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THE APPLICATION OF CRYOGENIC SPECTROSCOPY TO THE DETERMINATION OF IMPURITY CONCENTRATION IN COAL GASIFIERS*

by

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ABSTRACT

A number of small molecules are soluble at low-to-moderate concentrations in the ir-transparent liquefied rare gases.[1,2] As part of an effort to develop methods to measure concentrations of minor constituents in product gases from coal gasifiers, we have measured the infrared spectral absorbance of solutions produced by sampling cryogenically a mixture of gases and dissolving the sample in liquid xenon. Observations thus far include CO_2, CO, CH_4, and H_2 as major constituents and NO_2, NO, NH_3, N_2O, SO_2, and COS as minor constituents in the mixture.

For low concentrations in the cold solutions, solute absorption bands are narrow, with widths at half-maximum absorbance of 1-10 cm^{-1} compared with ~ 30-100 cm^{-1} for the gas phase. The band-narrowing enhances peak absorbance and reduces spectral overlapping for easier analysis of complex mixtures. In the sampling, we remove most CO and CH_4, so that only the CO_2 interferes with the spectrum of minor constituents. In the spectra we can distinguish bands of N_2O, SO_2, COS, and NO_2 (as N_2O_4) and estimate concentrations. The sensitivity and accuracy of the cryogenic solution technique for gas analysis are not yet established; however, detection of ~ 10 ppm appears possible with a half-inch absorption cell.

INTRODUCTION

The use of infrared absorption spectroscopy for determining the molecular composition of gas mixtures depends on identifying absorbing gas species from their spectral pattern and determining species concentrations from the magnitude of their absorbance in the spectrum of the mixture. As commonly applied, the ir absorption method is only moderately sensitive, so that analysis for low absorber concentrations in a gas may require long optical paths. In the analysis of complex mixtures, overlapping of spectral features can confuse identification, and strong absorption by major constituents of the mixture can mask absorption bands of species present at lower concentrations.

A method which earlier work at Los Alamos[1,2] has shown can effectively improve both the specificity and sensitivity of the ir technique involves condensing and dissolving a sample gas in a cryogenic liquid and observing the infrared absorbance of the cold solution.

We will describe preliminary experiments aimed at testing the applicability of this method to the analysis for minority species in coal gasifier product gases. We cryogenically sampled gas mixtures with NO, NO_2, N_2O, NH_3, SO_2, and COS representing minority species, and with CO, CO_2, CH_4, and H_2 present as majority species. The samples were dissolved in liquid xenon for the spectral observations.

BACKGROUND

The appeal of cryogenic solution spectroscopy for the minority species analysis rests on the following facts:[1,2]

(1) A number of small molecules have been shown to be soluble at low-to-moderate concentrations in the liquefied rare gases and a few other cold liquids that are optically clear for all or parts of the middle-ir spectral region.

(2) In the cold (100-200 K) solutions, ir absorption bands of the solute tend to be narrow, with full-widths at half-maximum absorbance typically 1-10 cm^{-1}, as compared with 50-200 cm^{-1} typically observed in gas-phase bands at room temperature. The band-narrowing reduces band overlap for easier analysis of complex mixtures. Also, since the absorbance per molecule is approximately the same in the liquid and gas phases, the narrowing increases the peak absorption and lowers the density required for detection. See Figs. 1 and 2, for example.

(3) Condensation of the gaseous species reduces the volume, permitting greater absorption for a given optical path length. Furthermore, differences in volatility permit the concentration and infrared absorption by some minority species to be enhanced relative to some of the absorbing majority species.

(4) Finally, infrared absorption bands of materials in the solutions, while narrower overall than in the gas phase, have no fine structure and are broad enough that the spectral resolution required for accurate absorbance measurements (1-2 cm^{-1}) is well within the capability of common infrared spectrometers.

EXPERIMENTAL PROCEDURE

To simulate a gasifier product gas, a gas mixture was prepared by combining 1-psi partial pressure each of minority species NO, NO_2, N_2O, NH_3, SO_2, and COS, in that order. To the mixture, we added 83 psi of CH_4, 200 psi of CO_2, 498 psi of CO, and 213 psi of H_2, for a total pressure of 1000 psi. It is understood that combination of the NO_2 with itself and with NO to produce N_2O_4 and N_2O_3 and possible other reaction products may occur. However, if this is ignored the mixture would consist of 0.1% of each minority species, and of 8.3% CH_4, 20% CO_2, 49.8% CO, and 21.3% H_2.

The gas mixture was admitted to a spectral cell (Fig. 2) at room temperature and 10,000 torr (193 psi) pressure. The cell was valved off just above the gas inlet and cooled to -186°C. Most of the H_2, CO, and CH_4 was then pumped out, reducing the pressure to 135 torr. The cell was then valved off again, warmed to -110°C, and Xe gas admitted to fill the cell with liquid xenon (LXe) to an overpressure of 1688 torr. The liquid was stirred and the cell was vented to reduce the overpressure to 876 torr (near the vapor pressure of the LXe)). The infrared transmittance of the solution in the middle infrared (4000-500 cm^{-1}) was then scanned with a Perkin-Elmer Model 180 grating spectrometer operating with a spectral resultion of ~ 2 cm^{-1}.

RESULTS

Spectra of the LXe solution for two interesting regions are shown in Figs. 4 and 5. Figure 4 shows the ν_3 bands of N_2O and COS, which are easily distinguished from the strong CO_2 absorption and the absorption by residual CO remaining in solution. Absorption in the two minor-species bands is about that expected for the N_2O and COS present in the dissolved gas mixture. By utilizing the same procedure, each could probably be detected at factors of 0.1 to 0.01 lower concentrations in the simulated gasifier product gas.

It should be pointed out that while the CO_2 present in the gas mixture has been retained and is dissolved in the xenon solvent, the CO, which was half the gas sample, has been reduced to a concentration not very much greater than the minority species. In the gas-phase spectrum (not shown) of the original mixtur , both the N_2O and COS ν_3 bands are strongly overlapped by the CO (0-1) band.

The spectrum of Fig. 5 shows the strong ν_3 band of SO_2 and the N_2O and N_2O_4 bands in the vicinity of the ν_4 band of CH_4. Like the CO the CH_4 concentration has been substantially reduced. This fact, and the band-narrowing in solution, permits easy resolution of the minority species features; whereas in the spectrum of the sample gas mixture, all would be strongly overlapped by the CH_4 ν_4 band. Absorbances of the SO_2 and N_2O bands are about as expected for the concentrations present in the gas sample.

The N_2O_4 band appears in Fig. 3, because NO_2 in the sample gas is converted to the dimer in the solution. No NO_2 bands were observed, so presumably all of the NO_2 was converted to N_2O_4.

No NH_3 bands nor NO bands were observed in the solution spectra, and the N_2O_4 concentrations appeared substantially lower than expected for the NO_2 present initially in the gas sample. A possible explanation is that a small amount of H_2O may have been introduced in the gas handling. This would permit reaction of NO_2, NO, H_2O, and NH_3 to make NH_4NO_2. No special precautions were taken to minimize H_2O, since it will be present in the gasifier product. However, it seems unlikely that both NH_3 and the acidic gases will then be present.

The results described above demonstrate some of the advantages of cryogenic solution spectroscopy noted in earlier work[1,2] and described above. The spectra of a synthetic mixture of gases dissolved in liquid Xe indicate that this approach may be useful in analysis of gasifier product gases for at least some minority species. A number of questions and possible problems should be mentioned. Among the most crucial problems is the elimination of water and particulate matter when present in substantial quantities, since they will tend to plug lines into a cooled cell. The solubility of minority species in cryogenic solvents has been measured for only a very few solvents and solute materials. Most transparent (or partially transparent) cryogenic liquids are poorer solvents than xenon. Xenon is moderately expensive (about $1/ per charge in our one-half-in. cell); however, the xenon may possibly be cleaned and recycled.

Finally, to reach the goal of part-per-million sensitivity, probably larger amounts of the gasifier product will have to be condensed, with possibly better provision for selective removal of some majority species.

FIGURE CAPTIONS

Figure 1. Infrared absorption spectrum of 100.3 torr of CO_2 vapor at 45°C (curve I) and that of 2 ppm (in mole ratio) of CO_2 in liquid Xe at -110°C (curve II). Note that the CO_2 molecular density in the liquid solution is one-hundredth that of the gas.

Figure 2. Infrared spectrum (curve I) of a mixture of CCl_2F_2 (0.3 ppm; features at 917.5 and 886.5 cm^{-1}) and C_2H_3Cl (2 ppm; features at 943.0 and 899.0 cm^{-1}) dissolved in liquid air at -188°C, and spectra of 25°C mixtures of 10 torr of CCl_2F_2 and 100 torr of C_2H_2Cl (curve II) and 10.6 torr of CCl_2F_2 and 6.8 torr of C_2H_3Cl (curve III). Notice the relative ease with which the solute bands are distinguished in the solution spectrum.

Figure 3. Cryogenic spectral cell. The cell body is copper. The interior of the cell is connected to a gas-handling manifold through the fill tube, a; liquid nitrogen coolant is forced through tubes, b, and channel, c, in pulses whose length is determined by a temperature controller. Spring washers and screws, d, hold the windows, e, (here AgCl) and window clamps, f, in place. Resistors, g, are used for rapid cell warmup, with coolant off or on, to warm the upper part of the cell when filling to help keep inlet lines free of solid condensate. Copper has been removed at h to decrease thermal conduction. Thermocouples are attached near top and bottom of the cell for temperature measurement and control. A maximum temperature differential of ~ 20°C can be maintained beteeen the top and bottom at -100°C. With temperature regulated and heaters off, the cell temperature at the top is within 1-2°C of that at the bottom. The cell is suspended from an appropriate flange, which fits into a vacuum jacket with KCl windows. The optical path length through the cell is 1.37 cm, and the cell volume is 2.5 cm^3.

Figure 4. Infrared transmittance of a solution prepared by dissolving a mixture simulating coal gasifier product gases in liquid xenon. The solute gas mixture originally included 0.1% each of NO, NO_2, N_2O, NH_3, COS, and SO_2 in 8.3% CH_4, 20% CO_2, 49.8% CO, and 21.3% H_2. Treatment of the mixture to remove most of the CO, H_2, and CH_4, and possible accidental removal of most of the NH_3, NO_2, and NO is discussed in the text. Densities of N_2O, COS, SO_2, N_2O_4, and CO_2 in solution correspond approximately to 10, 10, 10, 2, and 2000torr, respectively, of these gases at room temperature. Temperature of the solution is -110°C with LXe. The spectrometer cell used is that shown in Fig. 3. Absorption bands of solute species are marked.

Figure 5. Infrared transmittance of the same sample used for Fig. 4. Absorption bands of known solute species are marked, as are two bands, due to unidentified impurities in our xenon solvent.

References

1. S. M. Freund, W. B. Maier II, R. F. Holland, and W. H. Beattie, Anal. Chem. 50, 1261 (1978).

2. W. H. Beattie, W. B. Maier, II, R. F. Holland, S. M. Freund, and B. Stewart, SPIE Vol. 158 Laser Spectroscopy, p. 113 (1978).

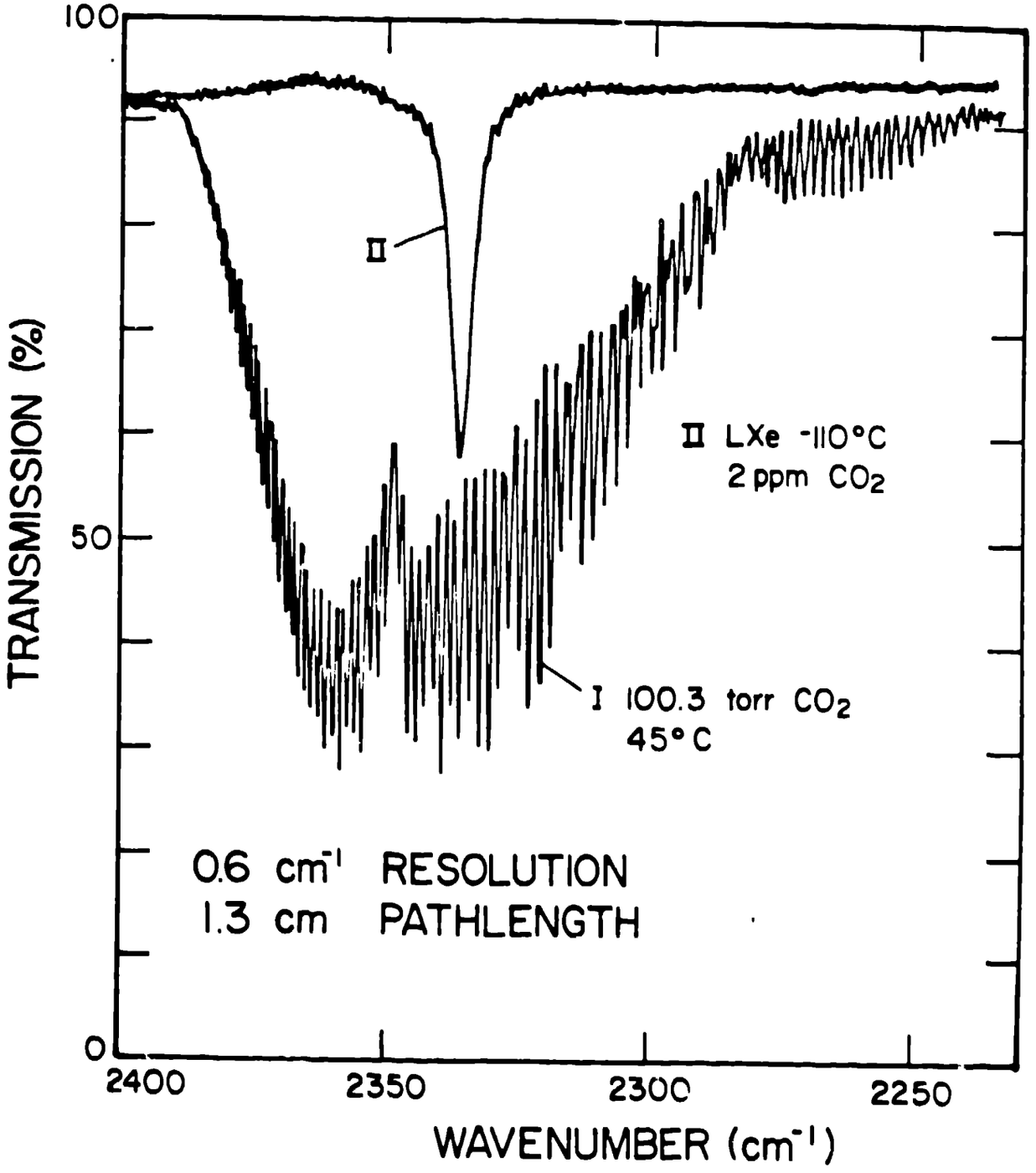

100
50
0
TRANSMISSION (%)
II
II LXe -110°C
2 ppm CO_2
I 100.3 torr CO_2
45°C
0.6 cm^{-1} RESOLUTION
1.3 cm PATHLENGTH
2400
2350
2300
2250
WAVENUMBER (cm^{-1})

Figure 1

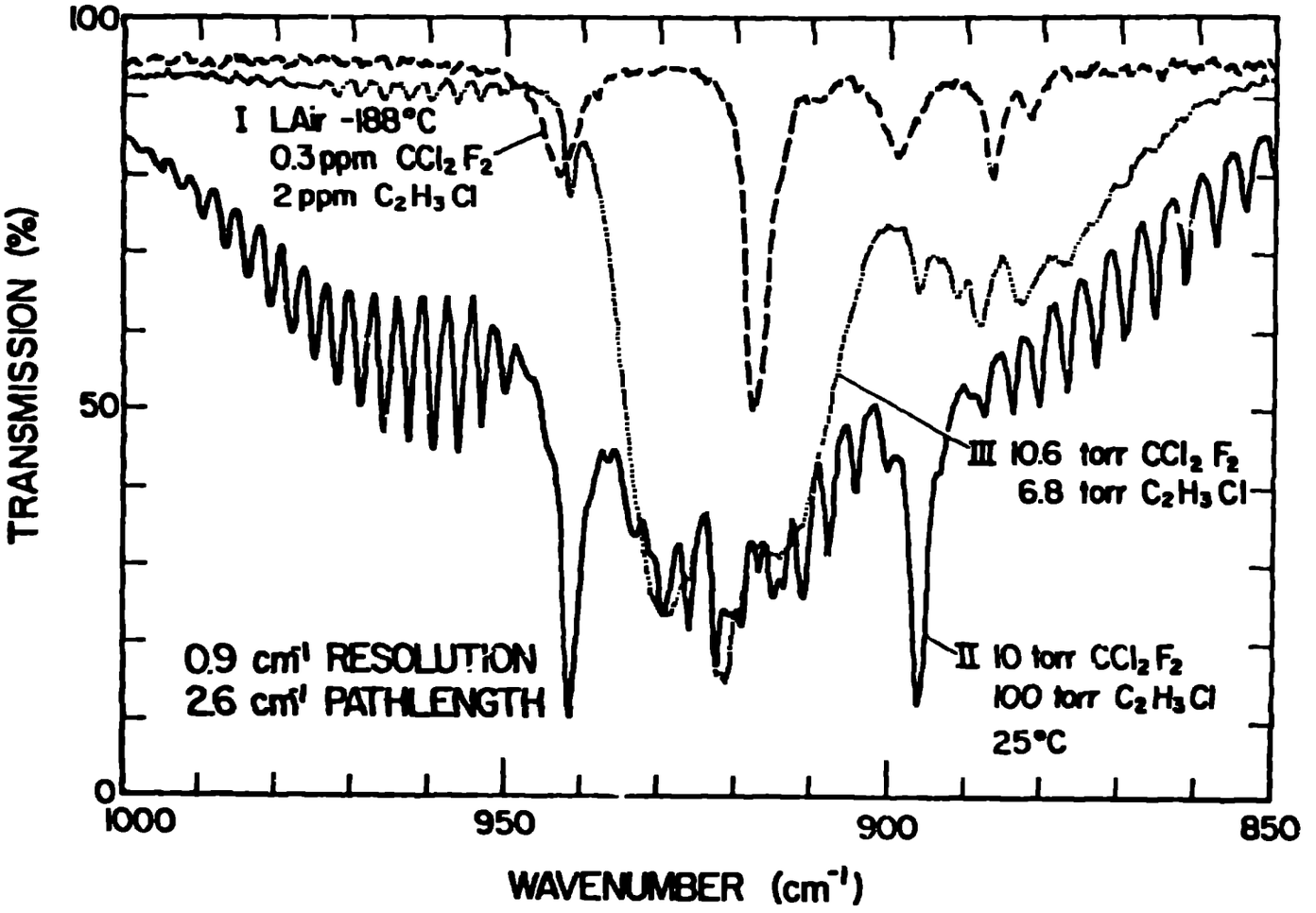
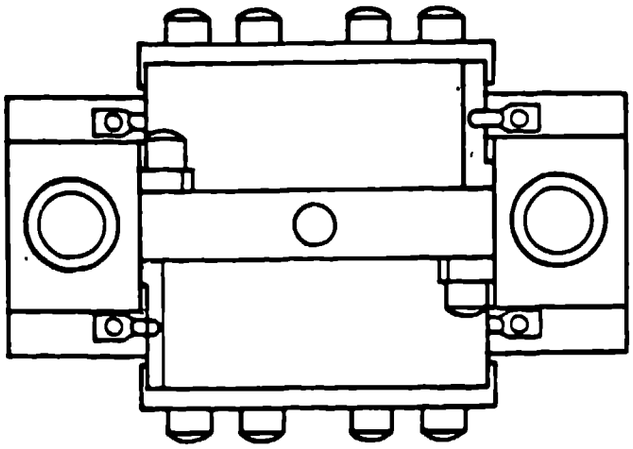
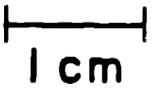
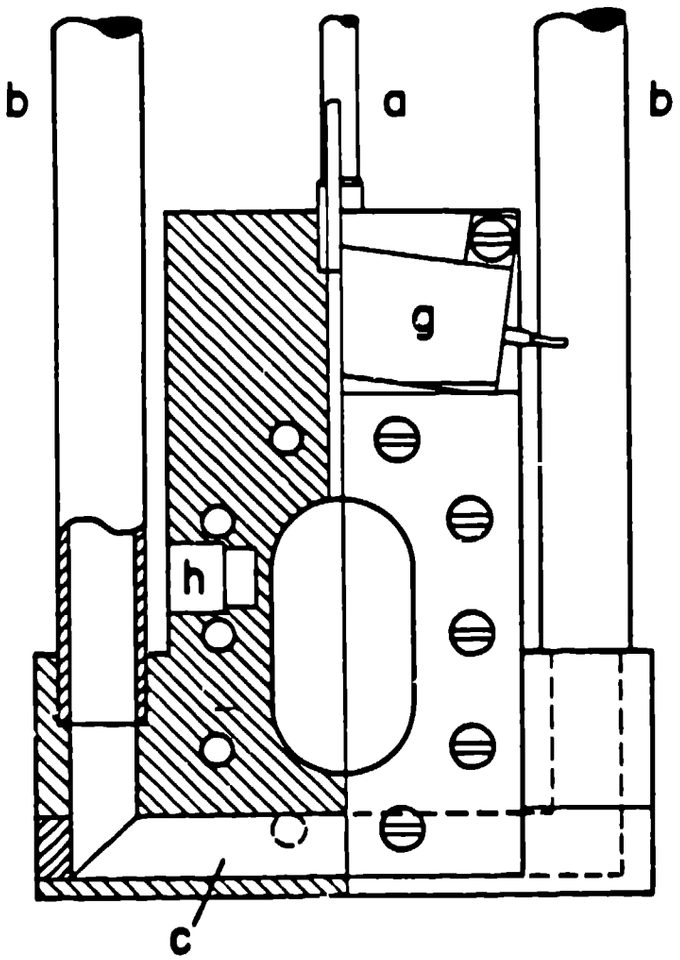

100
50
0
TRANSMISSION (%)
I LAir -188°C
0.3ppm CCl_2F_2
2ppm C_2H_3Cl
III 10.6 torr CCl_2F_2
6.8 torr C_2H_3Cl
II 10 torr CCl_2F_2
100 torr C_2H_3Cl
25°C
0.9 cm^{-1} RESOLUTION
2.6 cm^{-1} PATHLENGTH
1000
950
900
850
WAVENUMBER (cm^{-1})

Figure 2







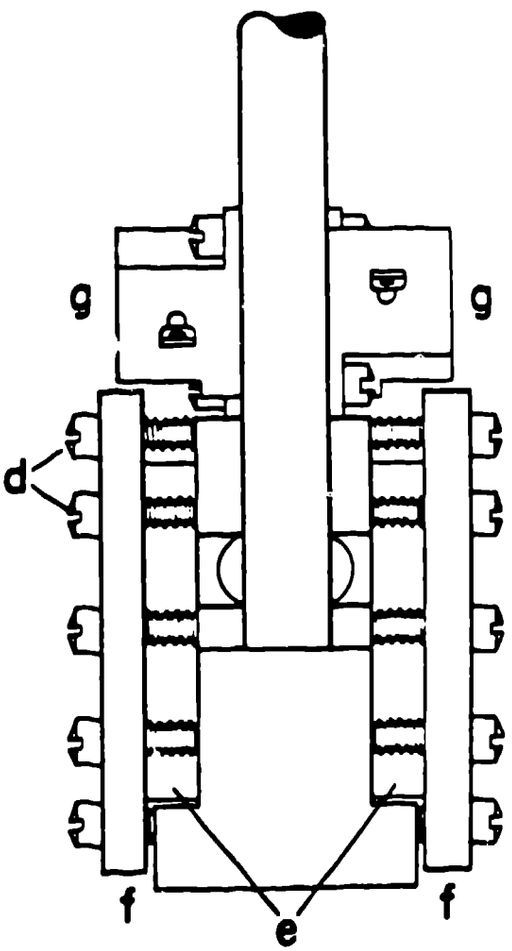


Figure 3

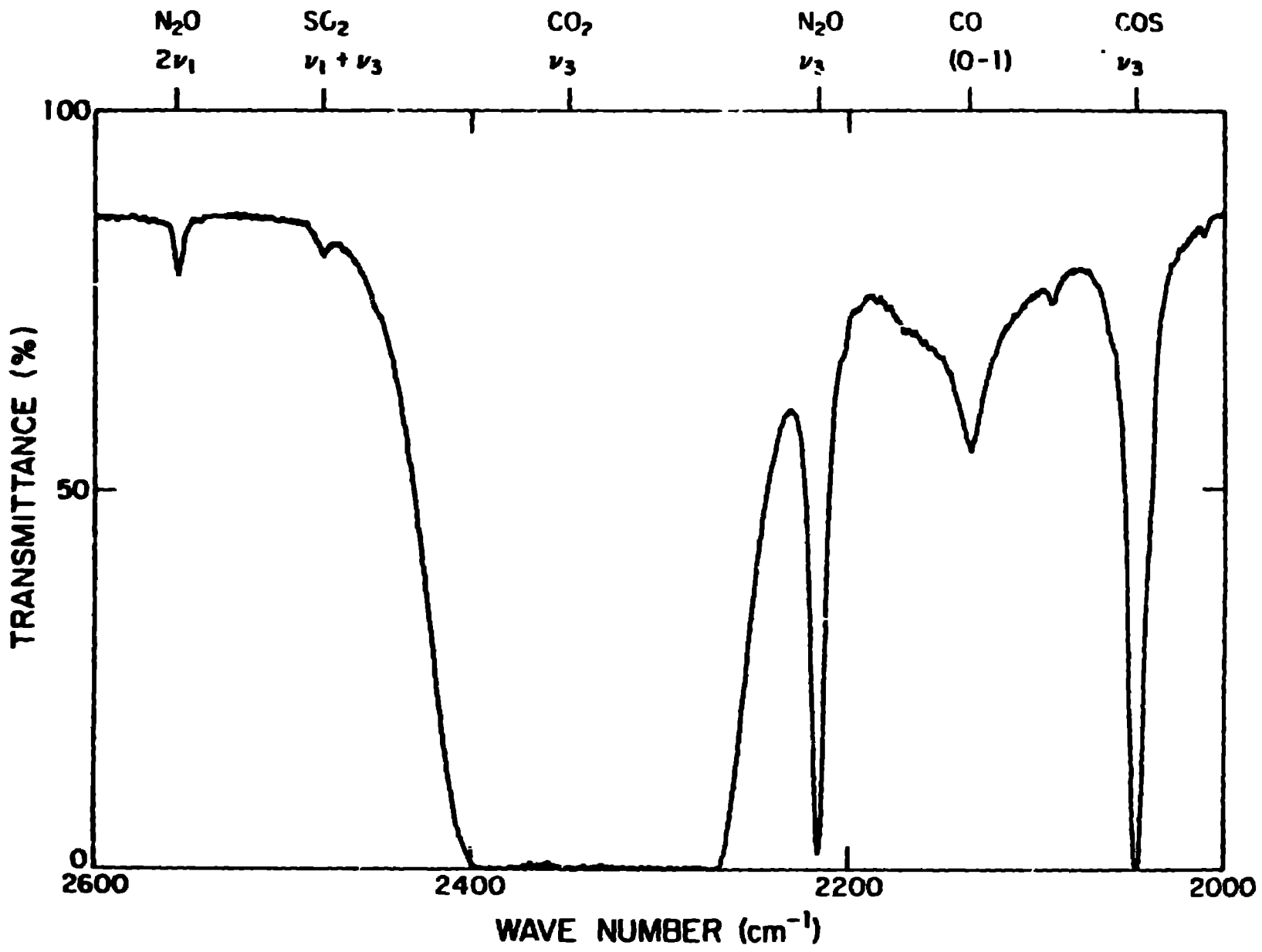

N_2O
$2\nu_1$
SO_2
$\nu_1 + \nu_3$
CO_2
ν_3
N_2O
ν_3
CO
(0-1)
COS
ν_3
100
50
0
TRANSMITTANCE (%)
2600
2400
2200
2000
WAVE NUMBER (cm^{-1})

Figure 1

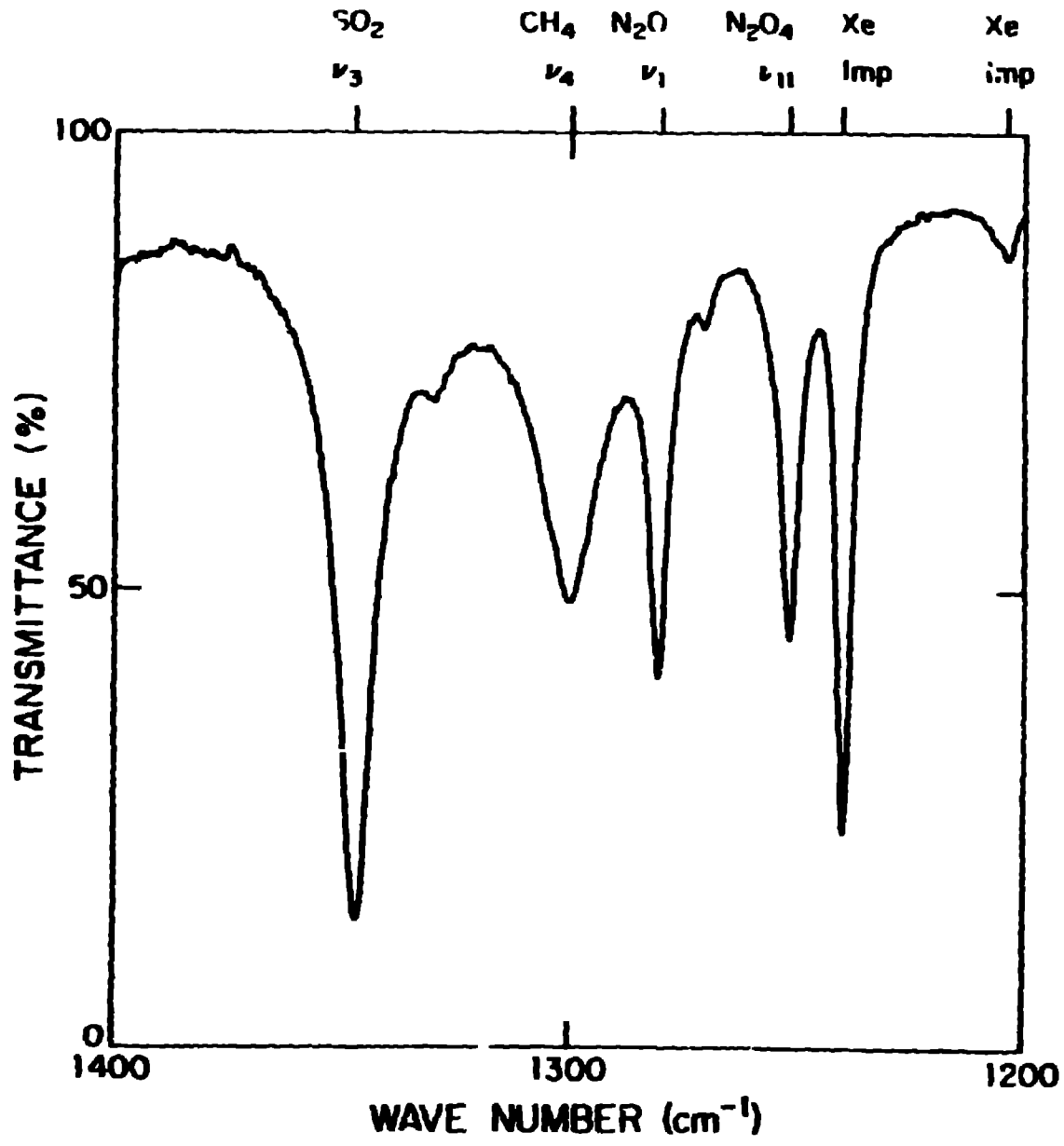

SO_2
ν_3
CH_4
ν_4
N_2O
ν_1
N_2O_4
ν_{11}
Xe
Imp
Xe
imp
100
50
0
TRANSMITTANCE (%)
1400
1300
1200
WAVE NUMBER (cm^{-1})

Figure 5

EXTRA FIGURES

Figure 1c. Spectral transmittance of a liquid xenon solution of gas from our NO_2 supply bottle. The difference between the dashed and solid curves is primarily due to evolution of NO impurity from the solution of the higher temperature. The spectral cell has 1/2-inch path length and thallium bromide iodide windows. Broad features near 1290 and 1380 cm^{-1} are "window bands." The Xe solvent contained impurities which produced the absorption bands marked with asterisks. Some positive-going peaks in the baseline are due to atmospheric absorption in the spectrometer reference beam. The spectral slit width is about 3 cm^{-1}.

Figure 2c. Solubilities of CO_2, CH_2O, CH_3OH, and HN_3 in liquid krypton versus 1/T. Data points are indicated. The dashed lines indicate the concentration corresponding to the total amount of solute used in the experiment.

Figure 3c. Transmission of saturated solutions of anthracene and phenanthrene in liquid xenon at two temperatures. Optical path length 2.6 cm, spectral resolution 1 cm^{-1}.

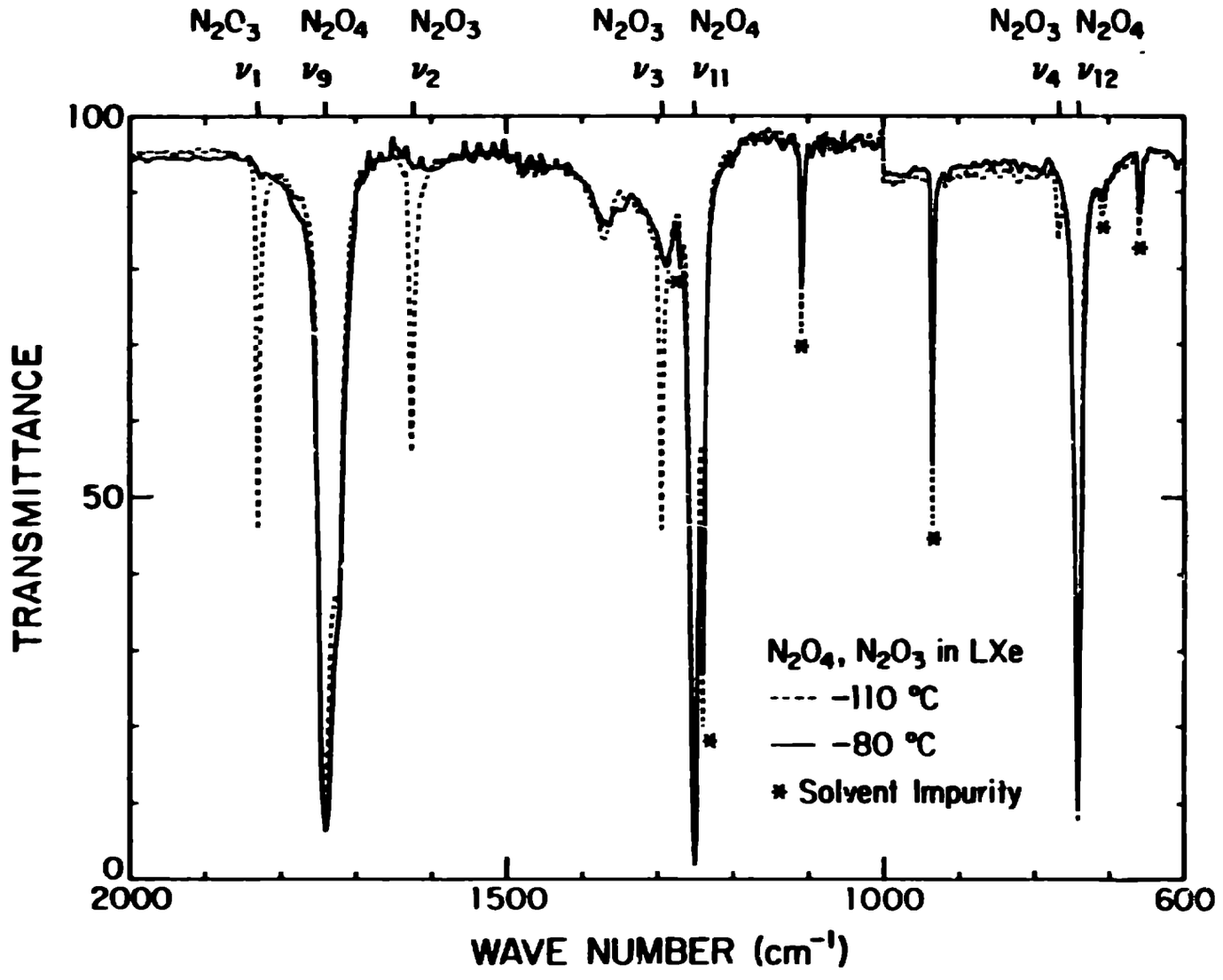

N_2O_3 ν_1
N_2O_4 ν_9
N_2O_3 ν_2
N_2O_3 ν_3
N_2O_4 ν_{11}
N_2O_3 ν_4
N_2O_4 ν_{12}
100
50
0
TRANSMITTANCE
2000
1500
1000
600
WAVE NUMBER (cm^{-1})
N_2O_4, N_2O_3 in LXe
---- -110 °C
—— -80 °C
* Solvent Impurity

Figure 1c

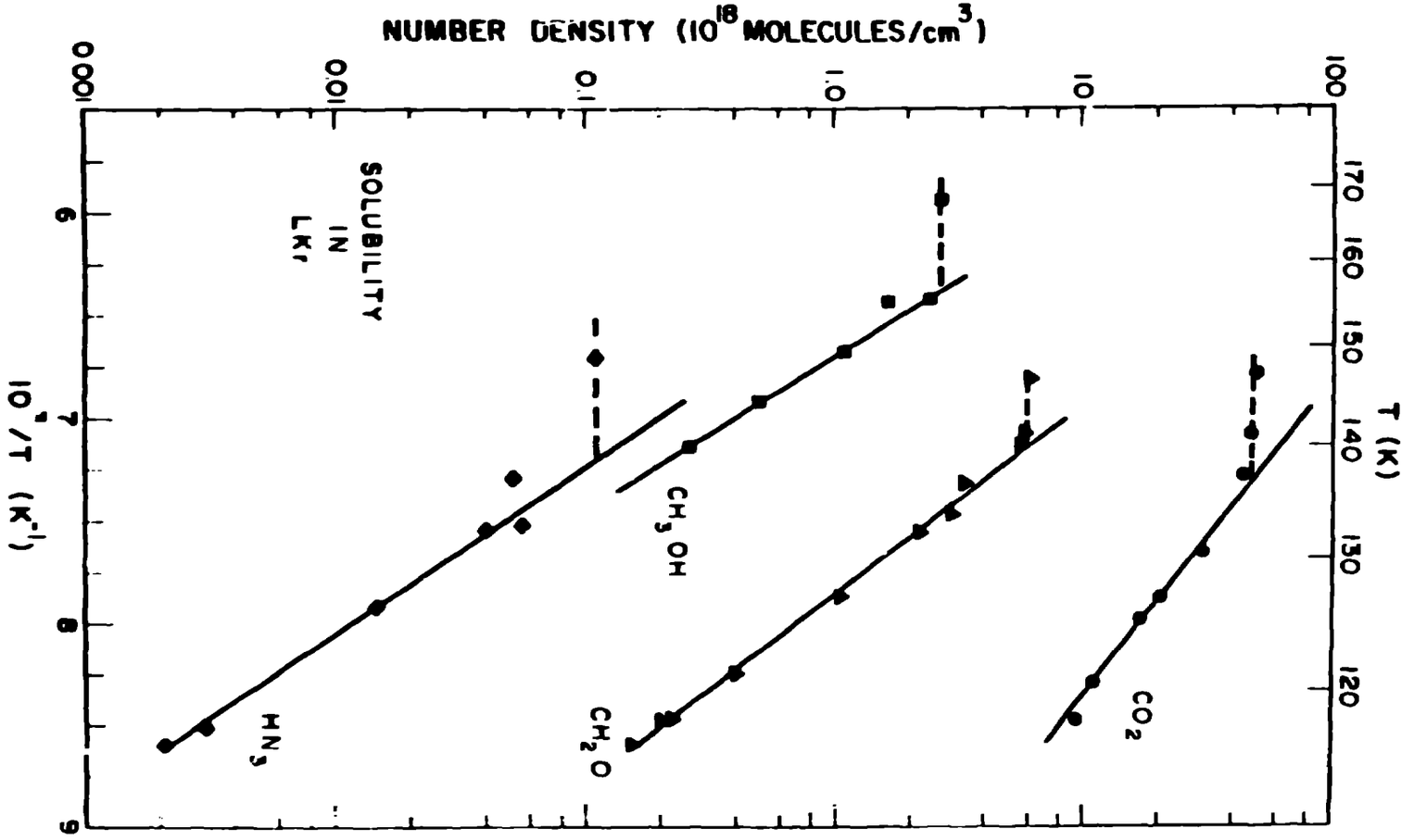

NUMBER DENSITY (10^{18} MOLECULES/cm^3)
0.001
0.01
0.1
1.0
10
100
SOLUBILITY IN LKr
HN_3
CH_3OH
CH_2O
CO_2
$10^4/T$ (K^{-1})
9
8
7
6
T (K)
120
130
140
150
160
170

Figure 2c

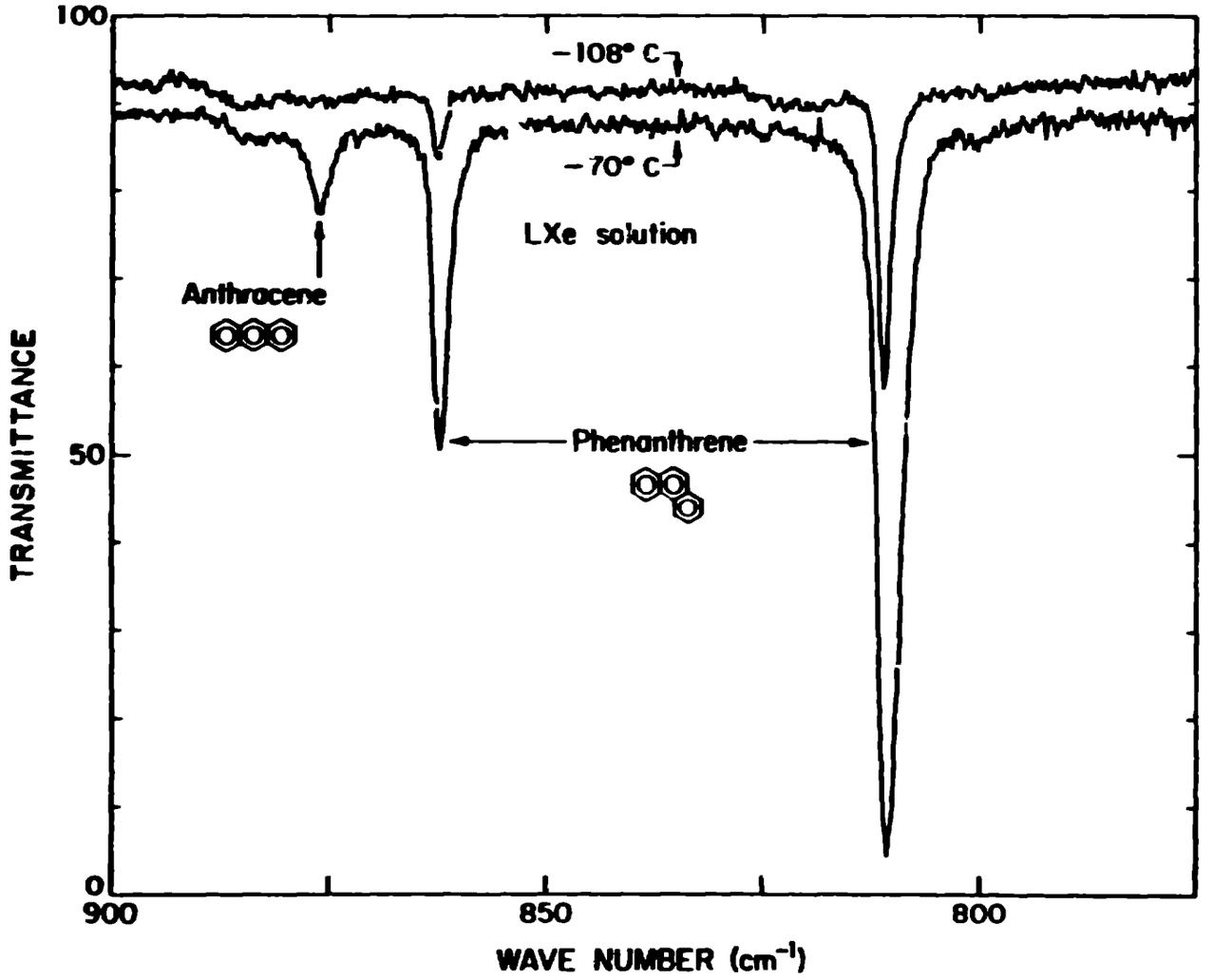

100
50
0
TRANSMITTANCE
-108° C
-70° C
LXe solution
Anthracene
Phenanthrene
900
850
800
WAVE NUMBER (cm⁻¹)

Figure 3c