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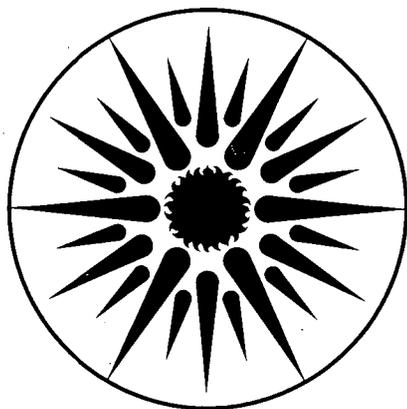
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## The Oxidation of $\text{HSO}_3^-$ by $\text{O}_2$

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### ABSTRACT

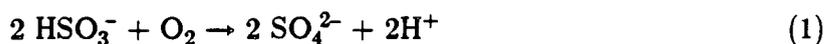
The oxidation of bisulfite ion by dissolved oxygen has been studied using a high pressure flow system and Raman spectroscopy. We have detected an intermediate in the reaction which appears to be formed from 2  $\text{HSO}_3^-$  and 1  $\text{O}_2$ . We propose that the intermediate is disulfate ion,  $\text{S}_2\text{O}_7^{2-}$ , which hydrolyzes into  $\text{SO}_4^{2-}$ ,  $\text{H}^+$  and/or  $\text{HSO}_4^{2-}$  with a hydrolysis rate constant of  $1.33 \pm .26 \times 10^{-2} \text{ sec}^{-1}$  at 25 °C.

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## Introduction

An improved understanding of the kinetics of the oxidation of dissolved  $\text{SO}_2$  by oxygen in aqueous solutions would benefit flue gas desulfurization programs in which control of the oxidation of  $\text{SO}_2$  is desirable.<sup>1</sup> This oxidation reaction has been studied for many years, yet the oxidation mechanism is unclear.<sup>2,4</sup> Previous studies of this reaction have reported conflicting results because the reaction is very sensitive to many kinds of impurities. Some of these impurities act as catalysts<sup>5</sup> while others are inhibitors at very low concentrations.<sup>3,6</sup> Studies of this reaction have generally monitored the rate of disappearance of one of the reactants or the rate of formation of sulfate ion using wet analytical techniques. The reaction stoichiometry,



was used to deduce the concentrations of the other species. We have studied this reaction using laser Raman spectroscopy (LRS) to monitor the behavior of all observable species during the reaction. Our results indicated that a mass balance for sulfur or oxygen could not be obtained from just the products and reactants. A signal due to an intermediate in the reaction was subsequently discovered. This intermediate has not been reported in earlier studies.

## Experimental

A high-pressure stopped-flow/continuous-flow mixing system was constructed for use with the Raman spectrometer. Two 20 l cylindrical stainless steel vessels were used for preparing and storing the reactant solution under pressure. The system is capable of being pressurized to 100 atm to obtain a sufficiently high dissolved oxygen concentration for detection by LRS. Besides dissolved oxygen, use of LRS permits the observation of the following species in the reaction system:  $\text{SO}_2$  (aq),  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_5^{2-}$

and  $\text{S}_2\text{O}_6^{2-}$ .<sup>7</sup> The reactants flowed through separate flowmeters into a mixer. The mixer was designed to efficiently mix the two solutions at flow rates above 2 ml/sec. This was confirmed by observing the mixing of Fe(II)(EDTA) with dissolved nitric oxide in a spectrophotometer. The Fe(II)(EDTA) + NO reaction is sufficiently rapid that the rate of product formation was limited by mixing. After mixing, the solution flowed through a quartz cell where it was illuminated by the 514 nm line from an argon ion laser. The light scattered by the solution was collected and passed through a Spex 1403 double spectrometer. A Spex Datamate computer was used to acquire and analyze the data. The solution then passed through a metering valve, where the pressure dropped to ambient levels, and past a pH electrode.

The bisulfite solution was prepared by adding reagent grade sodium metabisulfite to deionized water that had been deoxygenated by passing nitrogen through it. After it was prepared, it was sealed in one of the tanks and pressurized with nitrogen. Potassium perchlorate was added as a reference so that quantitative measurements could be made.

The oxygen solution was prepared by passing oxygen through a potassium perchlorate solution under pressure. The oxygen concentration was determined by comparing the oxygen Raman peak with the perchlorate Raman peak.

The species observed in these experiments, along with their Raman peaks and relative scattering efficiencies (RSE's) are listed in Table 1. The RSE for a compound is defined as

$$\text{RSE} = \frac{\text{compounds peak height}/\text{compounds molarity}}{981 \text{ cm}^{-1} \text{ SO}_4^{2-} \text{ peak height}/\text{SO}_4^{2-} \text{ molarity}}$$

Two types of experiments were carried out: continuous flow and stopped flow. In the former type of experiment, the mixed solution was flowed through the cell at a steady rate while the spectrometer was scanned over the desired region. The volume between the mixer and the cell could be changed to vary the time between mixing and observation.

In the stopped flow experiments, the desired flow through the cell was established, and the spectrometer was set at the desired wavenumber setting. The flow of solution through the cell was stopped under pressure, and the computer recorded the signal change due to the reaction. Afterwards, the spectrometer was set to another position, and the process was repeated under the same conditions until all the desired species had been observed.

A number of experiments have been done with dissolved oxygen concentrations ranging from  $8 \times 10^{-3}$  to  $4 \times 10^{-2}$  M (after mixing) and bisulfite concentrations ranging from  $6 \times 10^{-2}$  to  $5 \times 10^{-1}$  M (after mixing). Initial  $O_2$  to  $HSO_3^-$  concentration ratios ranged from 0.02 to 0.4. The pH of the solution immediately after mixing was in the range of 3.5 to 4. All runs were done at  $25^\circ C$  and at ionic strength  $\mu = 0.5$  M.

### Results and Discussion

Most experiments were carried out under stopped flow conditions. In these experiments, the signals due to  $SO_4^{2-}$ ,  $HSO_3^-$ ,  $SO_2(aq)$  and  $O_2$  were observed. After solution had reacted, the Raman spectrum  $900$  to  $1200\text{ cm}^{-1}$  and  $1540$  to  $1560\text{ cm}^{-1}$  was collected. From these data, the concentration vs. time profiles and the final concentrations of  $HSO_3^-$ ,  $O_2$ ,  $SO_4^{2-}$ , and  $SO_2(aq)$  could be determined by comparing their peaks with the  $ClO_4^-$  peak. The  $H^+$  concentration could be determined from the equilibrium

$$\frac{[H^+][HSO_3^-]}{[SO_2(aq)]} = .0139\text{ M} \quad (\text{ref. 8})$$

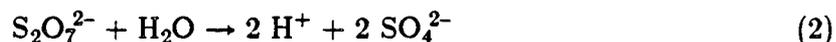
and the  $\text{HSO}_4^-$  concentration could be estimated from

$$\frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = .0102 \text{ M} \quad (\text{ref. 9})$$

With the concentration vs. time profiles established, mass balances for sulfur and oxygen could be obtained. For sulfur, the curves for  $\text{HSO}_3^-$ ,  $\text{SO}_2(\text{aq})$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$  were added together. For oxygen, the curves for  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  were added and multiplied by two, and then added to the oxygen curve. The concentrations of other species, such as  $\text{S}_2\text{O}_5^{2-}$ , were negligible and were not included in the mass balances. The mass balance plots for both sulfur and oxygen generally showed a dip shortly after mixing, which implied the presence of an intermediate. Figure 1 shows the rapid decrease in the  $\text{O}_2$  reactant and the slow build-up in  $\text{S(VI)}(\text{SO}_4^{2-} + \text{HSO}_4^-)$  after mixing. While attempting to observe  $\text{S}_2\text{O}_6^{2-}$  at  $1092 \text{ cm}^{-1}$ , we obtained a curve with a profile in time close to that expected for the intermediate. Subsequent study showed that the peak of the intermediate was centered at  $1090 \text{ cm}^{-1}$  and was somewhat broader than  $\text{S}_2\text{O}_6^{2-}$  (Fig. 2). Scans taken during continuous flow experiments indicated the presence of a second, weaker peak of the intermediate at about  $740 \text{ cm}^{-1}$ . We attribute the Raman peaks to S-O stretches. Other oxysulfur compounds with Raman peaks near  $1090 \text{ cm}^{-1}$  include  $\text{S}_2\text{O}_6^{2-}$  ( $1092 \text{ cm}^{-1}$ ) and  $\text{S}_2\text{O}_8^{2-}$  ( $1074 \text{ cm}^{-1}$ ). Dithionate ion is very stable and does not decay in the manner of the intermediate.

In runs where the intermediate was rapidly formed and then decayed away, the changes in concentrations of  $\text{O}_2$ ,  $\text{HSO}_3^-$ , and  $\text{S(VI)}$  could be used to determine the stoichiometry of the intermediate. Both the ratios of the change in  $\text{HSO}_3^-$  to the change in  $\text{O}_2$  and of the change in  $\text{S(VI)}$  to the change in  $\text{O}_2$  were two to one, indicating that the intermediate is formed from two  $\text{HSO}_3^-$  and one  $\text{O}_2$ . We have studied the reaction mixture by ESR spectroscopy and found no signal which can be ascribed to the

intermediate, indicating that it is not a free radical. We propose the intermediate has the formula of  $S_2O_7^{2-}$ . The decomposition of the intermediate does not appear to be significantly influenced by the experimental conditions. It appears that the decomposition occurs by:



Plots of  $\log_e[\text{intermediate}]$  vs. time (Fig. 3) are linear, indicating first order decomposition. The values of the decomposition rate constant are tabulated in Table 2, along with the initial reactant concentrations after mixing. The initial pH of the mixed reactants varied from 3.6 to 4.3. The values obtained from the decay of the intermediate agree well with the values obtained from the build-up of  $SO_4^{2-}$  and  $H^+$ . The average value of all determinations is  $k = .0133 \pm .0026 \text{ sec}^{-1}$  at  $25^\circ \text{C}$  and  $\mu = 0.5 \text{ M}$ . The decomposition rate did not appear to be influenced by the pH of the solution over the range of pH 2 to 5, nor was influenced by the presence of  $Fe^{3+}$  or  $Mn^{2+}$  at concentrations up to about  $10^{-4} \text{ M}$ .

The properties and behavior of the intermediate are very similar to those of the disulfate ion,  $S_2O_7^{2-}$ . To make a confirmation that the intermediate is indeed disulfate ion, we prepared sodium disulfate by heating sodium bisulfate to  $180^\circ \text{C}$  for five days.<sup>10</sup> The hydrolysis of the disulfate ion was observed by monitoring the decay of the  $1090 \text{ cm}^{-1}$  Raman peak with time. Values of the hydrolysis constant similar to those in Table 2 were obtained. There have been three previous studies<sup>10-12</sup> of the hydrolysis rate of the disulfate ion in aqueous solution. All of the studies found an activation energy of about 11 kcal/mole, although Hofmeister and Van Wazer obtained a lower rate constant at  $25^\circ \text{C}$  than the other groups. The hydrolysis rate constant we obtained in this study agrees well with the values reported.<sup>11, 12</sup> Thilo and von Lampe<sup>11</sup> reported that sodium ions accelerate the rate somewhat. This effect is sufficiently small that our value of the

rate constant requires no correction.

To obtain the Raman spectrum of  $S_2O_7^{2-}$  at 25 °C, about 0.2 g of the salt was mixed with about 5 ml of water for 5 seconds, and a sample was quickly collected. A Raman spectrum was collected over a 40  $cm^{-1}$  band for about 25 seconds. This was done for bands at 305-345  $cm^{-1}$ , 400-440  $cm^{-1}$ , 720-760  $cm^{-1}$ , 760-800  $cm^{-1}$ , 800-840  $cm^{-1}$  and 1070-1110  $cm^{-1}$ . A composite spectrum of these results is shown in Fig. 4A, after correcting for the background. The approximate peak maxima are located at 319  $cm^{-1}$ , 739  $cm^{-1}$  and 1090  $cm^{-1}$ . The only previously reported Raman spectrum of disulfate ion in aqueous solution was obtained by Millen<sup>13</sup>, who was uncertain of the peak at 735  $cm^{-1}$ . Frequency assignments for solid disulfate salts were made by Simon and Wagner<sup>14</sup>. The spectrum confirms the peak at about 740  $cm^{-1}$  in spectra of the reaction mixtures is due to disulfate ion and not another intermediate.

To obtain a mass balance for sulfur and oxygen, the relative scattering efficiency (RSE) for  $S_2O_7^{2-}$  is needed. To obtain a measure of the relative scattering efficiency of  $S_2O_7^{2-}$ , about 2 g of the sodium disulfate salt was mixed with 30 ml of water at 0 °C. After mixing for 30 seconds, it was added to a reservoir, in a 0 °C bath, which fed the solution through the spectrometer cell. Fresh aliquots of the solution were added every 90 seconds while the spectrum was collected. The spectrum is shown in Figure 4B. Some decomposition had occurred by the time the solution flowed through the cell, as indicated by the  $SO_4^{2-}$  peak at 981  $cm^{-1}$ . By the change of height of the  $SO_4^{2-}$  and  $HSO_4^-$  peaks between the flowing solution and the completely decomposed solution, the RSE of the  $S_2O_7^{2-}$  1090  $cm^{-1}$  peak was calculated to be about 0.33.

For comparison with the spectra of  $S_2O_7^{2-}$ , Figure 4C shows the difference between Raman spectra of the  $O_2 + HSO_3^-$  reaction during and after reaction.  $SO_4^{2-}$  and  $HSO_4^-$  are formed by the reaction and have negative peaks (not shown).  $HSO_3^-$  and the

intermediate decrease as the reaction goes to completion and have positive peaks. The spectra in Figure 4 suggest that the peak at about  $740\text{ cm}^{-1}$  has two components. It is possible that other intermediates are present in the reaction mixture. If they are present, they are at lower concentrations or exist for shorter times than  $\text{S}_2\text{O}_7^{2-}$ .

Connick and co-workers<sup>15</sup> have been studying the oxygen-bisulfite ion reaction and have found indirect evidence of the intermediate. They are studying the reaction at more dilute conditions than those used in this study, with reactant concentrations of about  $10^{-4}\text{ M}$  oxygen and  $10^{-2}\text{ M HSO}_3^-$ . Their measurements of the rate constant for the decay of the intermediate are in good agreement with our results.

The formation of the observed intermediate shows complicated dependence on reactant concentrations and trace amounts of metal ions such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . As the pH of the reaction mixture is raised above 4.5, the relative amount of intermediate formed decreases, suggesting the presence of another reaction channel. The fraction of S(IV) in the form of  $\text{SO}_3^{2-}$  increases rapidly as the pH increases. It may be that another oxidation reaction channel proceeds through the involvement of  $\text{SO}_3^{2-}$  at a faster rate than the reaction involving  $\text{HSO}_3^-$ . The observed intermediate does not seem to be involved in this process. The factors that govern the formation of the intermediate are under investigation.

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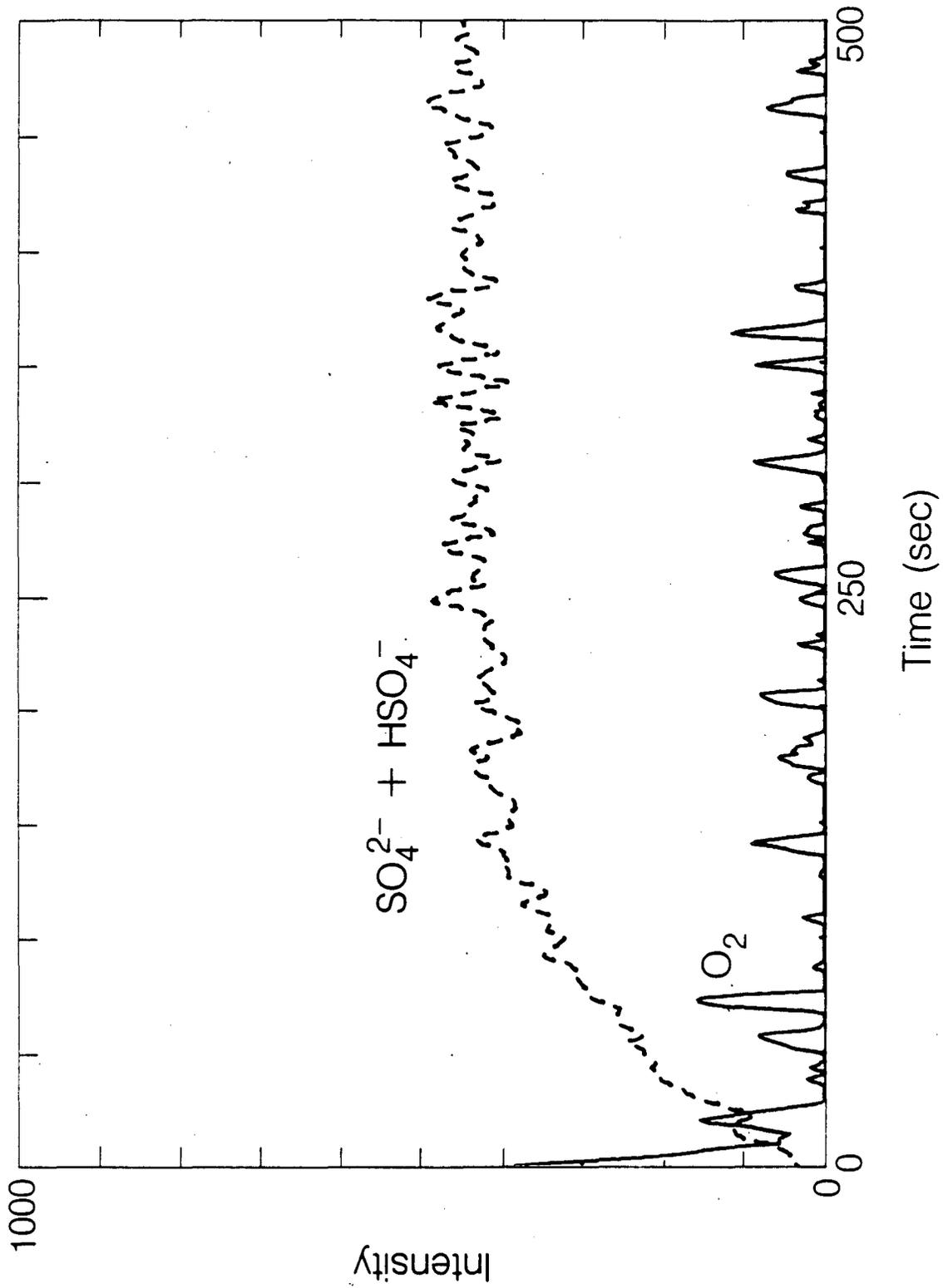
| <b>Table 1</b>  |   |                 |
|-----------------|---|-----------------|
| <i>Compound</i> | <i>Raman Peak<br/>(cm<sup>-1</sup>)</i> | <i>RSE*</i>     |
| $S_2O_5^{2-}$   | 235                                     | 0.15            |
| $ClO_4^-$       | 934                                     | 1.06            |
| $SO_3^{2-}$     | 967                                     | 0.10            |
| $SO_4^{2-}$     | 981                                     | 1.00            |
| $HSO_3^-$       | 1023                                    | 0.12            |
| $HSO_4^-$       | 1050                                    | 0.19            |
| $S_2O_7^{2-}$   | 1090                                    | <i>ca.</i> 0.33 |
| $S_2O_6^{2-}$   | 1092                                    | 0.48            |
| $SO_2$ (aq)     | 1152                                    | 0.94            |
| $O_2$           | 1550                                    | 0.38            |

\*Relative Scattering Efficiency — compared to  $SO_4^{2-}$ .

| Table 2  |                                     |  |                  |                           |
|--|-------------------------------------|--|------------------|---------------------------|
| Initial<br>[HSO <sub>3</sub> <sup>-</sup> ]<br>(M) | Initial<br>[O <sub>2</sub> ]<br>(M) | Decay Rate Constant (sec <sup>-1</sup> ) |                  |                           |
|  |                                     | from intermediate                        | from total S(VI) | from total H <sup>+</sup> |
| .19  | .014                                | .0135                                    | .010             | .0115                     |
| .22  | .012                                | .0141                                    | .0124            | .0130                     |
| .22  | .016                                | .0139                                    | .0130            | .0183                     |
| .22  | .032                                | .0112                                    | .0104            | .0116                     |
| .22  | .038                                | .0133                                    | .0153            | .0126                     |
| .22  | .0385                               | .0178                                    | .0132            | .0127                     |
| .23  | .014                                | .0139                                    | .0111            | .0114                     |
| .25  | .036                                | .0141                                    | .0138            | .0148                     |
| .27  | .014                                | .0099                                    | .0141            | .0141                     |
| .30  | .024                                | .0180                                    | .0168            | .0118                     |
| .34  | .016                                | .0126                                    | .0091            | .0104                     |
| .34  | .017                                | .0183                                    | .0116            | .0119                     |
| .34  | .017                                | .0125                                    | .0115            | .0099                     |
| .34  | .017                                | .0122                                    | .0086            | .0112                     |
| .475   | .014                                | .0150                                    | .0161            | .0113                     |
| .68  | .014                                | .0144                                    | .0203            | .0177                     |

### Figure Captions

- Fig.1 Relative concentrations of oxygen (solid line) and total S(IV) (dashed line) with time after mixing.
- Fig.2 Raman spectra of the intermediate (left peak) and  $S_2O_6^{2-}$  (right peak)
- Fig.3 Typical decomposition plots of the intermediate
- Fig.4 A: Composite Raman spectrum of disulfate ion in solution at 25 ° C  
B: Raman spectrum of flowing disulfate ion in solution at 0 ° C  
C: Difference between Raman spectra of the reaction mixture during and after reaction



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Fig. 1

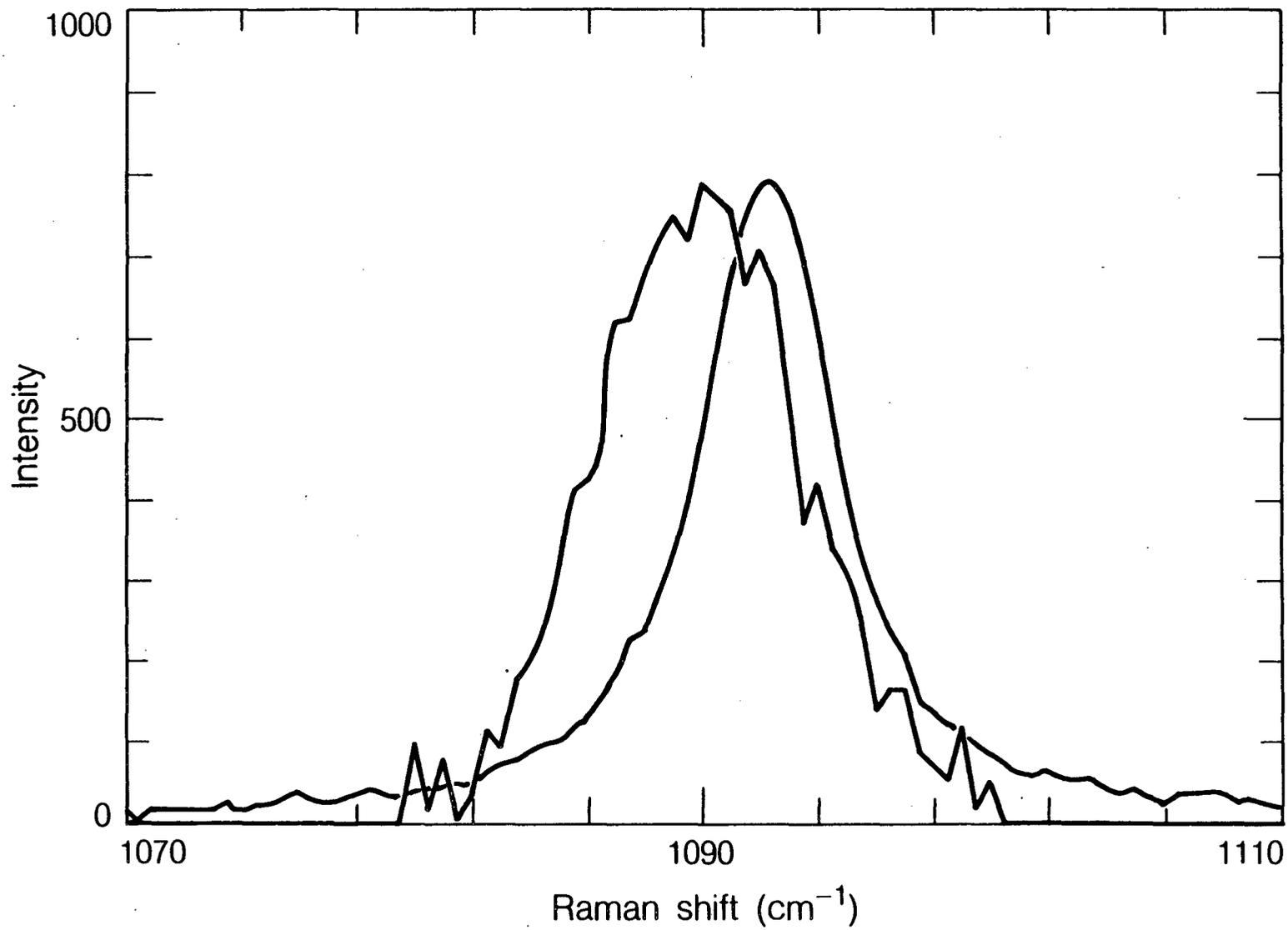
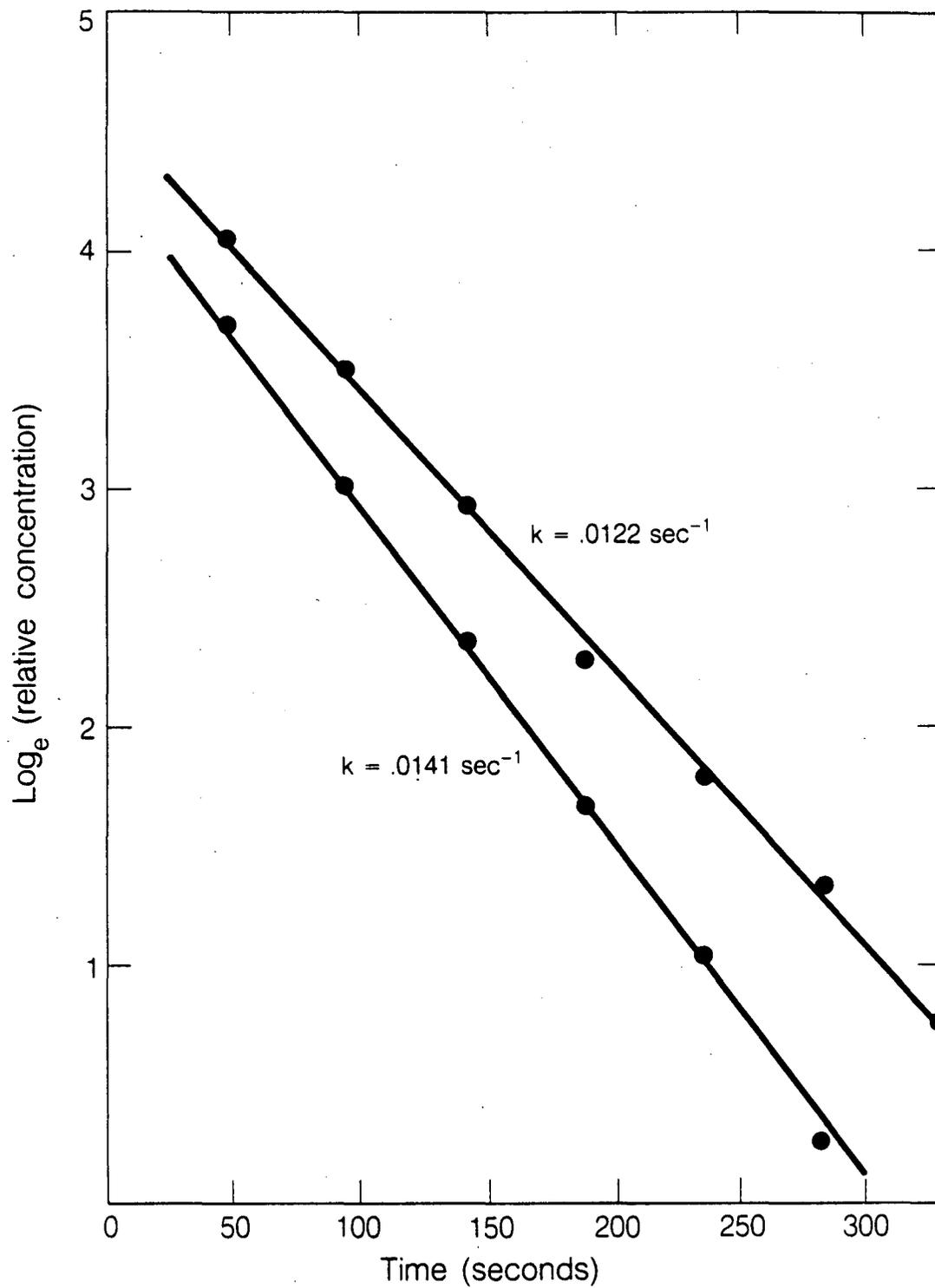


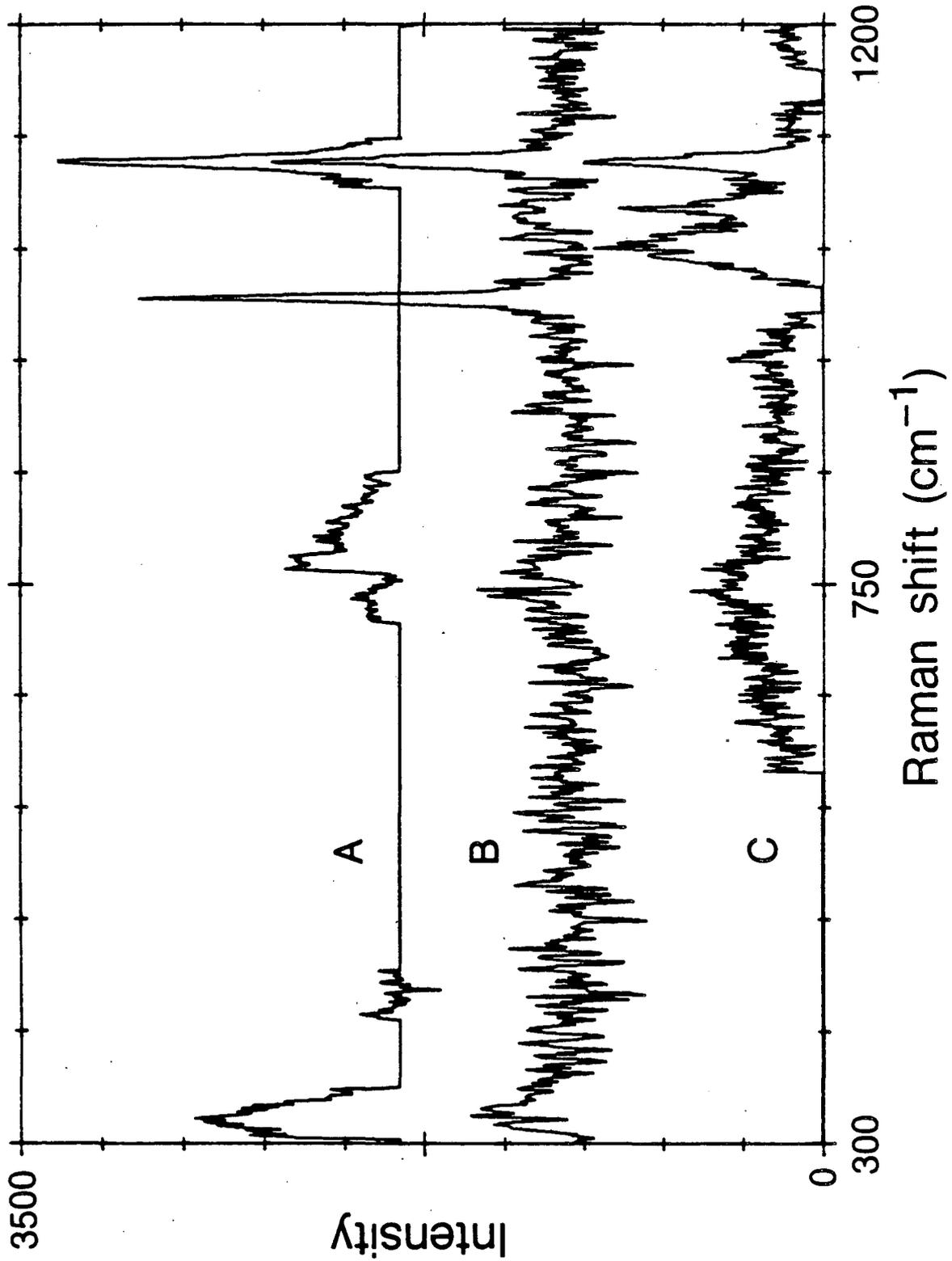
Fig. 2

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Fig. 3



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Fig. 4

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