Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DATE: January 18, 1982
IN REPLY REFER TO: AP-4-82:08
MAIL STOP: 567
TELEPHONE: 505-667-7121

MASTER

Dr. V. P. Kothari
Program Manager
Morgantown Energy Technology Center
P. O. Box 880
Morgantown, WV 26505

Dear Dr. Kothari:

Enclosed is our quarterly progress report for the Coal Gasification Instrumentation Program (PR 11734). The report covers the period from October 1, 1981 to December 31, 1981.

Sincerely yours,

Allen Hartford

Allen Hartford, Jr.
AP-4 Group Leader

AHJ:pag

xc: AP-4 MC File
CRMO (2) w/o enclosure
V. P. Kothari (5 enclosures)
J. Kovach, METC
M. Perlswieg, DOE
D. Smoot, BYU
J. H. Birely, ADCEL, MS 102
P. Gaetzens, PL, MS 717
D. C. Cartwright, AP-DO
H. Newman, AP-1
T. Loree, AP-2
F. Wampler, AP-4
R. McDowell, AP-4
R. Holland, AP-4
D. Taylor, AP-4
W. Miller, ADEP, MS 178
L. S. Germain, DAD/AE, MS 357
E. Leonard, DAD/AES, MS 682
F. Finch, ADEP, MS 178
J. Ackerman, ANL
J. Carr, DOE, Germantown
DOE Procurement & Property Management Section
DOE Technical Information Center

DOE/TIC--2006976

DE82 006976

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

COAL-GASIFICATION-INSTRUMENTATION
PROGRAM (PR 11734)

Quarterly Progress Report

For the Period

October 1, 1981 through December 31, 1981

by

The University of California, Los Alamos National Laboratory
Applied Photochemistry Division
P. O. Box 1663
Los Alamos, NM 87545

I. COHERENT RAMAN DIAGNOSTICS FOR COAL GASIFIERS

Coherent anti-Stokes Raman spectroscopy (CARS) is a promising spectroscopic technique for on-line, real-time monitoring of species concentrations and temperature in the gas-stream of coal gasifiers. During the past quarter we have continued to extend our data base for the purpose of improving minority species detectabilities and determining majority species sensitivities under various conditions of gas composition, total pressure, and temperature. We have also begun preparations for a CARS field test on the METC coal gasifier scheduled for winter, 1982.

Under some conditions, minority species detectability can be improved by using CARS lasers possessing higher spectral resolution. Therefore, we purchased a manufacturer-installed line-narrowing option for our Quantel YAG laser, which (according to the manufacturer) also required installation of a transverse-mode "Extrapolarex" upgrade for the YAG laser. After the laser modification, we found the 532-nm focal plane intensity to be about the same or perhaps somewhat lower than before, but the 532-nm spectral linewidth was significantly reduced, from 1.0 cm^{-1} to $<0.15 \text{ cm}^{-1}$ (spectrometer-limited). The CARS signatures now exhibit features with linewidths as narrow as 0.2 cm^{-1} , which corresponds to the dye laser resolution. We are presently determining the conditions under which this higher spectral resolution improves minority species detectability. The CARS signatures of pure H_2S and NH_3 at 15 psi do indeed exhibit narrower features. Whether this improvement in spectral resolution yields enhanced detectability, especially at the higher background pressures anticipated in the METC field tests, will be evaluated prior to the field tests. Based on the results of these tests, we can install a similar line-narrowing option in the QuantaRay YAG laser planned for use in the field tests.

We have proposed and begun to investigate a single-ended CARS scheme that would significantly simplify CARS access to gas regions of interest. In this approach only a single optical port is required rather than two diametrically opposing windows. Collinear CARS (or perhaps BOXCARS) would be initiated as before by focusing the pump and Stokes laser beams through the entrance window. A small fraction of the generated anti-Stokes beam would be Mie-scattered by the naturally resident particles back through the entrance window to a slightly off-axis focusing mirror and spectrometer. The normalization required for concentration measurements must be provided by measurements at two or more frequencies, as employed in the Differential Absorption Lidar (DIAL) technique. An additional advantage of this single-ended CARS scheme is that the signal-to-noise ratio, and hence detectability of minority species, should be less degraded by fluctuations in particulate loading. These fluctuations, proved to be the limiting factor in determining detectability during our field experiments on the BYU gasifier. Moreover, for determination of minority species concentrations the absolute back-scattering efficiency and the geometrical collection efficiency need not be measured, thanks to the CARS nonresonant susceptibility. The major concern in proving this technique is whether the magnitude of the anti-Stokes signal will be adequate. Our investigations thus far have utilized quite crude collection geometries, so we have not yet obtained the signal.

Among the minority species of interest, some of the Raman cross sections are not well known. Moreover, among the majority species some of the weak Raman cross sections are not known, but could cause interference with CARS measurements of minority species. Therefore, we have measured some of these unknown Raman cross sections and verified some known cross sections by spontaneous Raman scattering. In these studies cw Krypton-ion laser operating at 530.9 nm (1-W output) was used as the pump source in order to match the 532.1-nm CARS pump wavelength derived from a Nd:YAG laser.

A quartz cell mounted in front of the entrance slit of a Spex 14018 0.85-m double monochromator was evacuated and filled to 15 psi absolute with each gas in turn. The Raman spectra, taken using a triangular slit function of 4 cm^{-1} FWHM and an RCA C31034 cooled photomultiplier with flat responsivity, were compared to that of N_2 . The Raman differential cross section for N_2 , $d\sigma/d\Omega$ (N_2 , 532 nm), has been determined absolutely to be $0.37 \times 10^{-30}\text{ cm}^2/\text{sr}$. Some previously reported weak Raman bands were below our limit of detection ($0.03 \times 10^{-30}\text{ cm}^2/\text{sr}$), but probably would not cause interference in the CARS signal. Several Raman bands were partially spectrally resolved, notably H_2S with $\Delta\nu_{\text{FWHM}} = 6.7\text{ cm}^{-1}$ and OCS with a pair of red-shifted secondary peaks, the smaller of which could be attributed to the ^{34}S isotope. Agreement with previously tabulated values was best achieved by considering the integrated Raman strengths (areas), as would be measured with much lower resolution ($\sim 20\text{ cm}^{-1}$). The agreement was generally within $\pm 20\%$. The results of these measurements are given in Table I.

We have recently begun investigations of the CARS spectrum of NH_3 using the upgraded Quantel laser system. The CARS spectrum of the ν_1 vibrational mode of NH_3 at $\sim 3334\text{ cm}^{-1}$ is shown in Fig. 1 for pure NH_3 at 5 psi and room temperature. It exhibits substantial rotational structure. By running back-to-back spectra the peak CARS susceptibility of NH_3 with spectral resolution of 0.2 cm^{-1} was found to be equal to that of H_2S (to within 20%). The procedure involved tuning the Rhodamine 640 dye laser from 618 nm to 647 nm, slightly adjusting the beam deviation due to the dispersing prism, and replacing the band-pass filter that eliminates residual low-angle-scattered pump light at the photodiode detector. The similarity of CARS signals of NH_3 and H_2S was unexpected based upon tabulated Raman cross sections (see Table I), from which a CARS intensity ratio $I_{\text{AS}}(\text{NH}_3)/I_{\text{AS}}(\text{H}_2\text{S}) = (3.5/6.5)^2 = 0.29$ would have been

NH₃ CARS SPECTRUM

Figure 1

AP-4-82:08
January 12, 1982
Page 5

TABLE I

Molecule:	N ₂	O ₂	OCS		H ₂ S	NH ₃	CO ₂		CH ₄				
Vibrational mode:	--	--	v ₁	v ₃	v ₁	v ₁	v ₁	2v ₂	v ₁	v ₃	2v ₂	v ₂	v ₄
Raman shift(cm ⁻¹):	2331	1556	859	2079	2611	3334	1388	1286	2914	3020	3070	1526	1306
Ratio to N ₂ (this work):	1.0	1.18	6.0	b	7.2	3.8	1.98	1.32	8.1	0.2	b	b	b
Ratio to N ₂ (tabulated ^a):	1.0	1.27	c	c	6.5	3.5	1.5	c	7.0	4.6	c	c	c

^aA. C. Eckbreth, P. A. Bonczyk, and J. F. Verdick, Progress in Energy and Combustion Science, Table 5 (1978).

^bBelow limit of detectability.

^cNot previously measured.

predicted. The observed CARS intensity ratio of 1.0 ± 0.2 can be explained by the higher spectral concentration of Raman strength in NH_3 . The H_2S CARS spectral envelope of 6.3 cm^{-1} FWHM compares to the spontaneous Raman width observed above of 6.7 cm^{-1} , so it is reasonable that the NH_3 CARS spectral envelope of 3.9 cm^{-1} would correspond to an unresolved spontaneous Raman spectrum taken with 4 cm^{-1} spectral resolution.

We have also been preparing for the scheduled upcoming CARS field tests at METC. Following the visit to METC by Dave Taylor and John Weinbrecht on December 8, we have designed CARS window mounts. These mounts incorporate two METC-supplied high-temperature, high-pressure ball valves in series and appropriate gas-purge channels. The window mounts are presently being fabricated in the Los Alamos Shops. Fused-silica windows (2-in-diam $\times$ 0.5 in) to be used for both CARS and LIBS are scheduled for delivery January 11, 1982. Moreover, as indicated by the example discussed above regarding the potential benefits of higher spectral resolution, we are extending our CARS data base to provide more realistic laboratory simulations of the conditions anticipated at METC.

II. INFRARED SPECTROSCOPY OF COAL GASIFIER PRODUCTS

A. Introduction

This quarter we have investigated the use of 10-cm optical pathlengths in the infrared spectroscopic analysis of gas mixtures typical of coal gasifier product streams. We have established a reasonable lower concentration limit for the analysis of NH_3 in hot (220°C) mixtures containing substantial amounts of H_2O , CO_2 , and CH_4 . In the process, we have analyzed for CO_2 and H_2O by subtraction of weak spectral features and have examined the effect on the subtraction due to a small (20°C) temperature difference between conditions for reference and sample spectra. We note a possible concentration dependence of the H_2O spectrum not anticipated for 220°C .

This report includes a summary of estimated lower concentration limits for detection and analysis of minority species in coal gasifier product gases at $\sim 200^{\circ}\text{C}$ and 300 psi, with optimum optical pathlengths.

B. Analysis for NH_3 in Hot Gas Mixtures Containing CO_2 and H_2O

In the previous quarter¹ we simulated the spectrum of 30 ppm of NH_3 in a mixture with 6% CH_4 , 19.5% CO_2 , 50.2% CO , and 24.3% H_2 at room temperature, 150 psi, and 10-cm pathlength, by simply adding the NH_3 absorbance spectrum to that of a mixture containing the other compounds. The Q branches of the NH_3 ν_2 band near 950 cm^{-1} were readily distinguished from the background and noise, and 30 ppm NH_3 was taken as an estimated lower limit for detection of NH_3 by infrared spectroscopy of a gasifier product mixture. It was noted that this limit might have to be revised upward if the hot gasifier product had much stronger absorption or additional confusing spectral features near 950 cm^{-1} .

Because the NH_3 features were expected to broaden at higher temperature as well as the possibility of H_2O interference and the potential interference of a CO_2 "hot" band, it was thought worthwhile to make a more realistic simulation by analyzing for NH_3 in hot mixtures containing CO_2 and H_2O . In preparation for the experiment and for general reference, spectra of 18% CO_2 in N_2 , 30% CO_2 in N_2 , 6.0% CH_4 in N_2 , and 0.10% NH_3 in N_2 were obtained for a temperature of 220°C , total pressures of 150, 300, and 450 psi, and 10-cm optical pathlength.

Spectra of the 300-psi reference spectra for the CO_2 and H_2O are shown in Figs. 2 and 3 respectively. The CH_4 did not cause significant spectral interference in the NH_3 analysis, and no CH_4 reference spectrum is displayed here. A portion of the "hot" NH_3 reference spectrum is shown in Fig. 4. Note that in the H_2O reference spectrum of Fig. 3, a CO_2 band appears near 2350 cm^{-1} , which indicates about 0.02% CO_2 impurity probably retained in the cell from a previous run.

SPECTRUM OF 18% CO₂ IN N₂

10 cm PATH, 300 psi, 220 °C

Figure 2

SPECTRUM OF 30% H₂O IN N₂
10 cm PATH, 300 psi, 220 °C

Figure 3

1040 ppm NH_3 IN N_2
300 psi, 220 °C
10-cm PATH

Figure 4

Because it was anticipated that the addition of H_2O might result in NH_3 loss through reaction, the NH_3 analysis was first performed with a mixture of 17.0% CO_2 , 8.85% CH_4 , and 32 ppm NH_3 in N_2 . A spectrum obtained with this mixture at 300 psi and 220°C is shown in Fig. 5. An absorbance spectrum of the region near 950 cm^{-1} for the same mixture is shown in Fig. 6(b). Part (a) of Fig. 6 shows the NH_3 reference spectrum of Fig. 3, with the absorbance scale reversed to call attention to the NH_3 absorbance appearing as "shoulders" on the CO_2 ($\nu_3 - \nu_1$) difference band shown in part (b). An analysis for NH_3 was performed by subtraction of the NH_3 absorbance to remove the "shoulders," with the result is shown in Fig. 6(c). The multiplier of 0.025 times the absorbance of the reference spectrum of NH_3 corresponds to 26 ppm NH_3 in the sample mixture, which is in fair agreement with the mix value of 32 ppm.

An alternative procedure is illustrated in Fig. 7, where the CO_2 reference spectrum is subtracted from the original spectrum of Fig. 7(a) to give the spectrum of 7(b), clearly revealing the NH_3 Q branches. Subtraction of 0.024 times the NH_3 reference spectrum (Fig. 5) gives Fig. 7(c). The agreement with the subtraction of Fig. 6 suggests that the difference from the mix value of 32 ppm NH_3 is the result of a loss of NH_3 in the sample or a mixing error, and not an error in the subtraction. Note that the CO_2 absorbance subtracted, corresponding to 16.3% CO_2 , agrees well with the mix value of 17%. The oscillation in the residual spectrum of Fig. 7(c) appears due to a weak interference pattern of uncertain origin.

To see whether H_2O would cause serious spectral interference, a mixture of 83 ppm NH_3 , 30% H_2O , 15.6% CO_2 , and 7.3% CH_4 was prepared. The transmission spectrum of the mixture is shown in Fig. 8, and the absorbance spectrum in the region of interest is shown in Fig. 9(a). The NH_3 features appear to be cast into relief by the H_2O absorbance so that both Q branches are obvious in Fig. 9(a). The H_2O absorbance was subtracted, and the result is

MIX NO. 52:

17.0% CO₂, 8.85% CH₄, 32 ppm NH₃ IN N₂

10 cm PATH, 300 psi, 220 °C

Figure 5

ANALYSIS FOR NH_3 IN THE PRESENCE OF CO_2

10-cm PATH, 300 psi, 220° C

Figure 6

ANALYSIS FOR NH_3 IN THE PRESENCE OF CO_2 10-cm PATH, 300 psi, 220° C

Figure 7

MIX 60: 30% H₂O, 15.6% CO₂, 7.3% CH₄ IN N₂,
83 ppm NH₃ (MIX), 34 ppm NH₃ (ANALYSIS)
10 cm PATH, 300 psi, 220 °C

Figure 8

ANALYSIS FOR NH_3 IN THE PRESENCE OF CO_2 , H_2O 10-cm PATH, 300psi, 220°C

AP-4-82:08
January 12, 1982
Page 17

Figure 9

displayed in Fig. 9(b). The NH_3 Q branches are still observed but are less obvious in Fig. 9(b). Subtraction of CO_2 gives Fig. 9(c), which shows the NH_3 Q branches. Subtraction of NH_3 gives Fig. 9(d). Again, the background in (d) is not flat, for the same reason as that given to reconcile Fig. 8(c). Here the subtraction yields 33 ppm NH_3 . This is in poor agreement with the mix value of 83 ppm NH_3 . The low value is almost certainly due to loss of NH_3 through reactions that occur in the presence of the H_2O . We have established the integrated absorbance in the NH_3 ν_2 band as $600 \pm 30 \text{ cm}^{-1}$ per cm-atm at 0°C ,² and the NH_3 reference spectrum used here agrees with this value. We are therefore confident in the analysis and conclude that about 30 ppm is still a reasonable lower limit for analysis of NH_3 in the presence of CO_2 and H_2O in concentrations typical of a coal gasifier product.

C. Analysis for CO_2 and H_2O by Subtraction of Weak Spectral Features

It should be noted that the H_2O and CO_2 subtractions for Fig. 9 yielded 28% H_2O and 17.6% CO_2 , in reasonably good agreement with the mix values of 30% and 15.6%. Also, the subtraction of CO_2 absorbance for Fig. 7(b) yielded 16.3% CO_2 , in good agreement with the mix value of 17% CO_2 . This result is encouraging for the analysis for the majority species in a long optical path by subtraction of weak spectral features. It should be noted, however, that the H_2O and CO_2 concentrations for the sample are nearly identical to those in the reference mixes, so that conditions are favorable for the analysis for these compounds.

Because of the appearance of the H_2O reference spectra in Fig. 3, which shows a near continuum in the H_2O rotational spectra near $600\text{-}800 \text{ cm}^{-1}$, we are concerned about the possibility of absorption by water polymers. These polymers would make the relative spectral intensities depend strongly on concentration and temperature, in which case the subtraction procedure might require a close

match between concentrations and temperatures of sample and reference spectra. To test the dependence on concentration and temperature for H_2O , reference spectra of a mixture of 15% H_2O in N_2 have been obtained, for 220°C and total pressures of 150, 300, and 450 psi. One such spectrum (for 300 psi) is shown in Fig. 10. Reference spectra at the same pressures (not shown) have been obtained for 30% H_2O in N_2 at 200°C. Results of subtractions from the spectra of 30% H_2O in N_2 at 220°C are shown in Figs. 11 and 12.

The spectrum of Fig. 11(a) shows the H_2O (220°C, 450 psi) reference spectrum of the mixture used for Fig. 3, between 650 and 1350 cm^{-1} , and 11(b) shows the result of subtraction of a 200°C spectrum of a mixture at the same total pressure and with the same H_2O density (28.8% H_2O). The subtraction yielded a relatively flat residual spectrum over the region, indicating that the 20°C temperature difference is not very important. Note that the ν_2 band near 667 cm^{-1} of the CO_2 impurity in the 220°C sample is revealed by the subtraction.

The subtraction of the 15% H_2O reference from the 30% H_2O reference (both 220°C) is shown in Fig. 11. The slight "overshoot" of the peak near 910 cm^{-1} and the "plateau" remaining between 900 and 965 cm^{-1} in Fig. 12(c) probably are effects of the concentration dependence; however, the multiplier used in the subtraction corresponds to $1.8 \times 15\% = 27\%$, only 10% below the mix value for Fig. 12(a) of 30%. The result of this experiment indicates that, although there may be a concentration dependence for H_2O , a concentration match within a factor of two should be adequate for an H_2O analysis via subtraction of its weaker spectral features, and for analysis for NH_3 in this spectral region.

SPECTRUM OF 15% H₂O IN N₂

10 cm PATH, 300 psi, 220 °C

Figure 10

H₂O SUBTRACTION WITH TWO DIFFERENT TEMPERATURES (220-200°C)

Figure 11

H₂O SUBTRACTION - WEAK FEATURES

Figure 12

D. Estimated Lower Concentration Limits for Detection of Minority Species:
A Summary.

Based on the work reported here for NH_3 and on work done at Los Alamos previously, we have summarized in Table II the estimated lower limits of concentration for which specific minority species can be detected and their concentrations determined by ir spectroscopy of mixtures typical of a coal gasifier product gas.

Table II lists the species of interest, the bands selected for the analyses and their approximate frequencies, the interfering major gasifier product species, and their approximate concentrations. Based on our work, Table II also presents what appears to be the optimum optical pathlength. The detectivity quoted is appropriate for this pathlength and the temperature and total pressure indicated. However, in most cases extending the pressure range to 150-450 psi or changing the pathlength by 50% would not change the detectivity estimate. The temperature indicated is near the upper limit of our observations, and analysis would be somewhat easier at lower temperatures and perhaps more difficult at higher temperature.

In some cases numbers are enclosed in parentheses. For the pathlengths quoted, the parentheses indicate that we have not made observations at the particular pathlength. However, we estimate that the quoted pathlengths are more appropriate than those that were actually used. Parentheses on the detectivity indicate that it is based on room-temperature observations, but that some allowances have been made for effects such as decrease in density or band spreading at higher temperature.

The work on NO_2 is in progress but is not yet complete. SO_3 is a compound that we had intended to investigate. However, it appears that SO_3 is not likely to be present in the gasifier product. Consequently, we are not pursuing

TABLE II
FTIR ANALYSIS FOR COAL GAS MINORITY SPECIES

<u>Species</u>	<u>Band</u>	<u>Frequency (cm⁻¹)</u>	<u>Interference</u>	<u>Optimum Pathlength (cm)</u>	<u>Detectivity (300 psi, 200°C)</u>
COS	ν_3	2058	CO (20%)	0.2	100 ppm
SO ₂	ν_1	1149	CH ₄ (10%)	(2.0) ^a	100 ppm
N ₂ O	ν_3	2222	CO(20%), CO ₂ (20%)	1.0	500 ppm
N ₂ O	2 ν_1	2561	CH ₄	10.0	(200 ppm) ^b
NO ₂	ν_3	1615	H ₂ O	(2.0) ^a	--
NO	(0-1)	1875	H ₂ O(39%)	(2.0) ^a	(500 ppm) ^b
NH ₃	ν_2	950	CO ₂ (17%), H ₂ O(30%)	10.0	30 ppm
H ₂ S	ν_1	2680	CH ₄ (5-10%)	(20.0) ^a	(3%) ^b
SO ₃	--	--	--	--	--
(HCN)	--	--	--	--	--

^aParentheses indicate estimated optimum pathlength.

^bParentheses indicate only room-temperature measurements.

SO₃ detection. Although HCN is not one of the compounds that we had initially planned to study, but it appears to be an important species. Therefore, we are proceeding with the analysis of HCN.

III. LASER-INDUCED BREAKDOWN SPECTROSCOPY

A new task for LIBS this fiscal year is the detection of total sulfur, an interesting problem that has taken us in a new direction. Initial trials with LIBS and TRELIBS in SO₂ demonstrated poor sensitivity for sulfur, on the order of 100 ppm detectability. This was corroborated by others in parallel studies on sulfur-bearing organic molecules. Interestingly, only ionic S II was found to emit spectra; the expected strong neutral S I lines were not observed. Thus the usual enhanced detectability with time-delayed TRELIBS spectra is not realized for sulfur.

Due to the difficulty of sulfur detection with the basic LIBS process itself, a departure from the normal technique was required. We propose to pursue a double-pulsed approach involving laser-induced breakdown followed by fluorescence excitation with a second laser pulse. This will combine an initial laser pulse, which in our normal manner vaporizes the sample and reduces all the constituents to elemental form, while the second laser pulse is tuned to a favorable absorption in the element of interest. The selectively excited element will then radiate at a unique identifying wavelength. By itself, Laser-Induced Fluorescence is a well-established technique, and has been shown to have excellent sensitivity for the detection of both molecular and atomic species.

As a preliminary to a two-laser experiment, as described above, we tried two pulses of 1.06- μ m light from a single Nd:YAG laser, in which the Q-switch was adjusted to yield two output pulses separated by some 50 μ s. The first

pulse had just enough energy to break down air at the focus of a 10-cm lens, while the second pulse had about 20% as much energy. Thus, the second pulse did not produce breakdown again, but merely pumped the species present in the plasma after 50 μ s. The results of this experiment were quite favorable. The usual N II, N I, O II, and O I lines were seen from the initial breakdown with the normal time dependences. After some 20 μ s, all spectral emission terminated and nothing was observed until the second pulse arrived at about 50 μ s. At this point the spectra were regenerated, dominated by neutral emission, and lasted for another 15-20 μ s. We concluded from this nonselective pumping experiment that the constituents of the plasma can indeed be pumped late in time without having to produce another breakdown, and with minimal destruction or modification of the species present.

The proper approach to this type of double-pulse experiment requires two lasers and a timing system to introduce the appropriate delay. We have assembled such an apparatus, with the first laser being a Molelectron Nd:YAG laser, and the second a Quanta-Ray Nd:YAG configured to pump a dye laser. The dye laser will produce the required tuned wavelength to excite the species of interest. While the individual components of the system have been tested and run, at this time the system as a whole has not yet been tried.

This effort, and verification runs for our Na working curves, were slowed by the loss of our time-gated Tracor Northern detector array. We had borrowed that unit from another Division within the laboratory, and had to return it. At present, we are working on our own time-gating system for an ungated array. Our technique for doing this involves using a vacuum photodiode as a shutter, which should result in improved uv response over than the commercial detector.

The utility of the double-pulse technique is not limited to inducing fluorescence, which is of necessity a detection scheme for a single species.

A nonselective excitation, such as the two 1.06- μ m pulses used in the preliminary trials, should retain the LIBS advantage of exciting all species present. Separating the breakdown and probe pulses will provide more uniform starting samples in particulate-laden flows, thus reducing the shot-to-shot variations in spectral amplitudes. It should then require less time to gather statistically valid data from such samples, which currently require runs of hundreds of shots, or tens of seconds to obtain a reliable average value. One can envision situations involving feedback control in which increasing the reality of "real-time" detection will be of interest.

FIGURE CAPTIONS

- Fig. 1. NH_3 CARS spectrum.
- Fig. 2. Infrared transmission spectrum of 18% CO_2 in N_2 . Pressure is 300 psi, temperature 220°C , and optical pathlength 10 cm. Spectral resolution is 0.24 cm^{-1} .
- Fig. 3. Infrared transmission spectrum of 30% H_2O in N_2 . Pressure is 300 psi, temperature 220°C , and optical pathlength 10 cm. Spectral resolution is 0.24 cm^{-1} .
- Fig. 4. Spectrum of a mixture of 17.0% CO_2 , 8.85% CH_4 , and 32 ppm NH_3 in N_2 . The methane and CO_2 concentrations are similar to those in a BiGas gasifier product. The total gas pressure is 300 psi, the temperature is 220°C , and the pathlength is 10 cm. Spectral resolution is 0.24 cm^{-1} . The strongest (ν_2) absorption band of NH_3 is superposed on the CO_2 ($\nu_3 - \nu_1$) difference band near 961 cm^{-1} .
- Fig. 5. Absorbance (reference) spectrum of 0.1% NH_3 in N_2 , obtained with a 10-cm pathlength cell, 300 psi total pressure, and at 200°C . The two prominent features are the Q branches of the ν_2 band of NH_3 used in the ammonia analysis.
- Fig. 6. Analysis for NH_3 in the presence of CO_2 by direct subtraction of NH_3 absorbance. (a) NH_3 reference spectrum of Fig. 4 with absorbance scales reversed. (b) Absorbance of the $\text{NH}_3\text{-CO}_2\text{-CH}_4\text{-N}_2$ mixture of Fig. 4. Most of the absorbance is the $\text{CO}_2(\nu_3 - \nu_1)$ band; however, note the "shoulders" due to the NH_3 . (c) Spectrum resulting from the subtraction of 0.025 times the absorbance of (a) to remove the "shoulders." The subtraction indicates 26 ppm NH_3 in the mixture of (b).
- Fig. 7. Analysis for NH_3 by sequential subtraction of CO_2 and NH_3 absorbances. (a) Absorbance of the $\text{NH}_3\text{-CO}_2\text{-CH}_4\text{-N}_2$ mixture of Fig. 4. (b) Residual absorbance after subtraction of 0.905 times the absorbance of the (18%) CO_2 in Fig. 2. (c) Baseline after subtraction of 0.024 times the absorbance of the (1000 ppm) NH_3 of Fig. 4. The subtraction indicates 25 ppm of NH_3 .
- Fig. 8. Spectrum of a mixture of 30% H_2O , 15.6% CO_2 , 7.3% CH_4 , and 83 ppm NH_3 in N_2 . Water, methane, and CO_2 concentrations are similar to those of a BiGas product. Pressure is 300 psi, temperature 220°C , and optical pathlength 10 cm. Spectral resolution is 0.24 cm^{-1} .
- Fig. 9. Analysis for NH_3 in the presence of CO_2 and H_2O . (a) Absorbance plot of the 890 to 1010-cm^{-1} region of the spectrum of Fig. 8. (b) Absorbance remaining after subtraction of 0.923 times absorbance of (30%) H_2O in Fig. 3. (c) Absorbance after subtraction of 0.980 times absorbance of (18%) CO_2 in Fig. 2. (d) Residual spectrum after subtraction of 0.033 times absorbance of (1040 ppm) NH_3 . Pressure 300 psi, 10-cm pathlength, temperature 220°C . Resolution 0.24 cm^{-1} .

- Fig. 10. Transmission spectrum for 15% H₂O in N₂. Pressure is 300 psi, temperature is 220°C, and optical pathlength is 10 cm. Note that the CO₂ impurity is considerably less than in Fig. 3.
- Fig. 11. Subtraction of 28.8% H₂O in N₂ at 200°C from 30% H₂O in N₂ at 220°C. (a) Absorbance plot of the 650 to 1350-cm⁻¹ region of the 450-psi spectrum of the same mixture used to obtain Fig. 3. (b) Residual spectrum obtained after subtraction of the absorbance of 28.8% H₂O in N₂ at 200°C and 450 psi pressure. Resolution is 0.24 cm⁻¹.
- Fig. 12. Subtraction of 1.8 times the absorbance of 15% H₂O in N₂ from that of 30% H₂O in N₂. Pressure is 300 psi, optical pathlength is 10 cm, temperature is 220°C, and resolution 0.24 cm⁻¹ for each spectrum.

REFERENCES

1. "Quarterly Progress Report for the Coal Gasification Program (PR 11734)" for the period July 1 to September 30, 1981.
2. Our measured value. It is in reasonable agreement with values of $579 \text{ cm}^{-1}/\text{cm-atm}$ (0°C) obtained by P. Varanasi and P. Wyant, J. Quant. Spectros. Radiat. Transfer 25, 311 (1981) and $602 \text{ cm}^{-1}/\text{cm-atm}$ (0°C) from D. C. McKean and P. N. Schatz, J. Chem. Phys. 24, 316 (1956).