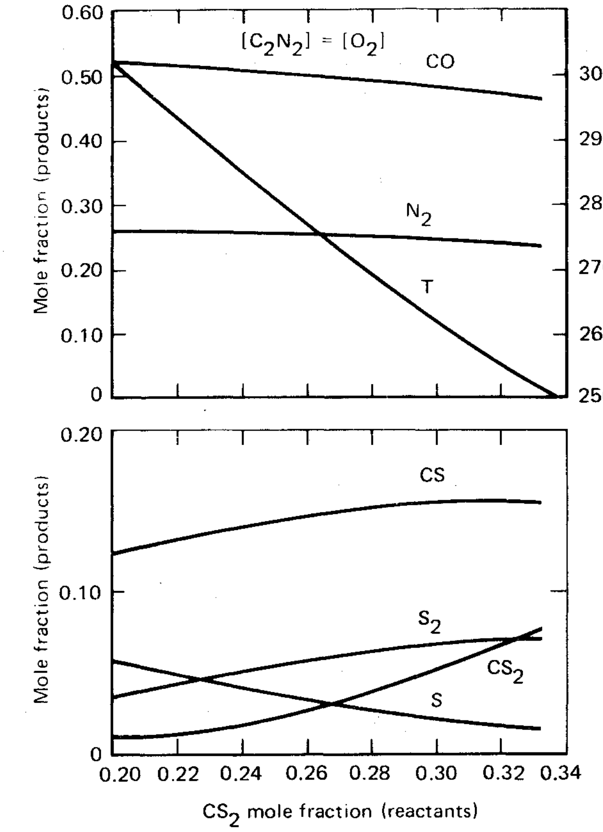

Fig. 1 Predicted products for cyanogen combustion with O_2 plus added CS_2. (Trace species are not shown.)

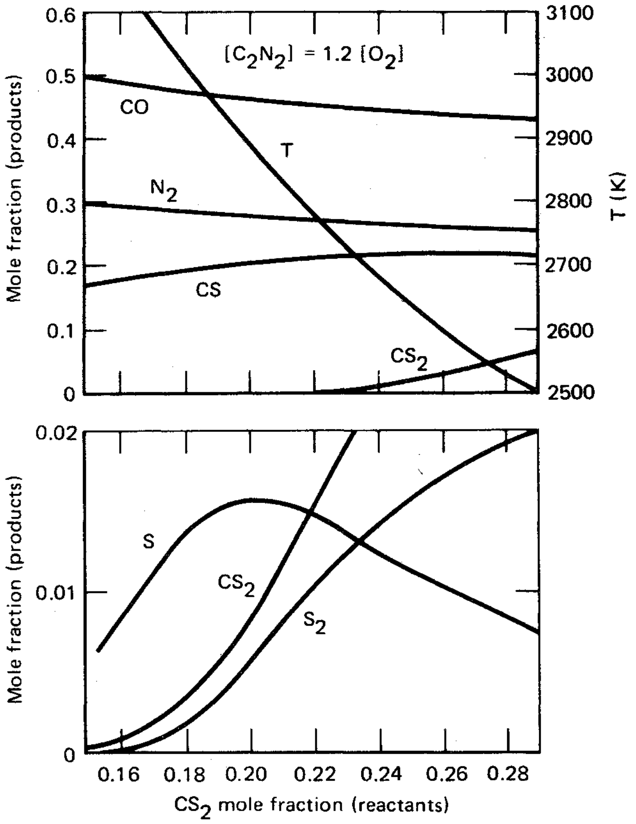

Fig. 2 Predicted products for cyanogen-rich combustion with O_2 plus added CS_2.

"freeze" (i.e., maintain constant chemical composition) the chemistry of the gas flow and to reduce the static exit pressure to a level suitable for the mass spectrometer sampling probe. The injector head contained a small mixing chamber where the CS_2 flow mixed with the C_2N_2-O_2 flow. A premixed gas feed system was chosen to insure a rapid approach to equilibrium in the combustor plenum. The injector head plug contained a sintered metal filter which acted as a flashback arrestor and pressure snubber. The gas was injected into the plenum through four 0.089-cm-diam orifices. The flame was initiated in the plenum by a spark from a Tesla coil. Flow rates of the three component gases were measured with precalibrated electronic flow meters (Matheson series 8116). The pressure in the plenum was monitored with a Bourdon pressure gage. The vacuum in the test cell was maintained by a 8.5-m^3/min (300-f^3/min) rotary vacuum pump (Stokes 412H). Although the data reported here were obtained with a test cell pressure of ~13 Pa (0.1 Torr), no significant variations in product ratios were observed when the pump was throttled [~2.5 kPa(20Torr)].

The C_2N_2 was obtained from Linde (technical grade, 98.5%) and the O_2 from Air Products (extra dry grade, 99.6%); both were used directly without further purification. The CS_2 was obtained from Taylor Chemical (reagent grade) and was degased before use. The supply pressure for the CS_2 was provided by its own vapor pressure (~5 atm) at 100°C.

The primary diagnostic equipment consisted of a flow-stream sampling probe connected to a high-vacuum chamber [$\sim 10^{-4}$ Pa (10^{-6} Torr)] containing a quadrupole mass spectrometer (UTI 100C). Two different mass spectrometer sampling probes were employed to intercept the flow stream: 1) a 0.78-rad (45°) half angle, 304 stainless steel, cone-shaped probe with a sharp 0.015-mm-diam orifice, and 2) a blunt-nosed 2.5-cm-o.d. quartz probe with a 0.015-mm-diam orifice. The steel probe was not cooled and typically was located a few millimeters downstream of the nozzle exit, well upstream of any Mach disk. The 0.78-rad (45°) cone angle ensured that the shock wave in the exit stream was attached to the cone tip. The quartz probe typically was located 8 cm downstream of the nozzle exit. Initial experiments indicated that no significant differences in species concentration profiles were observed for the two different probes for the same operating conditions. The steel probe, however, eroded at the probe tip, and the data reported here were obtained with the quartz probe. Experience with similar sampling techniques to monitor the presence of CS obtained from CS_2/Ar dc discharges[3] indicated that the concentration ratio of CS to CO and N_2 could be determined with this technique. No attempt was made to make quantitative measurements of the concentration of the short-lived species, S and S_2.

Calibration of the Mass Spectrometer

Mass spectrometer calibration factors relative to CS_2 were determined for N_2 in cold flow and static experiments and for CS and CO in a static experiment only. In the cold flow experiment, signal intensities obtained from known mass flows of CS_2 and N_2 through the combustor apparatus were compared to obtain the calibration factor $f_{N_2/CS_2} = 1.5 \pm 0.1$.

In the static experiments, a 5-liter sample bulb was filled sequentially with either N_2 or CO and CS_2, and the pressure in the bulb was determined with a capacitance manometer (MKS type 144 Baratron). The 5-liter bulb was connected to the mass spectrometer vacuum system through an 11-mm-diam quartz tube with a 0.015-mm-diam orifice in the tip. (The pressure loss in the sample bulb resulting from the sampling leak was negligible during the calibration procedure.) The mass spectrometer signal intensity then was determined as a function of pressure in the 5-liter sample bulb for each of the stable species. The mass spectrometer signal intensity for a given species did not depend on the total pressure [7-260 Pa (0.050-2.0 Torr)] in the bulb, and the calibration factors, f_{N_2/CS_2} and f_{CO/CS_2}, did not differ within the error limits from those for N_2 determined from the flow experiment.

The calibration factor f_{CS/CS_2}, for CS, was obtained according to the procedure of Ref. 3. The 5-liter bulb was filled

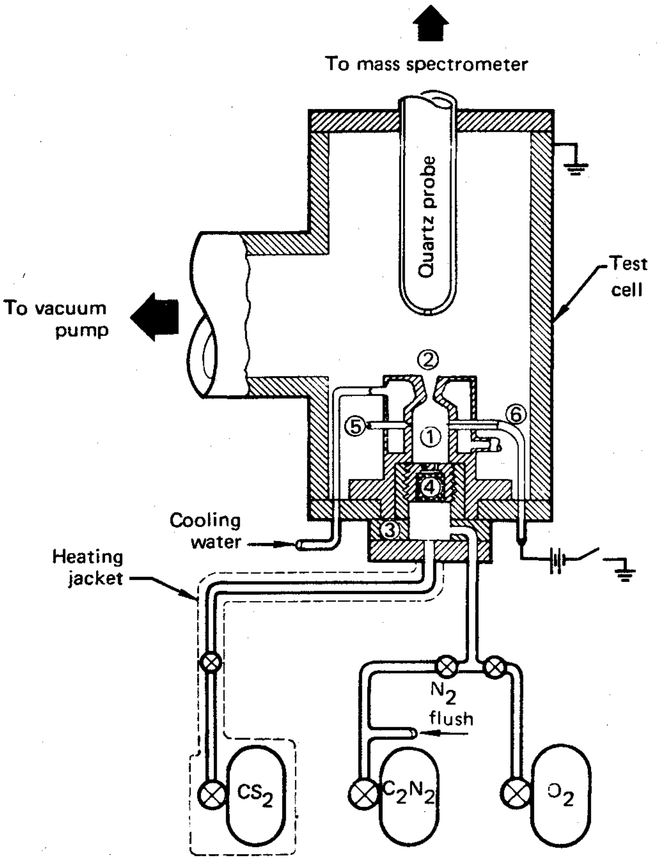

Fig. 3 Schematic of C_2N_2-O_2-CS_2 combustor experiment. Combustor details: 1) plenum, 2) nozzle, 3) injector head, 4) injector head plug, 5) plenum pressure measuring port, and 6) insulated ignitor wire.

with CS obtained from the dissociation of CS_2 in a microwave discharge. Solid products and some of the excess CS_2 were removed from the flowstream by an ethanol slurry trap (156 K). By monitoring the pressure rise and decay and comparing these values with the mass 44 and 76 peak intensities, a sensitivity factor for CS relative to CS_2, $f_{CS/CS_2} = 1.2 \pm 0.2$, was obtained.

Results

The combustor flame was ignited by flowing all three gases (C_2N_2-O_2-CS_2), premixed, into the plenum and sparking the igniter wire with a Tesla coil. The combustor originally was water-cooled, which resulted in excessive heat loss to the water, and little CS was produced. Without cooling water, temperatures near those calculated were obtained, and CS was observed in the flow stream. No adverse effects on the combustor or nozzle walls were observed as a result of excessive heating. Wall temperatures of 680 and 410°C were measured by thermocouples for the downstream and upstream ends of the plenum, respectively.

Plenum temperatures were estimated from the gasdynamic expression for mass flow through a choked nozzle:

$$T_0 = \frac{W}{R}\left[\frac{P_0}{\dot{m}}A^*\sqrt{\gamma}\left(\frac{2}{\gamma+1}\right)\frac{\gamma+1}{2(\gamma-1)}\right]^2 \qquad (1)$$

where W = molecular weight of gas, R = universal gas constant, P_0 = plenum stagnation pressure, $\dot{m}$ = mass flow, A^* = throat area, and γ = ratio of specific heats. The average W and γ of the gas were taken to be 35 and 1.3, respectively, as suggested by the equilibrium calculations. Measurements of P_0 were nominally 1 atm. The combined input mass flow for C_2N_2, O_2, and CS_2 was typically 0.1 g/sec. The throat area A^* was determined before each run by flowing room temperature N_2 through the nozzle and measuring P_0 and $\dot{m}$. The N_2 calibration flow was adjusted in such a way that the Reynolds number (based on plenum conditions and nozzle throat radius) was approximately equal to that for the combustor flame. The measured throat area A^* was valid only for the first few minutes of operation, because thermal effects and carbon deposits would soon alter the throat area. Mass flow measurements were considered accurate to ±2% for the C_2N_2 and O_2 flows and to ±10% for the CS_2 flow. For typical operating conditions, the temperature estimated on the basis of Eq. (1) was 2750±500 K. This temperature was consistent with calculated adiabatic flame temperature and estimated heat loss resulting from conduction from the hot plenum walls to the cool test-cell flange. Heat loss, based on the observed plenum-wall upstream and downstream temperatures and one-dimensional heat conduction, was calculated to be approximately 30 W. This represents a 10% loss of flow enthalpy based on calculated stagnation enthalpy and measured mass flow rates.

The average dwell time ($\sim 2\times10^{-3}$ sec) for a molecule in the combustor can be determined from the flow rate (~ 0.1 g/sec) through the combustor and the pressure [~ 100 kPa (760 Torr)], volume (~ 1.1 cm^3), and temperature of the plenum (~ 2500 K). Based on the known rate of the dissociation reaction for CS_2,[10,11] the average half-life ($\sim 2\times10^{-4}$ sec) of a CS_2 molecule is an order of magnitude shorter than the dwell time under the plenum conditions. The CS_2 should, therefore, reach equilibrium in transit through the combustor, since it is premixed with the C_2N_2 and O_2.

A typical mass scan from the mass spectrometer is illustrated in Fig. 4 for input combustor flows of $C_2N_2 = 1100$ std. cm^3/min, $O_2 = 1000$ std. cm^3/min, and $CS_2 = 375$ std. cm^3/min. The principal end products for these input conditions are CO and N_2 (mass 28), CS (mass 44), and CS_2 (mass 76). The signal at mass 32 is a sulfur cracking peak from CS. The magnitudes of this cracking peak and the peak at mass 46 from the CS with a sulfur isotope of mass 34 confirm that the peak at 44 is due to CS and not CO_2. Traces of $C_2N_2(52)$ and $S_2(64)$ also are visible in the mass scan. (The small peak at mass 18 is from H_2O which was the major background gas in the mass spectrometer vacuum system which was not "baked out" prior to the experiment.) Mass scans taken under stoichiometric C_2N_2-O_2 conditions showed the expected decrease in the CS signal and increase in the S_2 signal. Under very oxygen-rich conditions, CO_2 was observed, as well as SO_2, from a CS_2-O_2 flame. The ignition of the CS_2-O_2 flame in the oxygen-rich C_2N_2-O_2-CS_2 mixtures was observed to occur abruptly, indicating that the chain reaction for CS_2-O_2 is completely independent of the C_2N_2-O_2 chain.

A portion of the mass 44 signal is caused by a cracking peak from CS_2. Mass spectrometer data, obtained by flowing N_2 and CS_2 (no flame) through the combustor, indicated that 47% (±5%) of the CS_2 signal at 76 should be subtracted from the mass 44 signal to obtain the CS signal strength. Consequently, the CS/CS_2 and $CS/(CO+N_2)$ ratios were obtained as follows:

$$\frac{CS}{CS_2} = \frac{I(44) - 0.47I(76)}{I(76)}\,\frac{1}{f_{CS/CS_2}}$$

$$\frac{CS}{CO+N_2} = \frac{I(44) - 0.47I(76)}{I(28)}\,\frac{f_{N_2/CS_2}}{f_{CS/CS_2}}$$

where $I(xx)$ is the mass spectrometer signal strength at mass xx, and f_{N_2/CS_2} and f_{CS/CS_2} are the mass spectrometer calibration factors for N_2 to CS_2 (1.5±0.1) and CS to CS_2 (1.2±0.2), respectively,

The experimentally determined CS/CS_2 and $CS/(CO+N_2)$ ratios are plotted in Figs. 5 and 6 as a function of CS_2 reactant mole fraction for $C_2N_2/O_2 \simeq 1.00$ and 1.10, respectively. The theoretical values for these ratios, determined

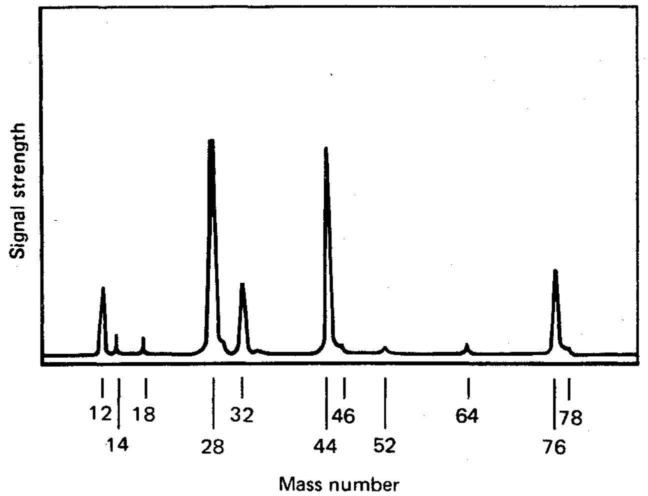

Fig. 4 Mass spectrometer scan of the C_2N_2-O_2-CS_2 combustor products. Reactant mole fractions were $C_2N_2/O_2/CS_2 = 0.44/0.41/0.15$ (the mass 28 signal is truncated).

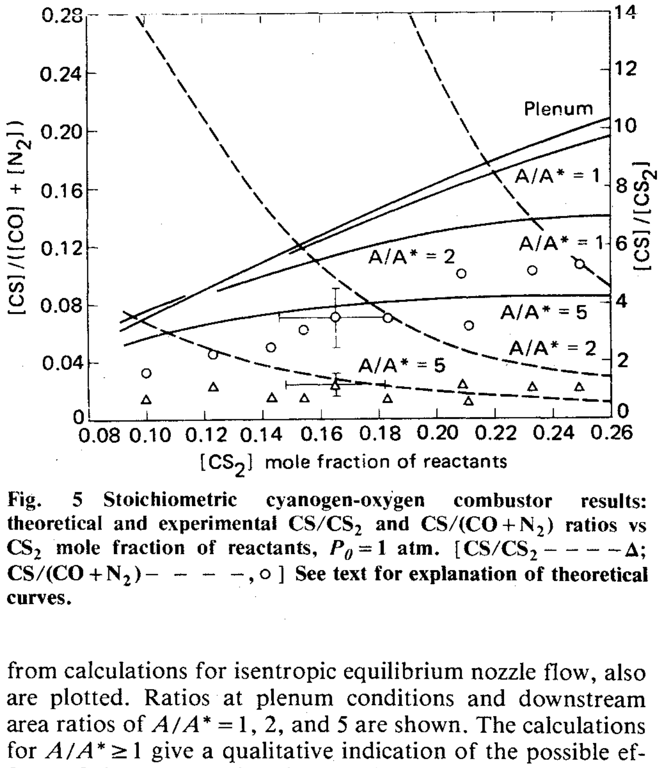

Fig. 5 Stoichiometric cyanogen-oxygen combustor results: theoretical and experimental CS/CS_2 and $CS/(CO+N_2)$ ratios vs CS_2 mole fraction of reactants, $P_0 = 1$ atm. [CS/CS_2 – – – – Δ; $CS/(CO+N_2)$ – – – –, o] See text for explanation of theoretical curves.

from calculations for isentropic equilibrium nozzle flow, also are plotted. Ratios at plenum conditions and downstream area ratios of $A/A^* = 1$, 2, and 5 are shown. The calculations for $A/A^* \geq 1$ give a qualitative indication of the possible effects of downstream freezing on the chemistry of the combustor products. No heat transfer losses are considered in these calculations.

The data for the C_2N_2-rich reactant mixture (Fig. 6) clearly show the predicted increase in the CS/CS_2 and $CS/(CO+N_2)$ ratios compared with the stoichiometric mixtures (Fig. 5). The data for all the mixtures suggest that the combustor chemisty is freezing at a location downstream of the nozzle throat, as characterized by the equilibrium flow calculations for $A/A^* = 2$ and 5. A maximum in the $CS/(CO+N_2)$ ratio occurs at a CS_2 reactant mole fraction of 0.17 for both cyanogen-rich mixtures. This maximum is near the maximum for the $A/A^* = 5$ calculation, again suggesting a downstream freezing of the combustor products.

The indications of downstream freezing are probably artificially caused by the mass spectrometer sampling system. Effects of the sampling process such as the bow shock in front of the quartz sampling probe, location of the Mach disk in the nozzle exit flow, and wall collisions inside the mass spectrometer vacuum system may alter the concentration ratios of the species detected from those present in the flow stream. For example, using a modulated-beam sampling technique, Peng and Lilenfeld[5] have found that the CS/CS_2 ratio in the residual gas of their mass spectrometer vacuum system was less than that found in the beam formed from the free jet expansion from a vitreous carbon oven used to dissociate CS_2 thermally in the presence of Ar. In addition, since the rate of the heterogeneous loss reaction increases with increasing temperature, the hot probe sampling orifice walls affect the CS/CS_2 ratio differently from the cold walls of the orifice used in the room-temperature static bulb calibration experiment. Most of these effects are expected to reduce the measured CS/CS_2 ratio from that actually present in the flow stream. Since the data clearly indicate that CS is produced in the combustor plenum and can be extracted successfully with CS/CS_2 ratios greater than 2, the substantial improvements in the mass spectrometer sampling system necessary to obtain more accurate quantitative sampling were not made.

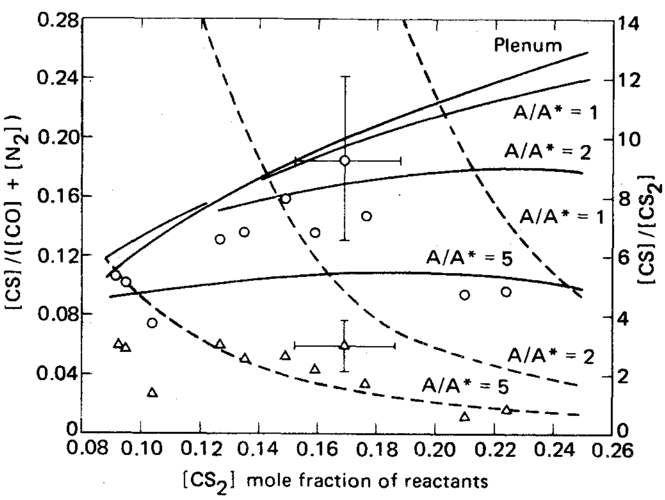

Fig. 6 Cyanogen-rich combustor results: theoretical and experimental CS/CS_2 and $CS/(CO+N_2)$ ratios vs CS_2 mole fraction of reactants for $C_2N_2/O_2 = 1.10$, $P_0 = 1$ atm. [CS/CS_2 – – – –, Δ; $CS/(CO+N_2)$ – – – –, o] See text for explanation of theoretical curves.

Conclusions

The feasibility of generating and extracting CS from a thermochemical combustor operating at 1 atm has been demonstrated. A C_2N_2-O_2-CS_2 flame has been achieved in a small-scale combustor, and the successful generation and detection of CS have been observed. This investigation provides experimental evidence that a CS-generating combustor has the potential to operate a CS-fueled CO chemical laser.

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