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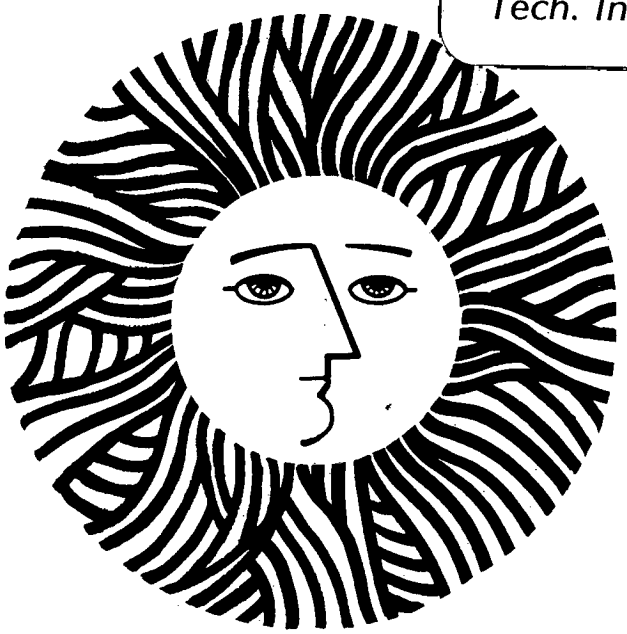

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INVESTIGATION OF THE PRODUCTS AND KINETICS OF THE REACTION OF NITRITE ION WITH BISULFITE ION BY LASER RAMAN SPECTROSCOPY **

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Abstract

Laser Raman spectroscopy (LRS) has been used to investigate the aqueous chemistry of nitrogen and sulfur oxyacids. Raman spectra have been obtained for a number of the nitrogen-sulfur compounds involved in this system. The products of the reaction of nitrite ion with bisulfite ion have been identified. The chemistry of this system has been studied and found to be in agreement with a reaction scheme previously proposed.

**This work was supported by the Morgantown Technology Center, Contract No. 82MC14002, through the Assistant Secretary of Fossil Energy of the U.S. Department of Energy under Contract No. DE-AC 03-76SF00098.

Introduction

Knowledge of the aqueous chemistry of nitrogen and sulfur oxyacids is needed for developing wet scrubber systems to remove NO_x (NO and NO_2) and SO_2 from power plant flue gases.[1-3] The chemistry is also of potential importance in air pollution involving nitrogen and sulfur oxides.[4] The system is complicated by the large number of reactions that occur and the large number of species involved.[1,5-7]

Some of the reactions that can occur in this system are illustrated in Fig. 1. The intermediate species nitrosulfonic acid (HO_3SNO) has never been identified, but its existence has been inferred from the behavior of the nitrite ion-bisulfite ion reaction.[8] The abbreviations used in the figure are HADS for hydroxylamine disulfonate, HAMS for hydroxylamine monosulfonate, HA for hydroxylamine, ATS for amine trisulfonate, ADS for amine disulfonate, and SA for sulfamic acid.

One of the problems in studying this system is the difficulty in quantitatively detecting all the species present under a wide range of solution conditions. Laser Raman spectrometry (LRS) has been suggested for chemical analysis of solutions,[9] although it has not yet been used extensively for this purpose. We decided to use LRS because one of its advantages over other analytical procedures is the ability to simultaneously determine the concentrations of a large number of species in solution. Other advantages include unambiguous identification of species in solution, a rapid and simple analysis procedure, and the ability to repeatedly study a solution over a period of time to observe changes in concentration of species involved in a reaction. Its major limitation is the difficulty in observing species at very low concentrations. We have not found any previous studies on this system utilizing LRS, so reference spectra were obtained for all the species present in it.

Experimental

The system used in this study consisted of a Coherent CR-2 argon ion laser and a Spectra Physics 165 krypton ion laser as excitation sources and a Jobin-Yvon Ramanor HG-2 double monochromator. Signals from a coded RCA 31034 photomultiplier tube were digitized by a Princeton Applied Research 1140A photometer and sent to a Nicolet 1280 Raman data processing system. Spectra were usually obtained with the 488.0-nm argon ion line.

It was necessary to synthesize HADS, HAMS, ATS, and ADS in order to obtain reference spectra of these compounds. HADS was synthesized from nitrite ion and bisulfite ion by the method of Rollefson and Oldershaw.[10] HAMS was prepared by the hydrolysis of HADS using Oblath's[8] modification of Seel and Degener's method.[11] ATS and ADS were synthesized from nitrite ion and bisulfite ion by the procedures given by Sisler and Audrieth.[12] The prepared compounds were stored in a vacuum dessicator over P_2O_5 at 5°C until use. The potassium sulfite, potassium nitrite, and potassium hydroxide used in the syntheses; the hydroxylamine hydrochloride, sulfamic acid, and sodium sulfate used to prepare samples for Raman spectra; and the sodium metabisulfite, sodium sulfite, and sodium nitrite used in preparing reaction mixtures were all standard reagent-grade compounds.

Samples containing bisulfite and sulfite ions were prepared by degassing the solution to which the sodium sulfite or sodium metabisulfite was to be added on vacuum line, adding the salt under an argon atmosphere, and again degassing the solution after addition. This was done to prevent oxidation of the ions into sulfate ion. The solution was then transferred to a Pyrex tube under an argon atmosphere and sealed off.

The sample used for obtaining the reference spectrum of N_2O was prepared by degassing the solution on a vacuum line and adding 1 atm of N_2O over the

solution. The solution was allowed to equilibrate with the N_2O for about 2 hours and then transferred to a Pyrex tube and sealed off. Because of the limited solubility of N_2O in water, the N_2O concentration in the sample was 0.025 M.

As indicated by Irish and Chen,[9] the simplest method to make quantitative measurements by LRS is to include a known amount of a reference compound in the samples so the other compounds can be compared with the reference compound. The reference also allows correction of the indicated Raman shift for any system errors. Sulfate ion was used in the samples with which the relative molar scattering intensities were determined. (Relative molar intensity = (ion peak height/ion molarity)/(981 cm^{-1} sulfate ion peak height/sulfate ion molarity).) There is still some uncertainty whether peak area or peak height is a more accurate indicator of a species concentration in solution.[13] Peak heights were used as a measure of the concentration of species in solution in this study.

Results and Discussion

The Raman shifts and relative molar intensities for the compounds investigated are given in Table 1. The hyponitrite ion ($N_2O_2^{=}$) was not studied, but Raman shifts obtained by Rauch and Decius[14] are given. The Raman shifts and relative molar intensities of nitrate ion, nitrite ion, and sulfate ion are in good agreement with those obtained by Miller[15] and Marson.[16]

Reference Raman spectra of HADS, HAMS, HA, ATS, ADS, and SA are shown in Fig. 2. The strong line at 980 cm^{-1} is the sulfate ion reference line and is off scale in all the spectra. No value for the relative molar intensity for sulfamic acid (SA) was obtained at very low pH since no work was planned for those conditions.

Knowledge of the Raman spectra of the potential product compounds of the reaction between nitrite and bisulfite ion allowed us to determine the concentrations of intermediates and products as a function of reaction time for various

reaction conditions. Mixtures of various ratios of nitrite ion and sulfite ion were prepared, and the Raman spectra of the mixtures were obtained. The initial concentrations of the ions used were:

A) 0.10 M NO_2^- + 0.50 M HSO_3^- ,

B) 0.26 M NO_2^- + 0.50 M HSO_3^- ,

C) 0.51 M NO_2^- + 0.50 M HSO_3^- , and

D) 1.02 M NO_2^- + 0.50 M HSO_3^- .

Spectra of the four solutions taken about 24 hours after mixing are shown in Fig. 3.

The spectrum of mixture A in Fig. 3A shows the presence of sulfite ion ($SO_3^=$) at 970 cm^{-1}, sulfate ion ($SO_4^=$) at 980 cm^{-1}, bisulfite ion (HSO_3^-) at 1040 cm^{-1}, disulfite ion ($S_2O_5^=$) at 1050 cm^{-1}, HADS at 1085 cm^{-1}, and ATS at 1100 cm^{-1}. The spectrum of mixture B, shown in Fig. 3B, is less complicated, with weak nitrite ion bands present at 820 and 1240 cm^{-1}, sulfite ion at 970 cm^{-1}, HADS at 1085 cm^{-1}, and ATS at 1100 cm^{-1}. Sulfate ion is much less prominent in the spectrum of mixture B. The spectra of mixtures C and D are similar to that of mixture B, except for increasingly strong nitrite ion bands and an increasingly weak ATS band.

Figures 4A and 4B illustrate the spectra of mixtures of HADS plus sulfate ion and HAMS plus sulfate ion respectively over a range of 500 to 2500 cm^{-1}. The HADS peak at 700 cm^{-1} and HAMS peak at 760 cm^{-1} are useful in determining the presence of HADS and HAMS when compounds with peaks that overlap the other peaks may be present. Figures 4C and 4D are spectra of mixtures B and C over 500 to 2500 cm^{-1}. Those confirm that the 1085-cm^{-1} peak is due to HADS, and not ADS, by the presence of the 700-cm^{-1} HADS peak. No unassigned peaks were observed in any of the spectra over the range of 500 to 2500 cm^{-1}. The peaks at 600, 1250, and 1650 cm^{-1} are due to water.

From the spectra, it can be seen that the pH has increased as a result of the reaction between bisulfite ion and nitrite ion. In Fig. 3A, some of the bisulfite ion has been converted to sulfite ion. In Figs. 3B, C, and D, all the bisulfite ion has been converted into sulfite ion. This is due to the reaction:

$$NO_2^- + 2HSO_3^- \rightarrow (^-O_3S)_2NOH\ (HADS) + OH^- \ .$$

The magnitude of the change in pH is proportional to the nitrite ion concentration when bisulfite ion is in excess, since nitrite ion will control the amount of hydroxyl ion produced. The occurrence of the hydrolysis reactions will cause a decrease in pH. For example:

$$(^-O_3S)_2NOH\ (HADS) + H_2O \rightarrow (^-O_3S)NHOH\ (HAMS) + SO_4^= + H^+ \ ;$$

$$(^-O_3S)_3N\ (ATS) + H_2O \rightarrow (^-O_3S)NH\ (ADS) + SO_4^= + H^+ \ .$$

The hydrolysis reactions in this reaction scheme are all hydrogen ion catalyzed. The increase in pH due to the reaction between nitrite ion and bisulfite ion was confirmed by monitoring the pH of the solution after mixing the reactants together. Prior to mixing, the bisulfite ion solution was pH 4.1. After the addition of nitrite ion, the solution pH rapidly increased to pH 7.0 or higher. Both the rate of pH increase and the amount of pH increase were proportional to the initial concentration of nitrite ion at a given bisulfite ion concentration.

As shown in Fig. 3, the nitrite ion/bisulfite ion ratio affects the products observed, as would be predicted from the reaction scheme in Fig. 1. The HNO_2: HSO_3^- molar ratio for production of HADS is 1:2 in the absence of interfering reactions. When the ratio is higher than this, as is the case of mixtures B, C, and D, most of the bisulfite ion will be consumed in the reaction with nitrite ion, so little will be available for conversion of HADS to ATS. As the nitrite ion concentration increases, it will compete more effectively with HADS for any

remaining HSO_3^-, resulting in lower ATS concentrations. Since the initial nitrite ion concentration affects the solution pH, the higher nitrite ion concentration mixtures will become basic more rapidly than lower concentration mixtures. The high pH will result in less hydrolysis of HADS and ATS and relatively lower concentrations of hydrolysis products in the higher nitrite ion concentration mixtures.

The compounds observed in spectra obtained from mixtures B, C, and D are what would be expected from the reactions in Fig. 1. No other reactions appear to be occurring. No unexpected peaks have been observed. Nitrosulfonic acid would not be expected to be present, since the spectra were not taken immediately after mixing; and nitrosulfonic acid should react fairly quickly under the given conditions.

Mixtures B, C, and D all show the presence of sulfite ion and nitrite ion in solution 24 hours after mixing, indicating the reaction between them and the reaction between HADS and sulfite ion is fairly slow. This was confirmed by preparing a solution of 1.02 M nitrite ion and 0.50 M sulfite ion at pH 10. A Raman spectrum obtained shortly after mixing showed no evidence of any reaction products and a spectrum taken one week later (Fig. 5) showed no change. From this, we conclude that the reaction between sulfite ion and nitrite ion occurs very slowly, if at all. This is consistent with the reaction mechanism proposed by Oblath et al.[5] and by Seel and Knorre[17] involving bisulfite ion for HADS and ATS production.

In mixture A, the nitrite ion-bisulfite ion ratio is much less than 1:2. Under these conditions, the kinetics of the system will be considerably different than in mixtures B, C, and D. In this situation, the amount of HADS produced should be limited by the amount of nitrite ion present. Since bisulfite ion should remain after the nitrite ion has been consumed, it can react with HADS

to produce ATS. There should be less hydroxyl ion produced than in the other mixtures, so that the hydrogen ion-catalyzed hydrolysis reactions should occur more rapidly. The relative amount of ATS in Fig. 3A is much larger than in the other spectra. Sulfate ion is produced only by the hydrolysis reactions, according to the reaction scheme in Fig. 1. The sulfate ion peak at 980 cm^{-1} is much more prominent in Fig. 3A than in the other figures, indicating more hydrolysis has occurred. Since no HAMS is apparent at 1060 cm^{-1}, the sulfate ion must be due to the hydrolysis of ATS to ADS. The 1085 cm^{-1} peak is therefore due to both ADS and HADS.

The spectra obtained of mixtures B, C, and D did not display much change with time. There appeared to be a small reduction in ATS and HADS peak heights relative to nitrite ion, probably due to hydrolysis or, in the case of HADS, a reaction with sulfite ion. The spectra obtained of mixture A with time changed considerably. The change with time is shown in Fig. 6, over the range of 900 to 1300 cm^{-1}. The times after mixing for the spectra are: Fig. 6A - 20 min, Fig. 6B - 2 hours, Fig. 6C - 24 hours, Fig. 6D - 105 days. In the first spectrum in Fig. 6A, HADS is prominent at 1085 cm^{-1}. The presence of ATS is indicated by the peak at 1100 cm^{-1}, and HSO_3^- and $S_2O_5^=$ are visible at 1020 and 1050 cm^{-1}. There is weak evidence for $SO_3^=$ and $SO_4^=$ at 960 and 980 cm^{-1}. In Fig. 6B, the ATS and sulfate ion peaks have become more prominent. In Fig. 6C, the ATS peak is very prominent, the HADS/ATS peak is smaller, sulfate ion is larger, and sulfite ion is still present. In the last spectrum in Fig. 5D, the peak due to ATS is absent, the 1085-cm^{-1} peak is due solely to ADS (because of the absence of the 700-cm^{-1} HADS peak), and the 970-cm^{-1} $SO_3^=$ peak is absent.

The chemistry that is occurring in the reaction mixture of 0.1-M nitrite ion and 0.5-M bisulfite ion is consistent with the reaction scheme shown in Fig. 1. The reaction to produce HADS is fairly rapid, and it was essentially

completed by the time the first spectrum was taken. The conversion of HADS to ATS has started as well. The second spectrum shows that further conversion of HADS to ATS has occurred. Hydrolysis is also occurring, evidenced by the growth of the sulfate ion peak at 980 cm^{-1}. The size of the sulfite ion peak relative to the bisulfite ion peak has increased from Fig. 6A, indicating the solution has become more basic from the production of HADS. In Fig. 6C, much of nitrogen from the nitrite ion is in the form of ATS, with the rest as ADS and a little HADS. Considerable hydrolysis of ATS has occurred, shown by the growth of the sulfate ion peak. The solution is at a higher pH than it was originally, as indicated by the presence of sulfite ion as well as bisulfite ion. In the last spectrum, all the ATS has been hydrolyzed to ADS; and hydrolysis of ADS to SA is beginning. The hydrolysis rate of ADS is much slower than that of ATS, so evidence of its occurrence will be much slower in appearing.

No reference compound was included in the nitrite ion-bisulfite ion mixture to act as a source of calibration for the other peaks because of potential interference with either the reaction system or overlap with other peaks in the spectra. Nitrate ion (NO_3^-), carbonate ion ($CO_3^=$), and dihydrogen phosphate ion ($H_2PO_4^-$) were considered; but nitrate ion interferes with the SA peak, and carbonate ion and phosphate ion act as buffers and exist in more than one charge state, making calibration more complicated. However, the reactions that are involved in the system of nitrite ion-bisulfite ion mixtures are fairly well understood, so that values of the concentrations of the species present can be determined.

For example, the concentrations of the species in Fig. 3 can be obtained from the spectra. In Fig. 3A, the concentrations are: (ATS) $\approx$ 0.08 M, (ADS) $\approx$ 0.01 M, (HADS) $\approx$ 0.01 M, (HSO_3^-) $\approx$ 0.05 M, ($SO_4^=$) $\approx$ 0.01 M, ($SO_3^=$) $\approx$ 0.05 M. In Fig. 3B, the concentrations are: (ATS) $\approx$ 0.1 M, (HADS) $\approx$ 0.05 M, ($SO_3^=$)

$\approx$ 0.1 M, (NO_2^-) $\approx$ 0.3 M. In Fig. 3D: (ATS) $\approx$ 0.06 M, (HADS) $\approx$ 0.1 M, ($SO_3^=$) $\approx$ 0.15 M, (NO_2^-) $\approx$ 0.8 M.

Studying the chemistry of the nitrogen oxyanion-sulfur oxyanion system is an excellent utilization of the analytical capabilities of LRS. Understanding of the kinetics and intermediates of this system is needed for the development of wet scrubber systems to remove NO_x and SO_2 from flue gases. Previous work on identification of species present in this system have been done by wet analytical techniques,[18] which are slow, tedious, and susceptible to interference from other species in solution. Use of LRS permits rapid, simultaneous determination of concentrations of a large number of species. It allows repeated measurement of a sample over time, which can provide useful kinetic information. This study provided unambiguous determination of all the reaction products present and showed that no previously undetected species exist in the system. We have confirmed the accuracy of the reaction scheme shown in Fig. 1. These results are of great value in developing and improving wet flue gas scrubber systems. Our work indicates that for optimum scrubber operation, the SO_2/NO_x ratio in the flue gases should be large enough so that the ratio of bisulfite on to nitrite ion in solution is greater than 2. The results also show that the pH of the scrubbing solution should by mildly acidic, so that bisulfite ion is the dominant form of sulfur oxyanion in solution. These scrubber conditions will permit optimum conversion of SO_2 and NO_x into other compounds. The LRS technique promises to be useful in investigating the kinetics of other reaction systems where a large number of species or a complicated reaction scheme make conventional techniques of limited value.

Acknowledgments

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Table 1. Raman shifts and relative molar intensities of species studied in this investigation.

Species	Raman shift (cm^{-1})	Relative molar intensity[a]
NO_2^-	818	0.053
	1240	∿ 0.025
	1331	0.125
NO_3^-	1050	0.95
$N_2O_2^=$	692[b]	weak[b]
	1115[b]	weak[b]
	1383[b]	strong[b]
N_2O^-	1285	∿ 0.18
$SO_3^=$	967	0.12
HSO_3^-	1023	0.10
$SO_4^=$	∿ 455	∿ 0.07
	981	1.00
HSO_4^-	1055	∿ 0.9
$S_2O_5^-$	1050	0.05
HADS	∿ 700	∿ 0.20
	1084	1.43
HAMS	∿ 420	∿ 0.13
	∿ 760	∿ 0.08
	1058	0.48
HA (pH ≤ 7)	1004	0.21
HA (pH ≥ 9)	918	0.09
ATS	1097	0.10
ADS	1084	0.056
SA (pH ≤ 1)	1063	[c]
SA (pH ≥ 3)	1049	0.41

[a] $SO_4^=$ 981 cm^{-1} line = 1.000

[b] Rauch, J.E.; Decius, J.C., Spectrochim. Acta 1966, 22, 1963.

[c] No value obtained.

Figure Captions

Figure 1. Reactions that occur in the nitrogen oxyacid-sulfur oxyacid system.

Figure 2. Raman shifts obtained for some nitrogen-sulfur compounds. A sulfate ion peak at 981 cm^{-1} is used as a reference.

Figure 3. Raman spectra of nitrite ion-bisulfite ion mixtures taken 24 hours after mixing.

A. 0.10 M NO_2^- + 0.50 M HSO_3^-

B. 0.26 M NO_2^- + 0.50 M HSO_3^-

C. 0.51 M NO_2^- + 0.50 M HSO_3^-

D. 1.02 M NO_2^- + 0.50 M HSO_3^-

Figure 4. Raman spectra of (A) HADS + $SO_4^=$, (B) HAMS + $SO_4^=$, (C) 0.26 M NO_2^- + 0.50 M HSO_3^-, and (D) 0.51 M NO_2^- + 0.50 M HSO_3^-.

Figure 5. Raman spectrum of a 1.02-M nitrite ion-0.50-M sulfite ion mixture taken one week after mixing.

Figure 6. Raman spectra of 0.10-M nitrite ion - 0.50 M-bisulfite ion mixture.

A. 20 minutes after mixing

B. 2 hours after mixing

C. 24 hours after mixing

D. 105 days after mixing

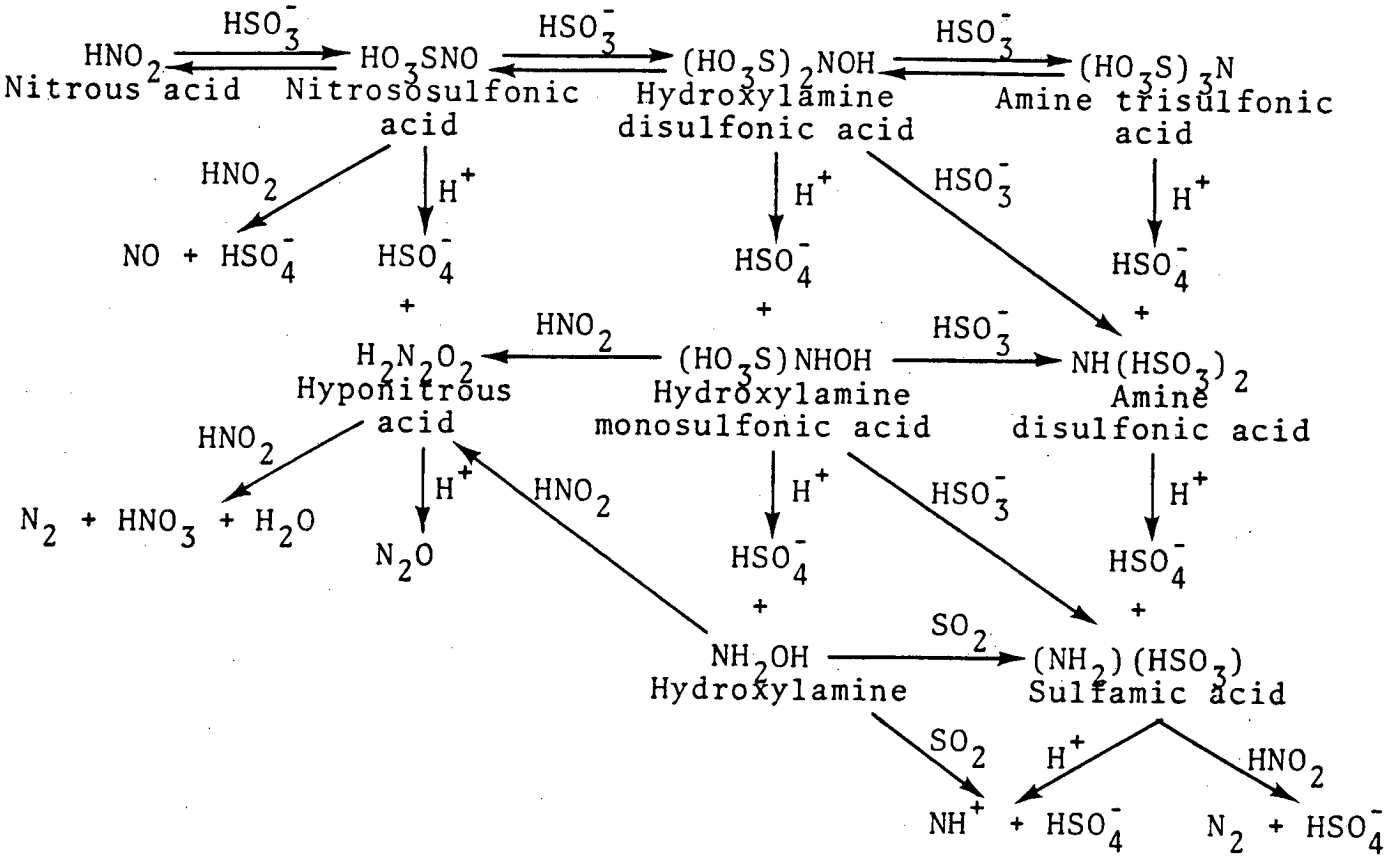
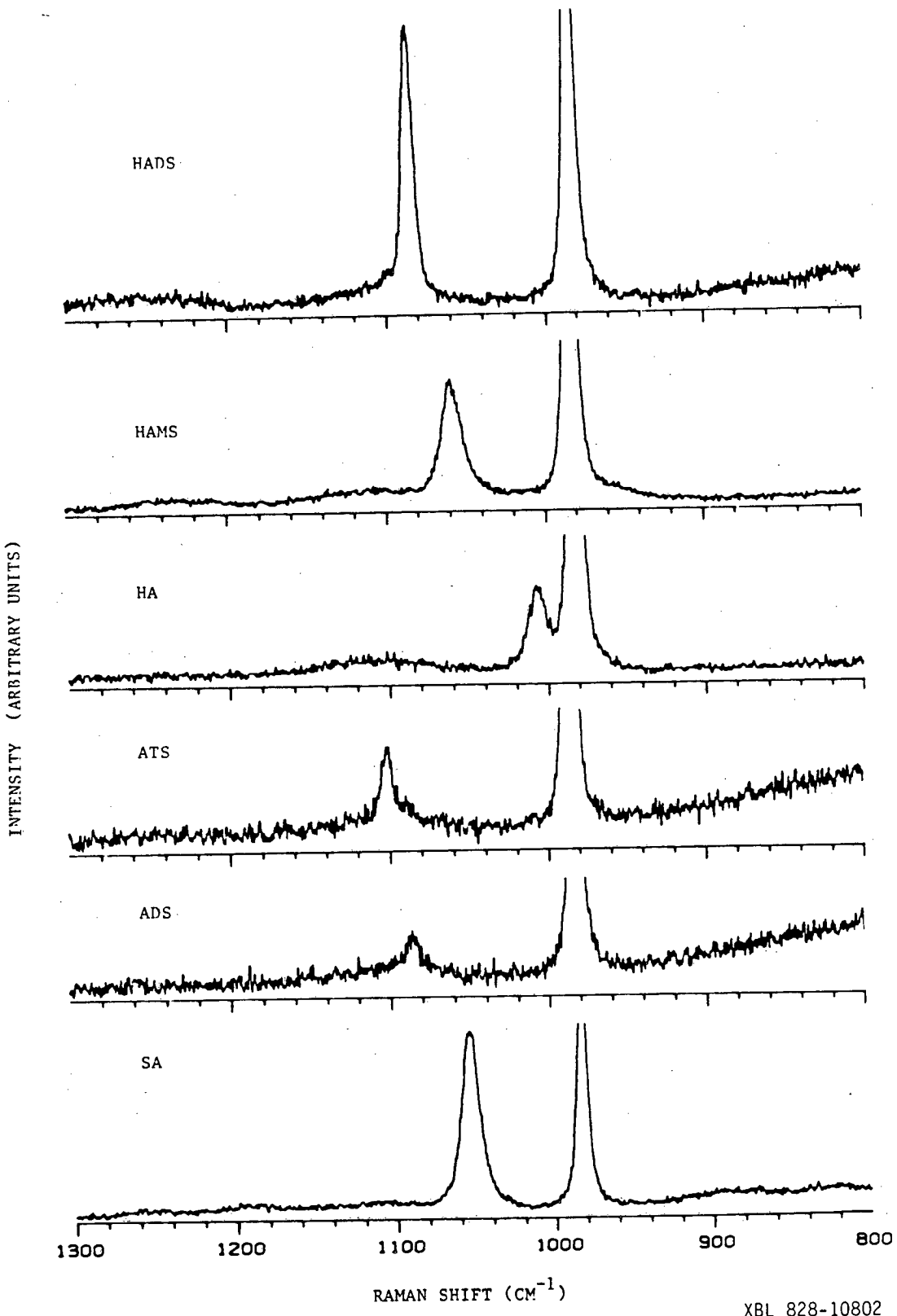

HNO2
Nitrous acid
HSO3-
HO3SNO
Nitrososulfonic acid
(HO3S)2NOH
Hydroxylamine disulfonic acid
(HO3S)3N
Amine trisulfonic acid
NO + HSO4-
H2N2O2
Hyponitrous acid
(HO3S)NHOH
Hydroxylamine monosulfonic acid
NH(HSO3)2
Amine disulfonic acid
N2 + HNO3 + H2O
N2O
NH2OH
Hydroxylamine
(NH2)(HSO3)
Sulfamic acid
SO2
NH+ + HSO4-
N2 + HSO4-

Figure 1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HAMS
HA
ATS
ADS
SA
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800
RAMAN SHIFT (CM^{-1})
XBL 828-10802

Figure 2

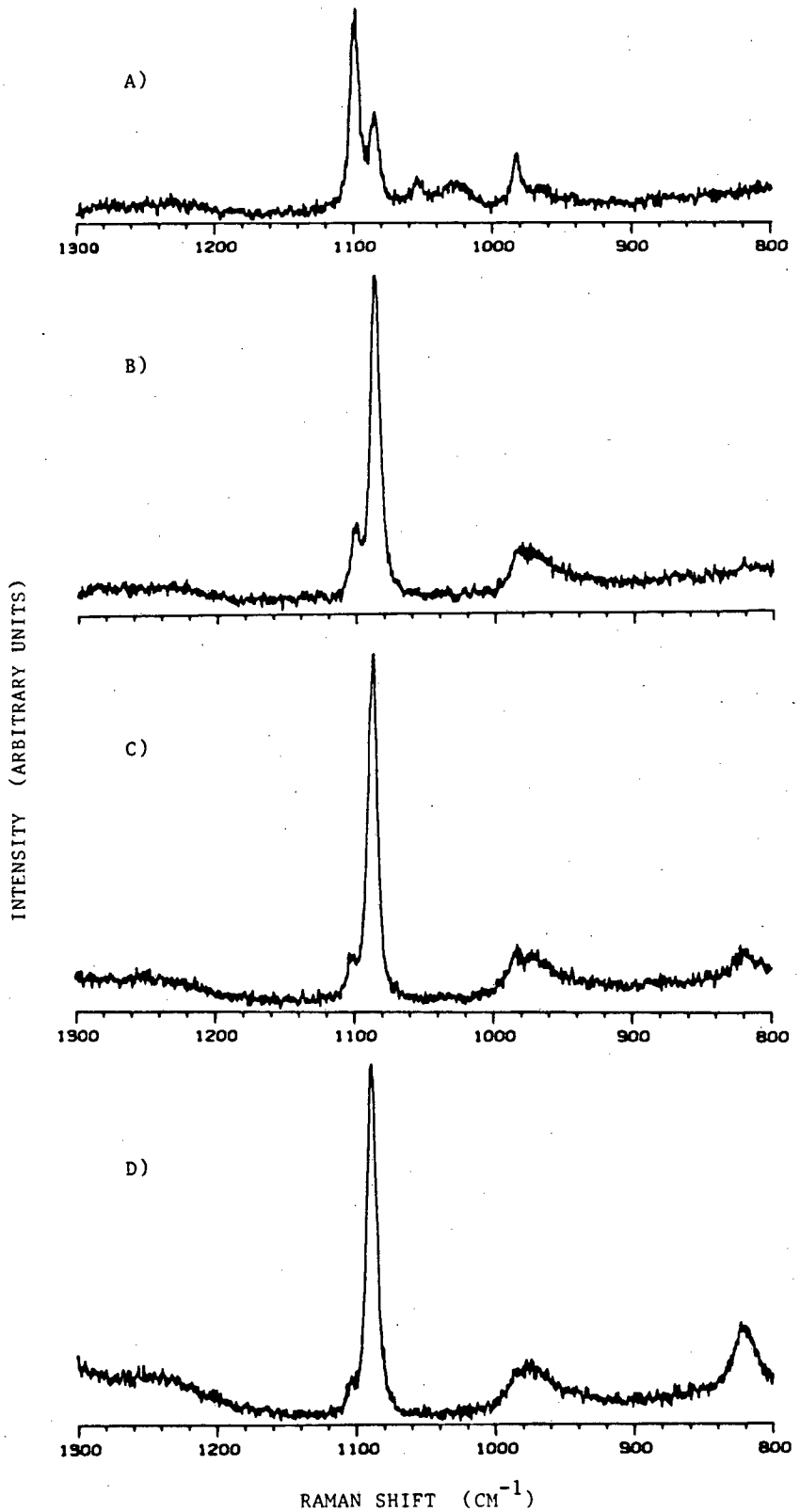

Figure 3

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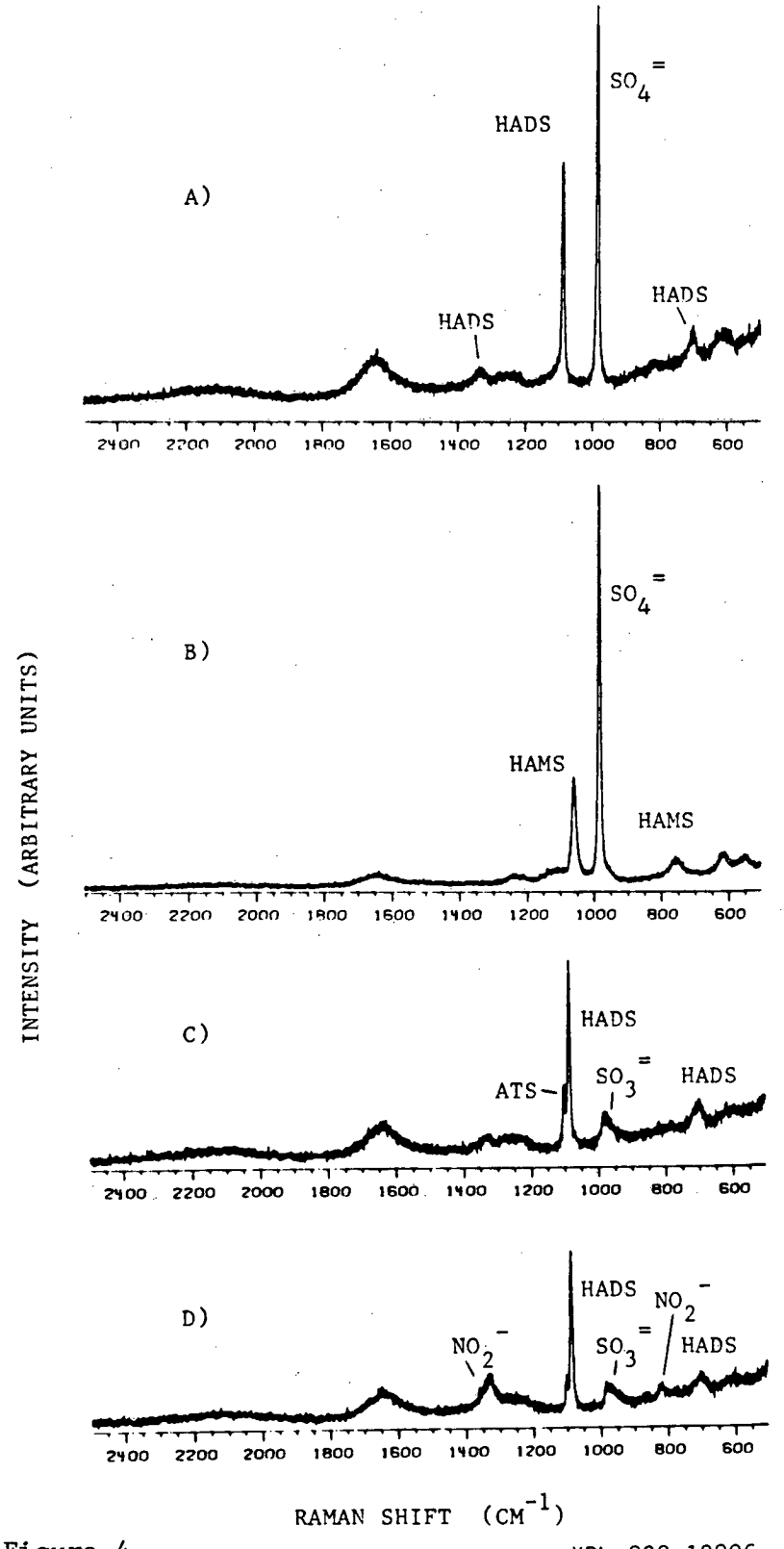

Figure 4

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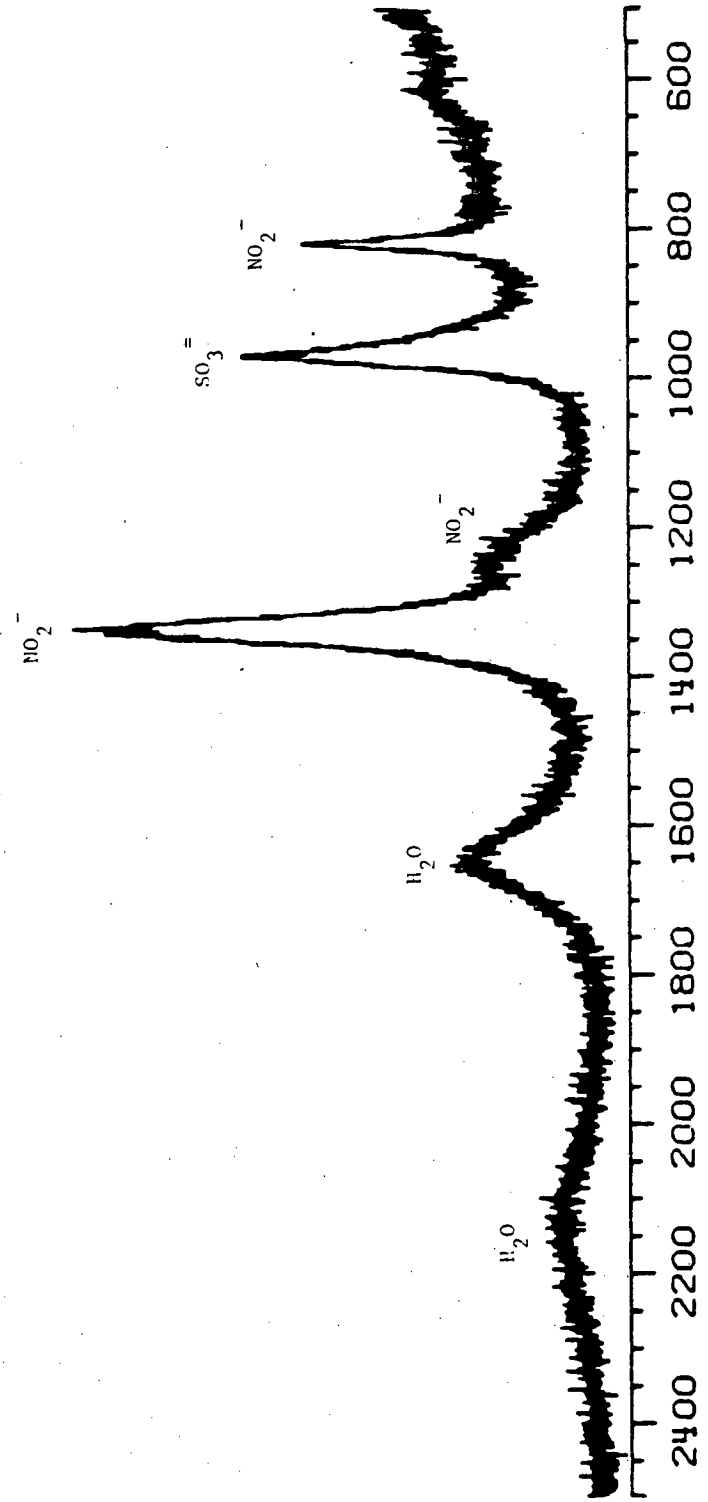

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Figure 5

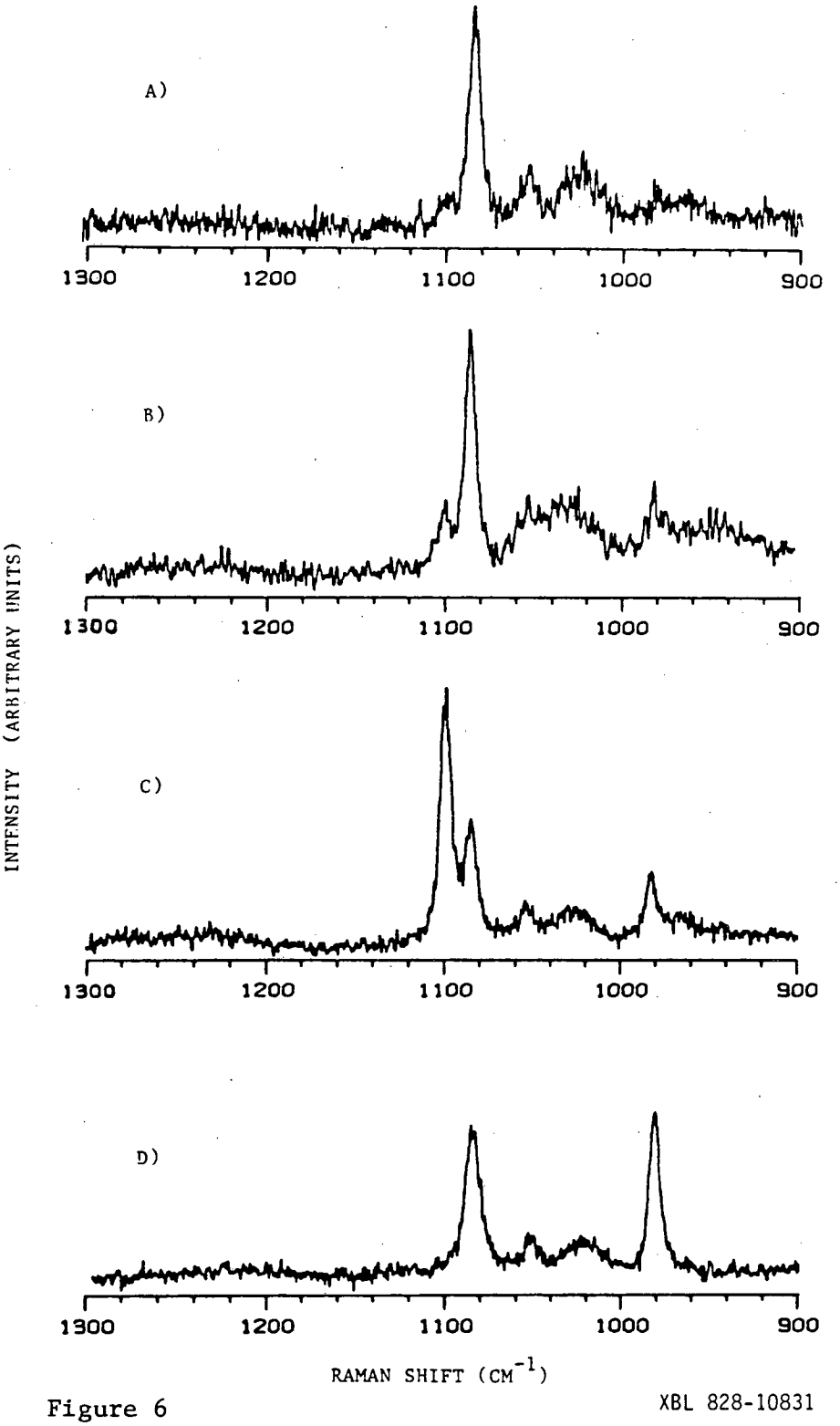

Figure 6

XBL 828-10831

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