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**U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards**



# **Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution**

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# Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution

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NSRDS-NBS no 69

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary  
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## Foreword

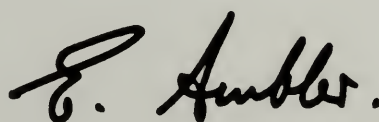
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NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.



ERNEST AMBLER, *Director*

## Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or  $G$  values (molecules formed or destroyed per 100 eV). Various indirect methods based on  $G$  values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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# Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution

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Optical absorption spectra are presented for 77 nonmetallic, inorganic radicals and radical ions, produced by radiolysis or photolysis in aqueous solution. This atlas results from the compilation, evaluation, and replotting of spectra from the literature. Additional information is included such as extinction coefficients, initial chemical conditions, methods of transient generation and spectral acquisition, references, mechanisms of transient formation, and notes on dosimetry.

Key words: Absorption spectra; aqueous solution; extinction coefficients; inorganic; radical ions; radicals; transients.

## Introduction

Simple inorganic radicals and radical ions in solution have been one of the favorite topics for study in radiation chemistry since the introduction of pulse radiolysis in the early 60's. Some of these radicals had been studied earlier by flash photolysis, but the number of flash photolysis studies increased in parallel with the radiolysis studies. The peak of the research activity on the simple inorganic species came in the late 60's and early 70's. Although many interesting problems remain in this field, a consensus seems to have been reached concerning the identity of the chemical composition of many of these inorganic transients. Such transients are currently being used to form more complicated species in organic and biological systems through oxidation and reduction.

One of the most fruitful techniques that has been used to study the chemistry of the simple inorganic species has been optical absorption spectroscopy. Most of these species absorb ultraviolet and visible radiation. Although optical spectroscopy is not very helpful in determining the exact structure of transients, it is very valuable in following the progress of reactions taking place on the nanosecond or microsecond time scale. Because of this use as a tool to study the kinetics and the use of transient spectra to identify reaction intermediates and individual steps in reaction mechanisms, the optical spectra have become useful data to the experimenter. Since many spectra are now scattered through the literature and since many of these are well characterized, it now seems like an opportune

time to collect all of these spectra together in one volume.

It is the purpose of this volume to collect as many spectra of nonmetallic inorganic transients in aqueous solution as possible. The main emphasis has been to collect the most complete and well-characterized spectra that are available in the literature. In addition, special effort was made to obtain extinction coefficients for these spectra.

## Explanation of Display and Definition of Symbols and Units

The spectra are displayed on a uniform grid, with a standard 0 to 100 relative absorbance scale and with a standard 500 nm long wavelength scale (1000 nm scale is used for hydrated electron spectrum). The relative absorbance,  $A$ , is defined by

$$A = N \times \log_{10} (I_0/I) \quad (1)$$

In this equation  $I_0$  is the incident intensity of the monitoring light beam at the wavelength being monitored,  $I$  is the intensity of the monitoring light beam, at the same wavelength, that is transmitted through the sample, and  $N$  is a normalization factor chosen so that the largest absorbance is 100. The wavelengths are given in nanometers (nm) =  $10^{-9}$  meters. An alternative abscissa scale is used in these spectra on the top line of the plots in a scale that is

proportional to energy. The units used are  $\text{cm}^{-1}$ . One eV is approximately  $8068 \text{ cm}^{-1}$ . To the right of the spectral plots is a sliding extinction coefficient scale.

$$\epsilon = (L[X])^{-1} \log_{10} (I_0/I) \quad (2)$$

$I_0$  and  $I$  are defined the same as above,  $L$  is the length of the optical path, and  $[X]$  is the concentration of the absorbing species, X.

In addition to the spectral display, additional information is given. Under the heading "Transient," the transient species is identified; other information which may be included under this heading is the wavelength of the maximum absorbance, an extinction coefficient, and a second-order decay constant,  $k$ , defined by

$$d[X]/dt = 2k[X]^2. \quad (3)$$

The wavelength of the absorption maximum and the extinction coefficient are given under this heading only when explicitly quoted by the experimenters or when taken from another reference. If  $\lambda(\text{max})$  and  $\epsilon$  are quoted by the experimenters, then the smoothed curves are normalized (see below) to these numbers, both with respect to the ordinate and the abscissa. Extinction coefficients are given in  $\text{L mol}^{-1} \text{ cm}^{-1}$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ); decay rate constants are given in  $\text{L mol}^{-1} \text{ s}^{-1}$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). No systematic attempt was made to include the second-order decay rate constants.

The information following the heading "System" concerns the chemical composition of the starting system. Under the headings of "Transient generation" and "Spectral acquisition" the physical equipment used to create the transients and detect them are given. Of particular interest in these two sections is the nature of the dosimetry (measurement of the amount of radiation absorbed in the sample) and actinometry plus the precautions taken to eliminate artifacts, like scattered light. The heading "Reference" contains the literature source of the displayed spectrum.

The information contained under the heading "Transient formation" is of particular interest when transients are prepared in a pulse radiolysis experiment. As opposed to near-ultraviolet or visible photolysis of aqueous solutions where the solutes form the transients in a relatively direct fashion, radiolysis experiments involve the decomposition of the water as a first step. The three major radicals from this process are OH,  $e(\text{aq})^-$ , and H. The amount of H formed is five or six times less than that of either OH or  $e(\text{aq})^-$ . These three primary radicals can react with solutes or other

transients to form the transients to be studied. Various scavengers are added to prevent the formation of interfering species or to maximize the yield of the transient to be studied. The detailed mechanisms of the authors are given in this section whenever possible, but in many cases these equations are given only as plausible formation equations and should not be understood as precise mechanisms endorsed by the authors who measured the spectrum.

The "Footnotes" are designed mainly to give additional information on alternate extinction coefficients, assumptions on  $G$  values,

$$G(X) = \text{number of X radicals formed for 100 eV} \\ \text{of the radiation absorbed by the system} \quad (4)$$

and additional information on special purifications and other precautions.

### Criterion for Inclusion

The following standards were set for the spectra to be included in this atlas. Attempts were made to include spectra that contain contributions from only one transient species, have chemical or physical proof of the chemical assignment, correct for instrumental effects like scattered light, give extinction coefficients, and contain a sufficient number of data points to indicate the precision of the smooth spectral curve. These criteria could not always be met. However, in cases where the transients were considered to be important, the spectra were included with some documentation indicating appropriate qualifications. One common problem, for example, is the failure to correct for spectral contributions of species resulting from H atom reactions in pulse radiolysis experiments in aqueous solutions. This is often neglected on the basis of the low yield of hydrogen atoms relative to hydroxyl radicals and hydrated electrons. However, this contribution is not always negligible, and a spectrum must be viewed with some caution when this type of omission occurs.

All of the spectra in this atlas are taken from the literature. Since the pioneering works on these inorganic transients are approximately 10 to 20 years old, newer spectra often exist in private collections and in the literature. These later spectra are often better characterized than the original works. This has been due in large part to refinements in techniques and to better understanding of the chemical processes. One improvement in equipment that has resulted in more reliable spectral shapes has been the interfacing of the experiment to computers. This has allowed the use of



convenient signal averaging techniques [1]<sup>1</sup>. In addition, the case of data handling with these systems has allowed the experimenter to explore a larger set of wavelengths [2]. Because of these general advances, spectra that have appeared later in the literature than the pioneering works are often chosen for this atlas over the original works.

Even though spectra obtained from private collections often have these same advantages, it was decided that they should be excluded from the atlas since so many of them were inaccessible to this Data Center. However, the Radiation Chemistry Data Center is collecting these newer spectra and is storing them in a computer-readable form. Spectra will be updated as the Center is made aware of new measurements. Some spectra from private collections are already on file.

### **Difficulties with Yields and Extinction Coefficients**

There is probably much less variability among the various reported spectra of a given transient than among the various reported extinction coefficients of that transient. Many factors could contribute to this difficulty. Among the possible causes are nonuniform irradiation of sample, poor wavelength calibration, faulty dosimetry, scattered light problems, and poor time resolution. Discussion of these and other experimental problems has been thoroughly covered elsewhere [3,4]. However, even when the normal experimental precautions are taken, there remain difficulties. The ultimate source of the problem with extinction coefficients lies in the difficulty of knowing the concentration of a short-lived transient (see eq (2)). Since most of the extinction coefficients in this work are taken from radiolysis works, this means that it is crucial to know the yields (or  $G$  values) of the primary radicals, the mechanism of production of the transients from these radicals, and the dose of radiation absorbed by the sample in order to calculate the concentration of the species of interest.

The problem of knowing the  $G$  value is particularly acute, for both the sample itself and for the dosimetry. Usually  $G(X)$ , itself, is not measured directly. It is usually based on a yield of primary radicals that has been estimated from measured yields at infinite dilution of all scavengers. These yields represent the number of primary radicals that diffuse out of the tracks formed by the ionizing radiation and their secondary electrons. Immediately after the arrival of the high energy radiation, the tracks contain a high density of radicals

and other fragments, and many of the radicals combine with each other. Thus only a fraction of the original primary radicals escape into the bulk solution and are measured.

In a usual radiolysis experiment in which absorption spectra are to be measured, scavengers and/or solutes must be added at some finite concentration to react with the primary radicals. However, as the concentration of the scavenger is raised, the chance that the scavenger molecule will initially be present in the volume of a track increases. If this eventually takes place, the primary radicals which would normally combine with other primary radicals in the track will react with the scavenger instead. Thus at high scavenger concentration, scavenging in the track increases the effective yield of primary radicals. The increase in yield depends not only on the scavenger or solute concentration but on the rate constant of the reaction of the scavenger or solute with the primary radicals. This problem has been treated for hydrated electrons [5] and has recently been addressed for hydroxyl radicals [6].

Extinction coefficients can be corrected for scavenging of primary radicals in tracks if the scavenger concentration is known, if the rate constant of the scavenging reaction is known, and if a calibration curve is available. Some calibration curves do now exist [5], but not enough supplementary information is available to make corrections for many cases in the literature. For example, since dosimetry usually involves measuring some well-known transient, it is necessary to know concentrations in the dosimeter as well as in the sample under study. Since corrections cannot be made in many cases, none of the extinction coefficients reported within have these corrections. However, much of the supplementary information that would be needed to make these corrections is included.

### **Digitization Methods and Their Sources of Errors**

The transcription of the spectra from the literature to the standard format reported in this atlas has led to some unavoidable errors in the resulting data. In order to document the errors, a brief description of the transcription procedure and the possible errors in each step are presented for reference. The data were taken from the literature by first photocopying and then digitizing the spectra from the photocopy. If the drawing was too small for accurate digitization, the photocopy was enlarged before the spectrum was digitized. Where possible the spectra were digitized directly from reprints of journal articles. The digitizer consisted of a digital voltmeter connected to the slide wires of an X-Y

<sup>1</sup> Figures in brackets indicate literature references at the end of the text.

recorder. A seven-power comparator was attached to the slide wires to improve both accuracy and precision of each reading.

For normal-sized, full-column graphs taken from an American Chemical Society journal with the ordinate ranging from 0 to 100 and the abscissa covering a 200 nm range, the reproducibility of the digitizer was  $\pm 0.5\%$  for the ordinate and  $\pm 1$  nm for the abscissa. Most of the curves reproduced will have similar uncertainties in the ordinate from the digitization process itself. However, the uncertainties in the abscissa will vary since the wavelength range of the original figures cover a wide range. When the original drawing has the full 500 nm range, the uncertainty in the abscissa might be as large as  $\pm 3$  nm.

In general, the ultimate accuracy is probably not limited by the reproducibility of the digitizer. Other sources of error enter between the data from the author and the final reproduction. One source of distortions is the optics of the xerography and enlarging processes. Some pincushion distortions were found, particularly in the xerography process. In some cases it was found that figures in the literature had their own inherent distortions that had entered in the processing of the initial raw data to the final journal spectrum. Thus a loss in accuracy due to these processes is very difficult to estimate. However, in the overall reproduction process from the literature, it is estimated that the data presented here are accurate to better than  $\pm 2\%$  of the maximum extinction coefficient. The spectral plots were made with a Versatec electrostatic plotter. The resolution of the plots is 200 dots per inch.

All of the continuous spectral curves, but not the data points themselves, that were digitized from the literature were put through a smoothing procedure involving a fast Fourier transform [7]. This procedure had the advantage of averaging the digitization of the spectral curves from the literature, which have the best likelihood of representing the shape of the spectra. Intermediate steps in the smoothing process were displayed on a video GT 62 terminal made by the Digital Equipment Corporation. The output from the smoothing routine is a set of extinction coefficients at regular wavelength intervals. This output was stored in permanent computer files and was plotted along with the individual, digitized data points to give the displayed spectra in this volume. When an  $\epsilon(\text{max})$  was quoted by the authors, the ordinate and abscissa of the plots containing the digitized data were checked and adjusted to match the quoted values.

## Acknowledgements

The Radiation Laboratory is operated under Contract DE-AC02-76ER00038 with the Department of Energy. The Radiation Chemistry Data Center is supported jointly by the National Bureau of Standards, Office of Standard Reference Data and the Office of Basic Energy Sciences and the Office of Health and Environmental Research of the Department of Energy. This is Radiation Laboratory Document No. NDRL-2109.

I would like to thank my coworkers in the Radiation Chemistry Data Center, Drs. A. B. Ross and W. P. Helman, for much good advice, criticism, and encouragement. Also, I would like to thank Professor R. H. Schuler and Drs. C. L. Greenstock, P. Neta, and L. K. Patterson for many discussions of the science and technology in this volume. Finally, I would like to thank Dr. A. K. E. Hagopian, who set up this spectral project initially.

## Symbols and Abbreviations

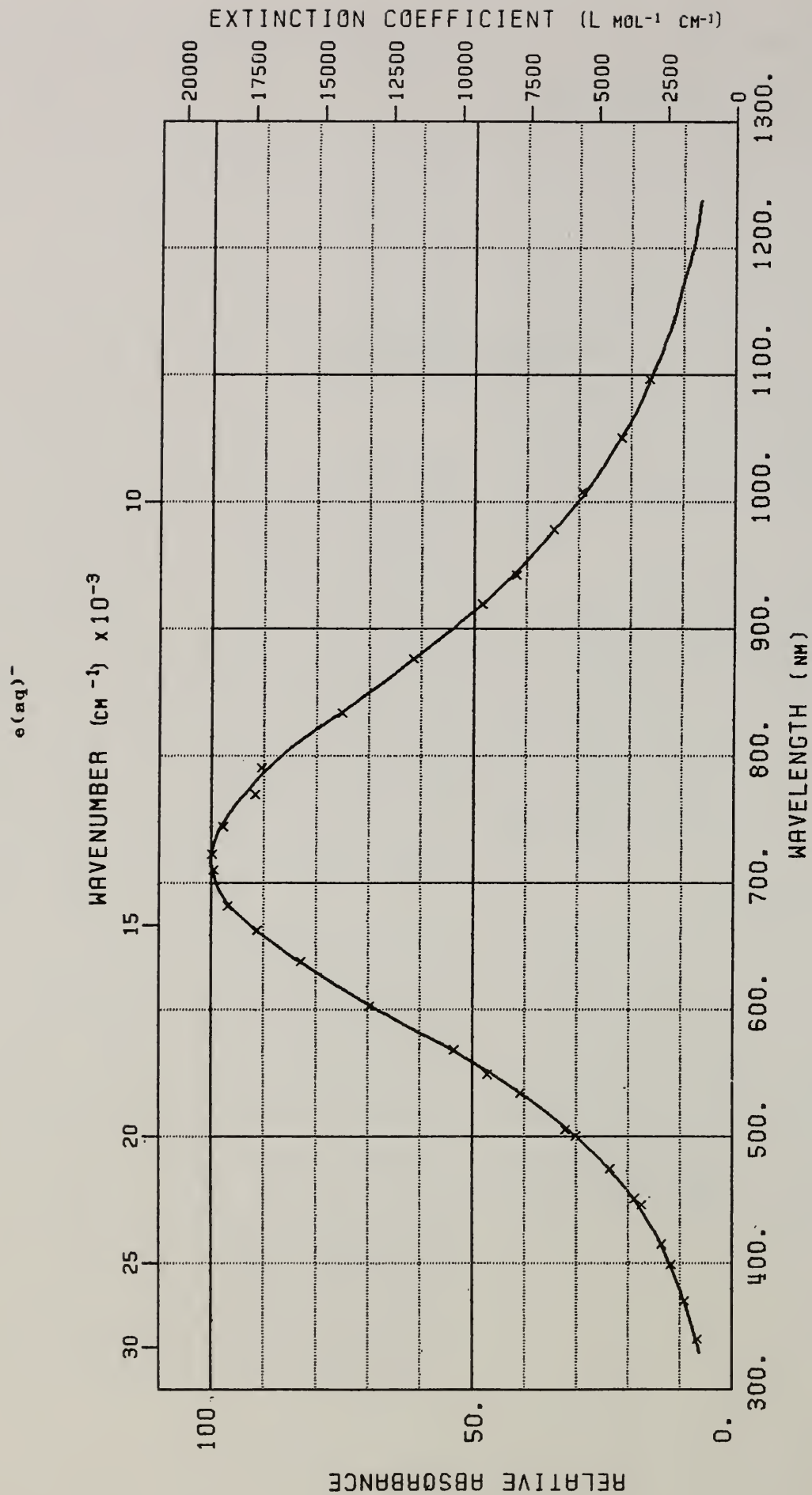
<i>A</i>	absorbance (optical density)
$\epsilon$	extinction coefficient (molar absorption coefficient)
<i>G</i>	radiation yield (molecules per 100 eV)
<i>k</i>	rate constant
krad	dose absorbed ( $6.24 \times 10^{16}$ eV per g) = 10 Gy
<i>K</i>	equilibrium constant
$\lambda$	wavelength (nm)
$\text{p}K_a$	$-\log_{10}$ dissociation constant
PMT	photomultiplier tube

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## **Spectra of Transients**



Transients:  $e(aq)^-$ , hydrated electron,  $\lambda(\text{max}) = 720 \text{ nm}$ ,  $\epsilon_{720} = 1.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: water (triply distilled), 300 K, 1 bar

e(aq)<sup>-</sup>

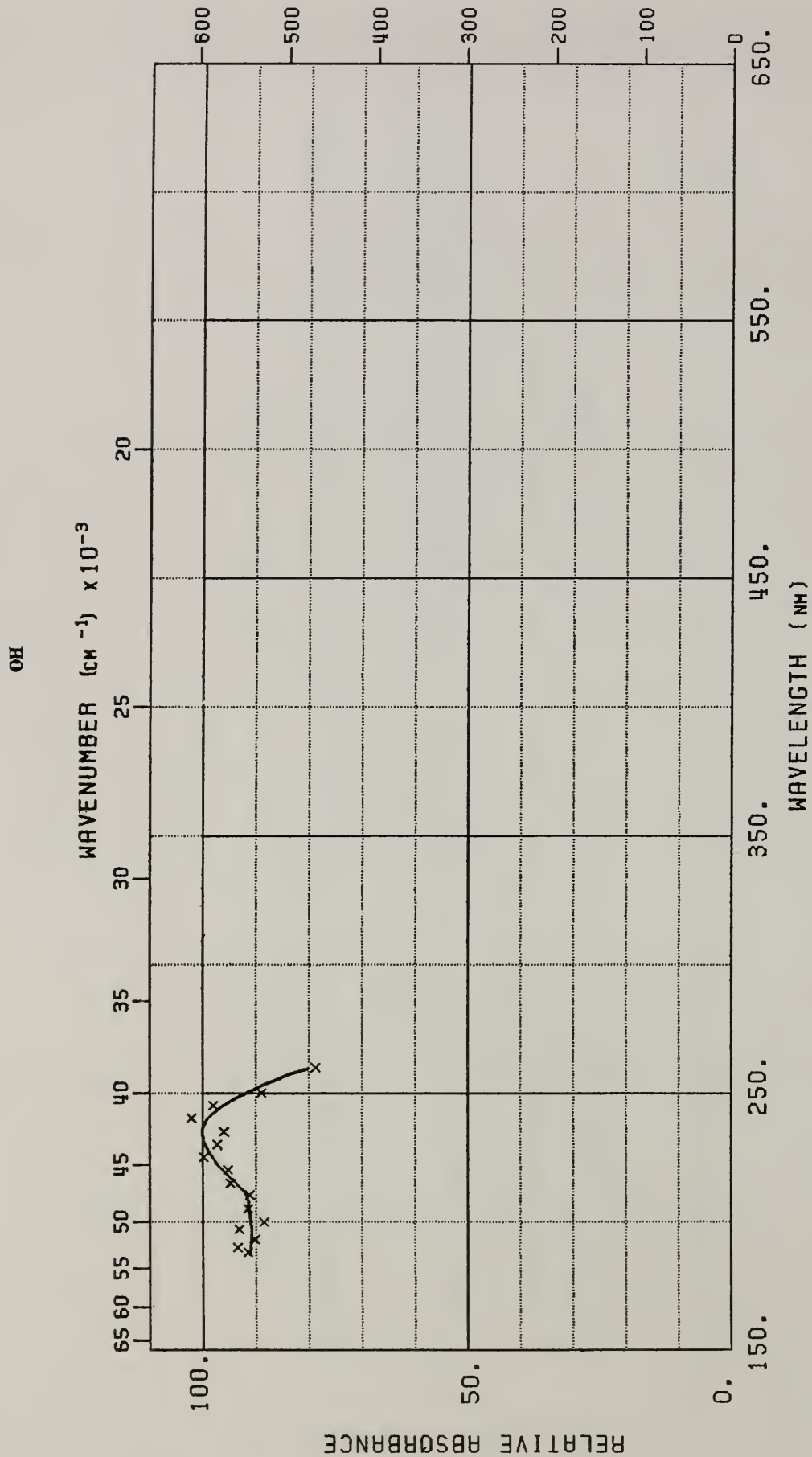
Reference: F.-Y. Jou and G.R. Freeman, J. Phys. Chem. 81(9): 909-15 (1977)

Transient generation: 2.1 MeV electrons; pulse width 1.0  $\mu$ s; dosimetry KSCN [2]; steel pressure cell

Spectral acquisition: In UV range: Bausch & Lomb 33-86-07 grating in monochromator, band pass = 7 nm; RCA 1P28 PMT; Corning filter were used to eliminate higher order light interference. In visible and ir region [3] gratings were 33-86-02, -03, and -78; infrared photocell, Barnes Engineering A-10D/D10S InSb diode cooled to 77 K.

Footnotes: [1] G.L. Bolton, K.N. Jha, and G.R. Freeman, Can. J. Chem., 54(10): 1497-506 (1976).  
[2] Dosimetry oxygen saturated  $5 \times 10^{-3}$  mol L<sup>-1</sup> KSCN using  $\text{Ce}_{478}(\text{SCN})_2^- = 21000$  (100 eV mol L<sup>-1</sup> cm)<sup>-1</sup>.  
[3] F.-Y. Jou and G.R. Freeman, Can. J. Chem. 54(23): 3693-704 (1976).

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1]: OH, hydroxyl radical,  $\epsilon_{138} = 540 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $5.25 \times 10^{-5} \text{ mol L}^{-1}$  NaOH and  $5.0 \times 10^{-4} \text{ mol L}^{-1}$  N<sub>2</sub>O, T = 302 K



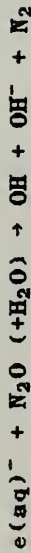
Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, *J. Phys. Chem.* **80**(22): 2482-8 (1976)

Transient generation: pulse radiolysis using 0.5  $\mu$ s pulses of 7 MeV electrons; dose per pulse 6.6 krad [3]; dose variations monitored by charge collection method [4]

Spectral acquisition: two Bausch & Lomb high-intensity grating monochromators connected in series [5]; bandwidth at half-max intensity = 4.8 nm; light path purged with N<sub>2</sub> [6]; solar-blind PMT (R166, H.T.V. Co., Japan) [7]; XBO 450 W/4 xenon lamp (Osram) with Suprasil envelope operated with a transistorized pulser which intensifies lamp by 30-fold; time delay 0.8  $\mu$ s after pulse

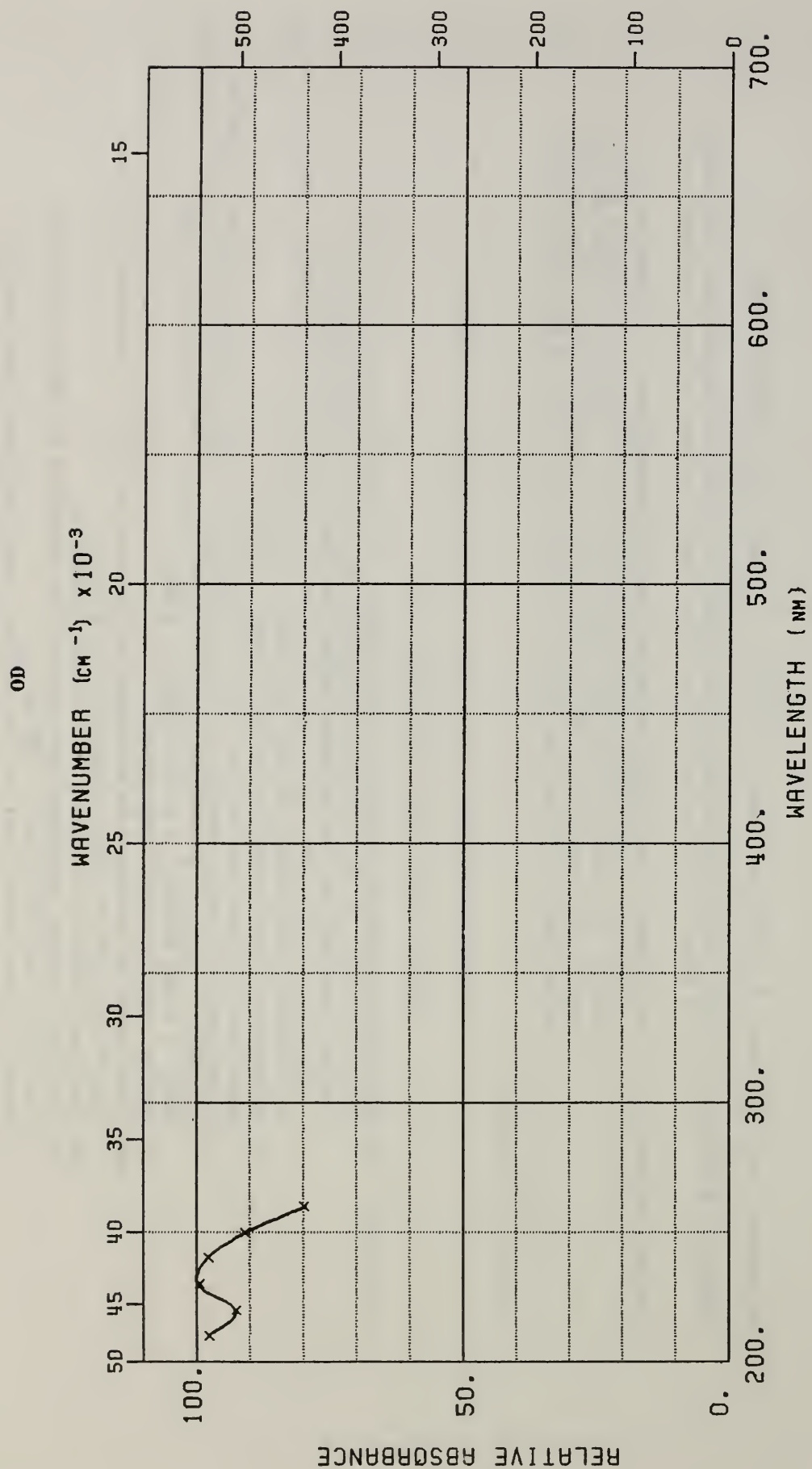
Transient formation:

OH formed in primary processes of radiolysis of H<sub>2</sub>O also



- Footnotes: [1] The long wavelength portion of the spectrum is thought to be a  $2\Pi \rightarrow 2\Sigma^+$  transition that is perturbed by H-bonding to H<sub>2</sub>O. At wavelengths shorter than 200 nm, the authors think that the intensity may be from a transition in H<sub>2</sub>O that is perturbed by the presence of an OH radical. There is an alternate explanation of the spectrum in the literature.
- [2] Absorbances were corrected for OH<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, and N<sub>2</sub>O. Reactions of these species and the transients were simulated by a computer program using available rate constants. Rate of 2k(H+H) = 1.55 x 10<sup>10</sup> L mol<sup>-1</sup> s<sup>-1</sup> and G(e(aq)<sup>-</sup>) = 2.80; G(H<sup>+</sup>) = 2.90; G(OH) = 2.70; G(OH<sup>-</sup>) = 0.10; G(H) = 0.48; G(H<sub>2</sub>) = 0.45; G(H<sub>2</sub>O<sub>2</sub>) = 0.70; G(HO<sub>2</sub>) = 0.02.
- [3] Sample changed after each pulse.
- [4] Total dose was obtained by matching the calculated e(aq)<sup>-</sup> transient with that observed at 600 nm using alkaline solution.
- [5] Gratings blazed for maximum efficiency at 250 nm.
- [6] With this system transient spectra could be measured to 182 nm, but H<sub>2</sub>O absorption interfered below 188 nm.
- [7] Amount of scattered light at the shortest wavelength was less than 1%.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1,2]: OD

System: D<sub>2</sub>O solution of 3 x 10<sup>-5</sup> mol L<sup>-1</sup> DC10<sub>4</sub> and 2 x 10<sup>-3</sup> mol L<sup>-1</sup> N<sub>2</sub>O

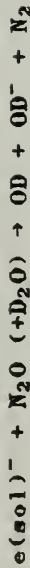
Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, J. Phys. Chem. 80(22): 2482-8 (1976)

Transient generation [3]: pulse radiolysis; pulse energy 10-11 MeV; pulse length 1.0  $\mu$ s; dosimetry  $K_4Fe(CN)_6$  [4]; dose per pulse  $\approx$  5 krad

Spectral acquisition [3]: Osram xenon lamp XB0 450 with Suprasil quartz bulb; lamp pulsed resulting in an increase in brightness of 25-30 times the nonpulsed lamp; optical windows of cell were of Suprasil quartz; lenses were of Suprasil quartz; Zeiss MM 12 double quartz prism monochromator [5]; EMI 955BQ PMT [6]; time delay, extrapolated back to zero

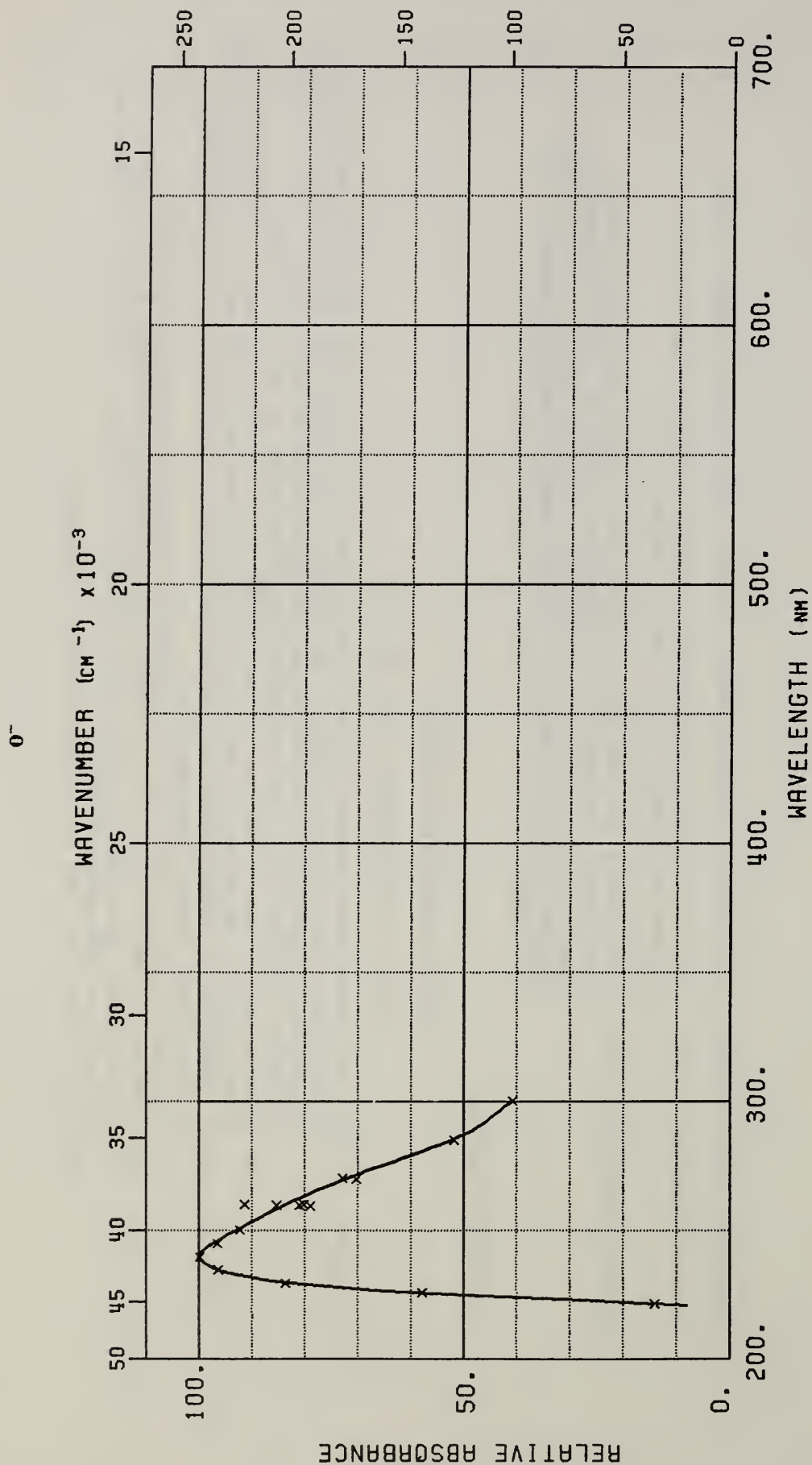
Transient formation:

OD from radiolysis of  $D_2O$



- Footnotes: [1] The long wavelength portion of the spectrum is thought to be a  $2^1\Pi \rightarrow 2^2\Sigma^+$  transition. At wavelengths shorter than 200 nm, the authors think that the intensity may be from a transition in  $D_2O$  that is perturbed by the presence of an OD radical. There is an alternate explanation of the corresponding OH spectrum in the literature.
- [2] Calculation of concentrations were made using  $G(D) = 0.44$ ,  $G(e(sol)^-) = 2.90$ ,  $G(OD) = 2.90$ ,  $G(D_2O_2) = 0.62$  with a small correction for radical recombination during pulse.
- [3] P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S.O. Nielsen, J. Phys. Chem. 73(4): 1029-38 (1969).
- [4] Aqueous solution of  $10^{-3}$  mol  $L^{-1}$   $K_4Fe(CN)_6$  saturated with  $N_2O$ ;  $G(Fe(CN)_6^{3-}) = G(OH) + G(e(aq)^-) = 2.65 + 2.6 = 5.25$  and  $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000 L mol^{-1} cm^{-1}$ .
- [5] No scattered light could be detected at 200 nm; at maximum slit width of 2.0 mm the bandwidth at 200 nm was 0.95 nm.
- [6] Monochromator and PMT set behind a 10 cm lead shield.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: O<sup>-</sup>, λ(max) = 240 nm, ε<sub>240</sub> = 240 L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of 0.105 mol L<sup>-1</sup> NaOH, pH = 13, 0.5 atmospheres N<sub>2</sub>O, carbonate free

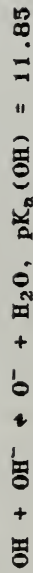
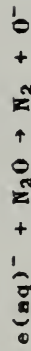
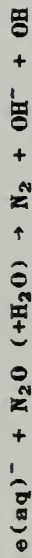
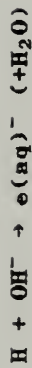


Reference: J. Rabani, Advan. Chem. Ser. 81: 131-52 (1968)

Transient generation: pulse radiolysis using syringe technique; electron beam monitored by split beam technique [2]

Spectral acquisition: 450 W Osram xenon monitoring lamp, corrections made for scattered light [3]; Bausch & Lomb monochromators

Transient formation:

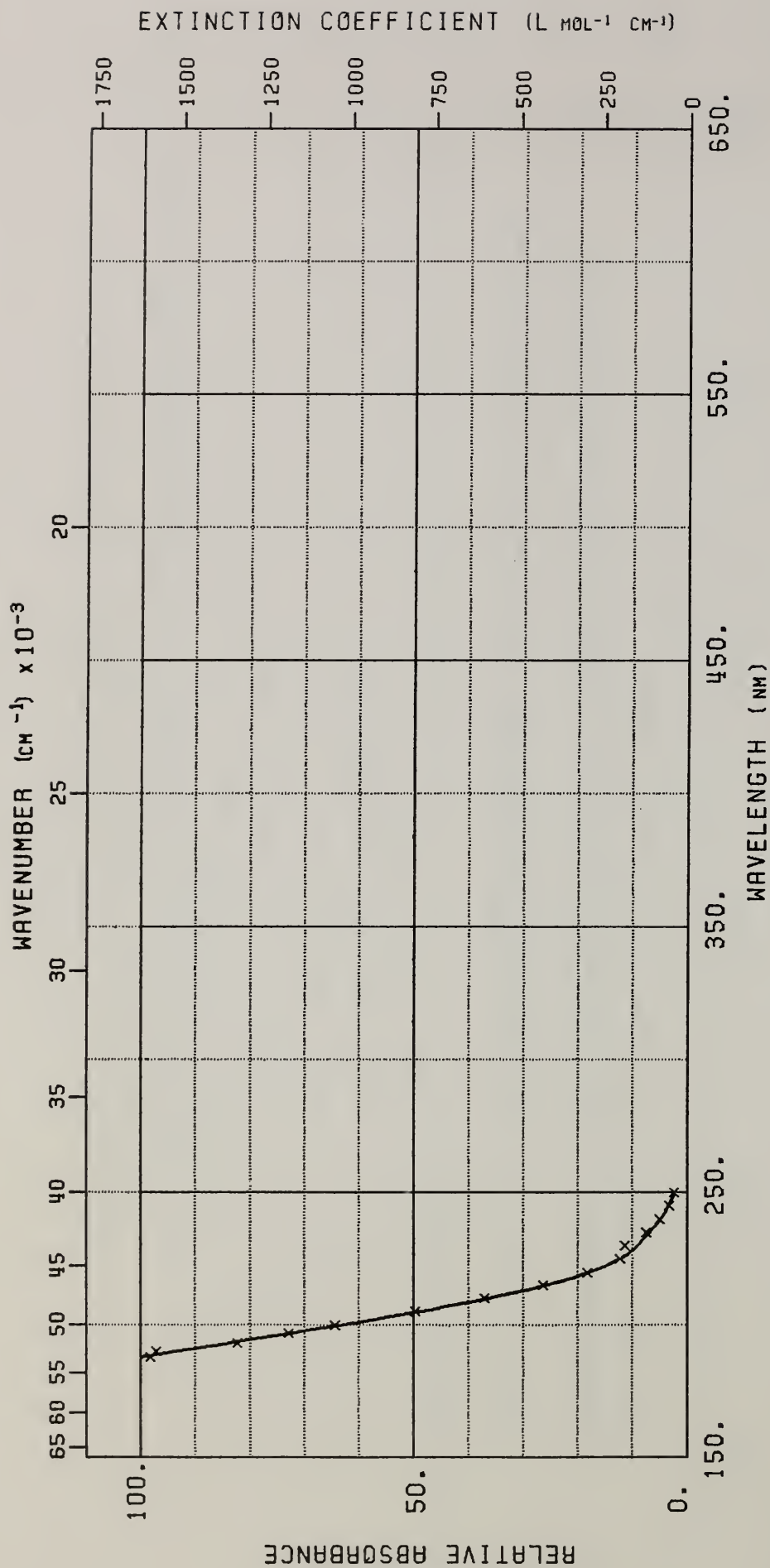


Footnotes: [1] Using  $G(\text{OH}) + G(\text{O}^-) = 5.8$  and  $G(\text{H}_2\text{O}_2) = 0.7$ . Corrections were made for the absorption of OH and  $\text{H}_2\text{O}_2$ .

[2] One beam was passed through a monochromator set at 260 nm to monitor the electron beam intensity. Absolute dosimetry used  $5 \times 10^{-4}$  mol  $\text{L}^{-1}$   $\text{K}_4\text{Fe}(\text{CN})_6$  under experimental conditions, taking  $\epsilon_{420} = 1000$  L mol $^{-1}$  cm $^{-1}$ .

[3] Depending on the optical alignment, the scattered light was 3-6% at 260 nm, 8% at 250 nm, 10-15% at 240 nm, 20-25% at 230 nm, and 50% at 222 nm.

H in H<sub>2</sub>O



Transient [1]: H atom in H<sub>2</sub>O,  $\epsilon_{188} = 1620 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $3.39 \times 10^{-4} \text{ mol L}^{-1} \text{ HClO}_4$ ,  $2.82 \times 10^{-2} \text{ mol L}^{-1} \text{ H}_2$  (30 atm), and  $4.5 \times 10^{-5} \text{ mol L}^{-1} \text{ H}_2\text{O}_2$  (steady state concentration from radiolysis),  $T = 307 \text{ K}$

## H in H<sub>2</sub>O

Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, *J. Phys. Chem.* **80**(22): 2482-8 (1976)

Transient generation: pulse radiolysis using 1.0  $\mu$ s pulses of 7 MeV electrons; dose per pulse 3.3 krad; dose variations monitored by charge collection method [3]

Spectral acquisition: two Bausch & Lomb high-intensity grating monochromators connected in series [4]; bandwidth at half-max intensity = 4.8 nm; light path purged with N<sub>2</sub> [5]; solar-blind PMF (RI166, H.T.V. Co., Jpn) [6]; XBO 450 W/4 xenon lamp (Osram) with Suprasil envelope operated with transistorized pulser which intensifies lamp by 30-fold; time delay 1.0  $\mu$ s after pulse

Transient formation:

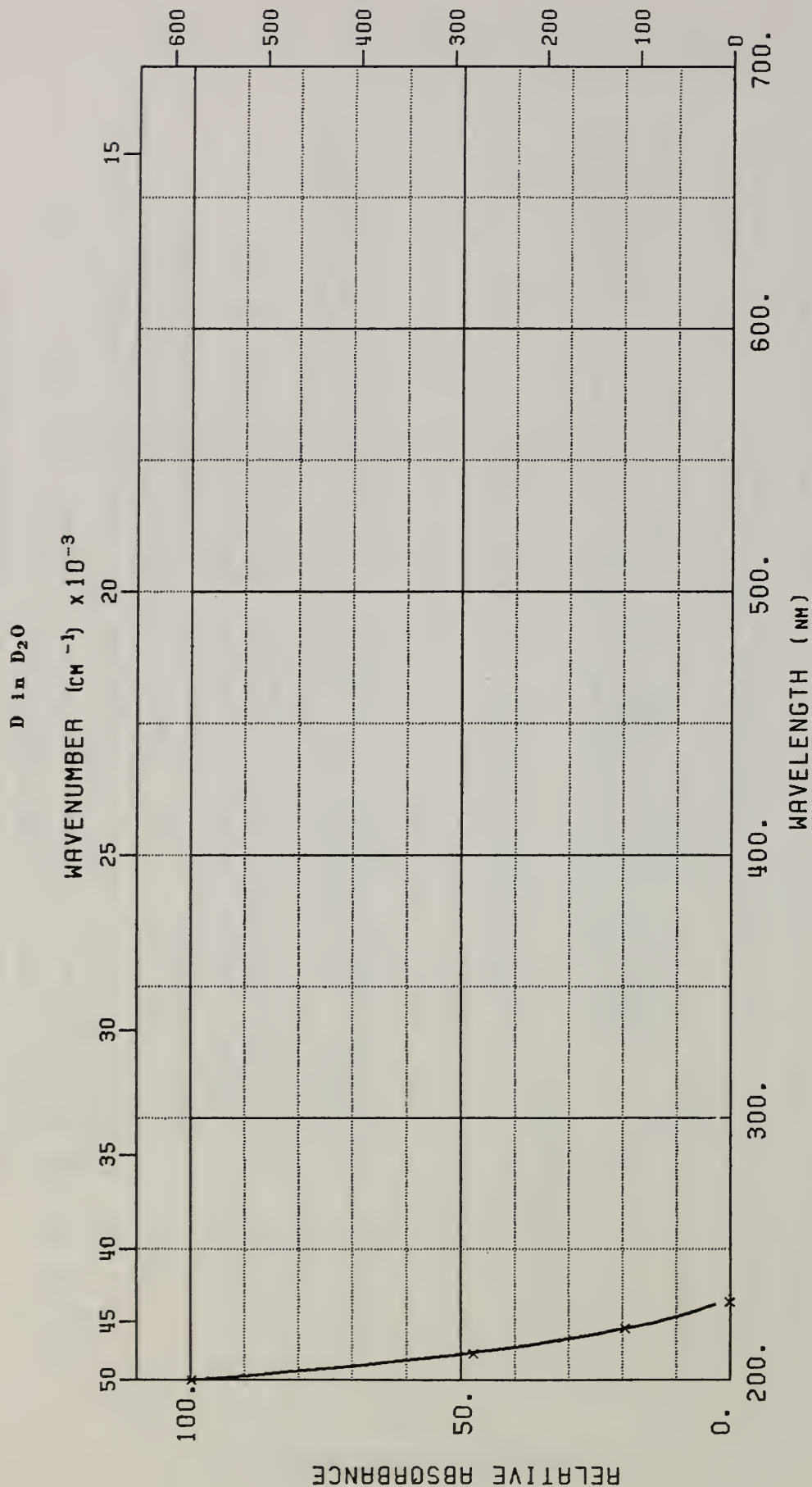
H from primary processes in radiolysis of H<sub>2</sub>O



- Footnotes: [1] Authors assign the spectrum to a transition that mainly involves the H<sub>2</sub>O molecule. The excited state was thought to involve a partial negative charge transfer to a neighboring H atom. The ground state was not perturbed by the H atom. There are alternate assignments of this spectrum in the literature.
- [2] Absorbances were corrected for presence of H<sub>2</sub>O<sub>2</sub>. This correction was made using the calculated concentrations for H<sub>2</sub>O<sub>2</sub> and transient species that were obtained by a computer simulation of the overall reaction using available rate constants. Yields used were G(e(aq)<sup>·-</sup>) = 2.80; G(H<sup>·</sup>) = 2.90; G(OH) = 2.70; G(OH<sup>-</sup>) = 0.10; G(H) = 0.48; G(H<sub>2</sub>) = 0.45; G(H<sub>2</sub>O<sub>2</sub>) = 0.70; G(HO<sub>2</sub>) = 0.02. Correction was made for radiation-induced absorption of quartz cell used for high pressures.
- [3] Total dose was obtained by matching the calculated e(aq)<sup>·-</sup> transient with that observed at 600 nm using alkaline solution.
- [4] Gratings blazed for maximum efficiency at 250 nm.
- [5] With this system transient spectra could be measured to 182 nm, but H<sub>2</sub>O absorption interfered below 188 nm.
- [6] Amount of scattered light at the shortest wavelength was less than 1%.



EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1,2]: D atom in D<sub>2</sub>O

System: D<sub>2</sub>O solution of 10<sup>-3</sup> mol L<sup>-1</sup> DC10<sub>4</sub>

## D in D<sub>2</sub>O

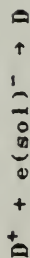
Reference: S.O. Nielsen, B.D. Michael, and E.J. Hart, *J. Phys. Chem.* **80**(22): 2482-8 (1976)

Transient generation [3]: pulse radiolysis; pulse energy 10-11 MeV; pulse length 1.0  $\mu$ s; dosimetry K<sub>4</sub>Fe(CN)<sub>6</sub> [4]; dose per pulse  $\approx$  5 krad

Spectral acquisition [3]: Osram xenon lamp XB0 450 with Suprasil quartz bulb; lamp pulsed resulting in an increase in brightness of 25-30 times the nonpulsed lamp; optical windows of cell were of Suprasil quartz; lenses were of Suprasil quartz; Zeiss MM 12 double quartz prism monochromator [5]; EMI 9558Q PMT [6]; time delay, extrapolated back to zero

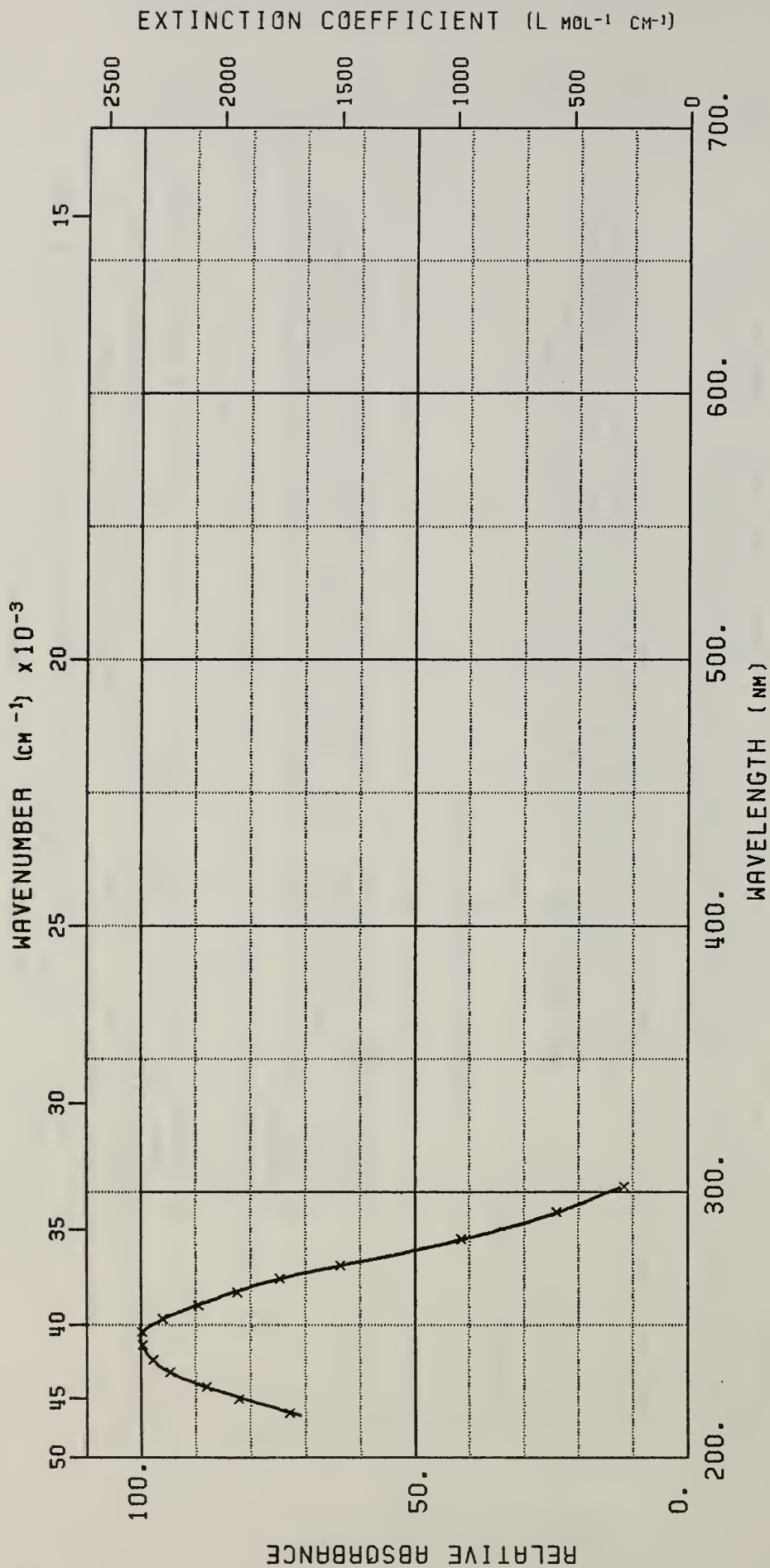
Transient formation:

D from radiolysis of D<sub>2</sub>O



- Footnotes: [1] Authors assign the spectrum to a transition that mainly involves the D<sub>2</sub>O molecule. The excited state was thought to involve a partial negative charge transfer to a neighboring D atom. The ground state was not perturbed by the D atom. There are alternate assignments of the corresponding H atom spectrum in the literature.
- [2] Calculation of concentrations were made using  $G(D) = 0.44$ ,  $G(e(sol)^-) = 2.90$ ,  $G(OD) = 2.90$ ,  $G(D_2O_2) = 0.62$  with a small correction for radical recombination during pulse.
- [3] P. Pagsberg, H. Christensen, J. Rabani, G. Nilsson, J. Fenger, and S.O. Nielsen, *J. Phys. Chem.* **73**(4): 1029-38 (1969).
- [4] Aqueous solution of  $10^{-3}$  mol L<sup>-1</sup> K<sub>4</sub>Fe(CN)<sub>6</sub> saturated with N<sub>2</sub>O;  $G(Fe(CN)_6^{3-}) = G(OH) + G(e(aq)^-) = 2.65 + 2.6 = 5.25$  and  $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000$  L mol<sup>-1</sup> cm<sup>-1</sup>.
- [5] No scattered light could be detected at 200 nm; at maximum slit width of 2.0 mm, the bandwidth at 200 nm was 0.95 nm.
- [6] Monochromator and PMT set behind a 10 cm lead shield.

$O_2^-$



Transient:  $O_2^-$ , superoxide radical ion,  $\lambda(\text{max}) = 245 \text{ nm}$ ,  $\epsilon_{245} = (2350 \pm 12) \text{ L mol}^{-1} \text{ cm}^{-1}$  [1,2],  
 $k(O_2^- + O_2^-)$  less than  $0.35 \text{ L mol}^{-1} \text{ s}^{-1}$

System: air-saturated, aqueous  $[3] 10^{-2} \text{ mol L}^{-1}$  sodium formate solution, containing  $10^{-4} \text{ mol L}^{-1}$  EDTA [4] and  $\text{Na}_3\text{PO}_4$  [5] added to adjust pH to 10.5



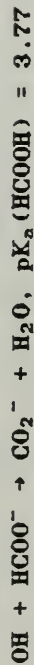
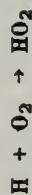


Reference: B.H.J. Bielski, Photochem. Photobiol. 28: 645-9 (1978)

Transient generation: pulse radiolysis, using stopped-flow technique [6]

Spectral acquisition:

Transient formation:



Footnotes: [1] Based (a) on extinction coefficient of nitroform radical anion,  $\text{C}(\text{NO}_2)_3^-$ , which was formed by the reaction of  $\text{O}_2^-$  and tetranitromethane and (b) on difference in 550 nm extinction coefficients of ferrocyanide and ferricyanide. The ferrocyanide was formed by the reaction of  $\text{O}_2^-$  with ferricyanide. No  $\text{G}(\text{O}_2^-)$  was assumed with this method.

[2] Earlier values for  $\epsilon(\text{max})$  are listed in the review by G. Czapski, Ann. Rev. Phys. Chem. 22: 171-208 (1971).

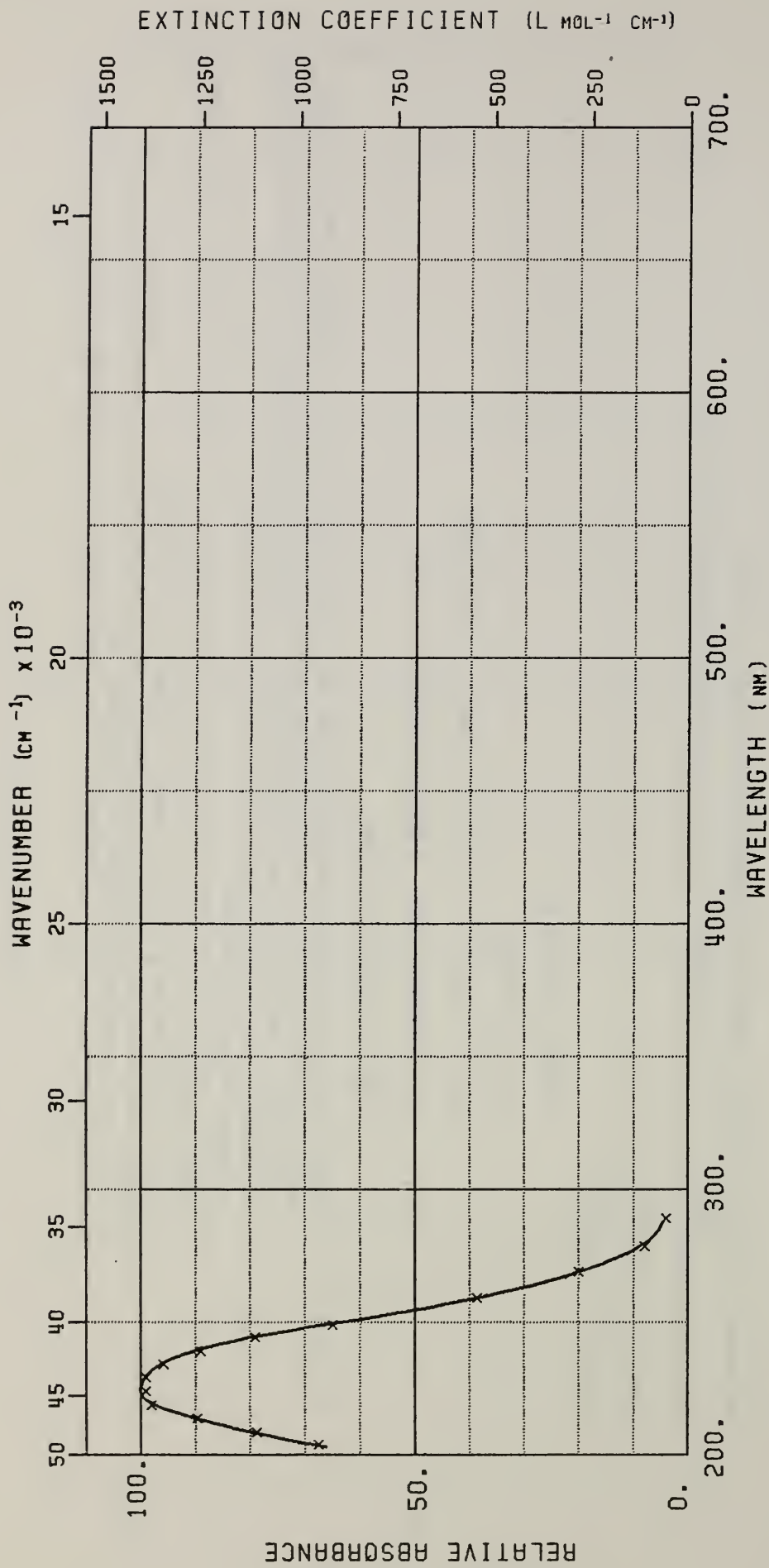
[3] Water purified by a Milli-Q reagent grade water system.

[4] Added to remove heavy metal ions which can catalyze  $\text{O}_2^-$  disproportionation.

[5] Purified using method given in reference [6].

[6] B.H.J. Bielski and H.W. Richter, J. Am. Chem. Soc. 99(9): 3019-23 (1977).

HO<sub>2</sub>



Transient: HO<sub>2</sub>, perhydroxyl radical,  $\lambda(\text{max}) = 225 \text{ nm}$ ,  $\epsilon_{225} = (1400 \pm 80) \text{ L mol}^{-1} \text{ cm}^{-1}$  [1,2],  
 $k(\text{HO}_2 + \text{HO}_2) = (8.60 \pm 0.62) \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$

System: air-saturated, aqueous [3]  $10^{-2} \text{ mol L}^{-1}$  sodium formate solution with pH adjusted to 1.5 using perchloric acid

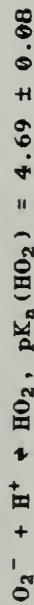
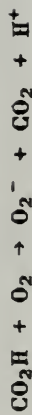
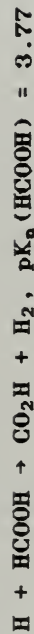
## HO<sub>2</sub>

Reference: B.H.J. Bielski, Photochem. Photobiol. 28: 645-9 (1978)

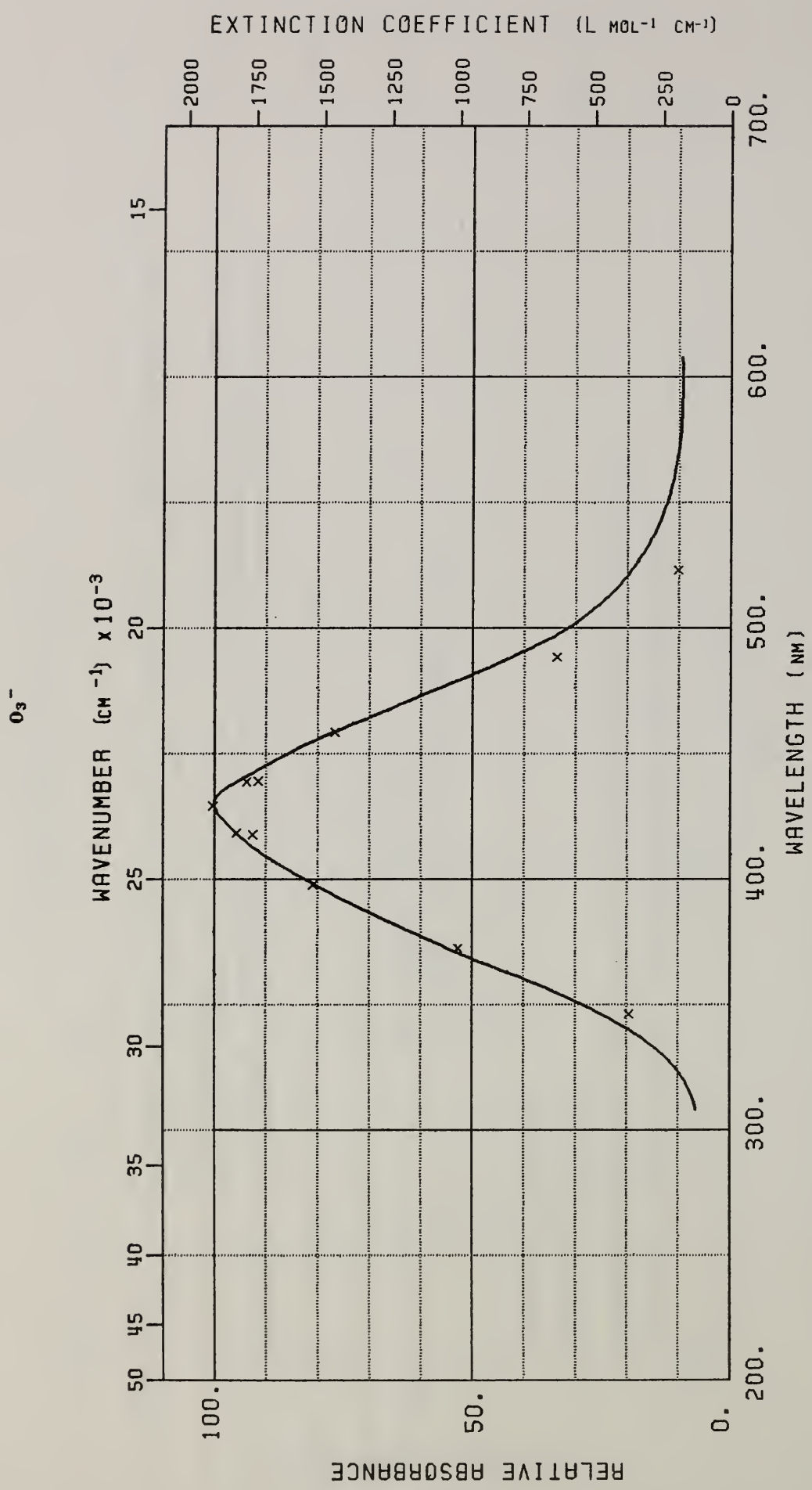
Transient generation: pulse radiolysis, using stopped-flow technique [4]

Spectral acquisition:

Transient formation:



- Footnotes: [1] Determined from calibrations of beam current based on O<sub>2</sub><sup>-</sup> concentration, where O<sub>2</sub><sup>-</sup> concentration was obtained without assuming a G(O<sub>2</sub><sup>-</sup>).
- [2] Earlier values for ε(max) are given by G. Czapski in Ann. Rev. Phys. Chem. 22: 171-208 (1971).
- [3] Water purified by a Milli-Q reagent grade water system.
- [4] B.H.J. Bielski and H.W. Richter, J. Am. Chem. Soc. 99(9): 3019-23 (1977).



Transient [1]:  $O_3^-$ , ozonide ion,  $\epsilon_{430} = (1900 \pm 120) L \text{ mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $O_2$  and  $N_2O$  with  $[N_2O]/[O_2] \approx 20$ ,  $pH \approx 13.5$  [3]

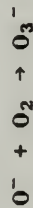


Reference: W.D. Felix, B.L. Gall, and L.M. Dorfman, J. Phys. Chem. 71(2): 384-92 (1967)

Transient generation: pulse radiolysis using a Varian V-7715A linear accelerator, syringe technique; dosimetry [4]

Spectral acquisition: 500 W Osram xenon lamp (Type XB0 450 W); 1P28 PMT; two Bausch & Lomb grating monochromators (Type 33-86-25, f/3.5) with light beam split by partially reflecting mirror; bandwidth: less than 1.8 nm

Transient formation:



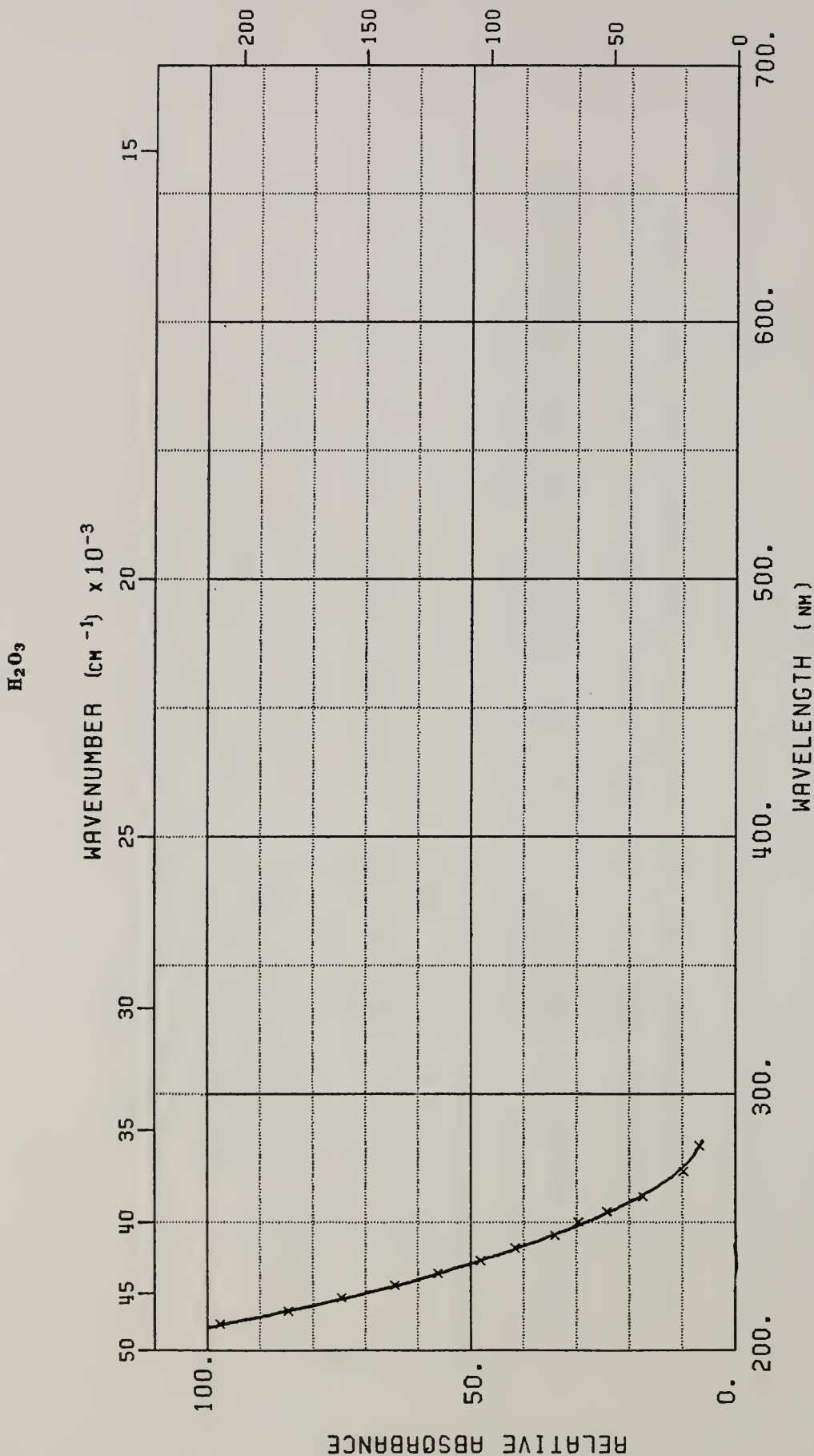
Footnotes: [1] Solid curve is drawn from a composite of the data presented plus data from a solution free of N<sub>2</sub>O.

[2] Based on  $G(\text{O}^-) = 3.3$  at pH = 13.1 in O<sub>2</sub>-saturated solution.

[3] Under these conditions most  $e(\text{aq})^-$  are converted to O<sup>-</sup>.

[4] Dosimeter was an O<sub>2</sub>-saturated sulfuric acid solution with no chloride ions and with 10<sup>-2</sup> mol L<sup>-1</sup> Fe<sup>2+</sup>. At high dose rates,  $G(\text{Fe}^{3+}) = 15.6$ . At low dose,  $\epsilon_{304}(\text{Fe}^{3+}) = 2200 \text{ L mol}^{-1} \text{ cm}^{-1}$  was used to calculate dose. At high intensity, dose was calculated by monitoring 366 nm and by using  $\epsilon_{304}/\epsilon_{366} = 8.9$  for Fe<sup>3+</sup>.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: H<sub>2</sub>O<sub>3</sub>, hydrogen sesquioxide [1]

System: air-saturated, aqueous 10<sup>-2</sup> mol L<sup>-1</sup> HClO<sub>4</sub>, pH ≈ 2

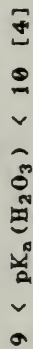
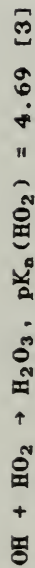
## H<sub>2</sub>O<sub>3</sub>

Reference: B.H.J. Bielski and H.A. Schwarz, J. Phys. Chem. 72(11): 3836-41 (1968)

Transient generation: electrons from 2 MeV Van de Graaff generator; variable pulse length, a few hundred microseconds to several tenths of a second; ferrous dosimetry

Spectral acquisition: deuterium analyzing lamp; optical path length = 6.1 cm; Bausch & Lomb f/3.5 monochromator; tandem monochromators used below 240 nm [2]; dual beam oscilloscope

Transient formation:



Footnotes: [1] Extinction coefficients were calculated using  $G(\text{H}_2\text{O}_3) = 1.7$  from reference in footnote 4.

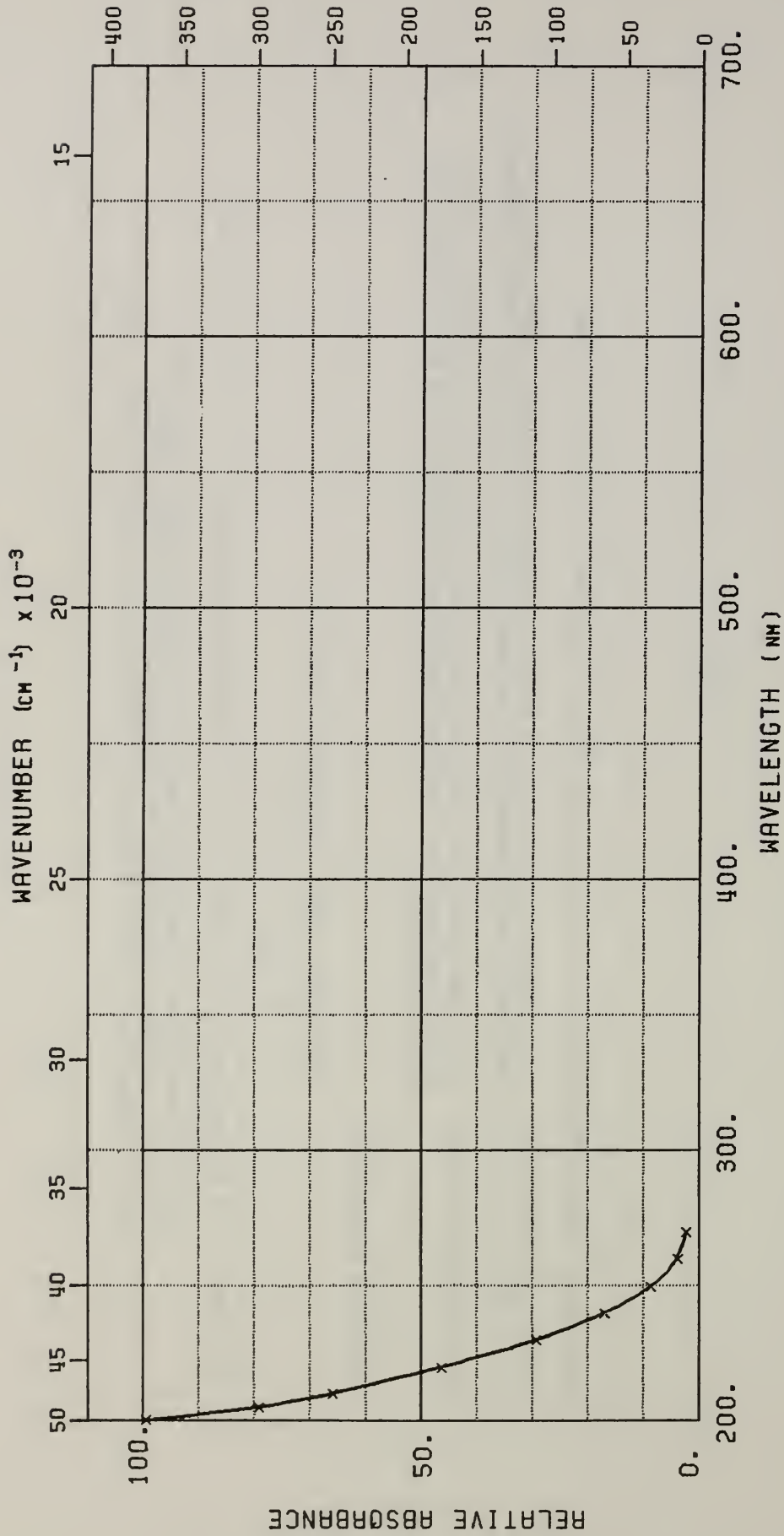
[2] Scattered light always kept below 2% of the analyzed light beam.

[3] B.H.J. Bielski, Photochem. Photobiol. 28(4-5): 645-9 (1978).

[4] G. Czapski and B.H.J. Bielski, J. Phys. Chem. 67(10): 2180-4 (1963).

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

D<sub>2</sub>O<sub>3</sub>



Transient [1]: D<sub>2</sub>O<sub>3</sub>, deuterium sesquioxide

System: oxygenated D<sub>2</sub>O [1]



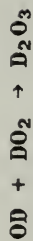
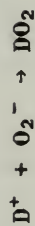
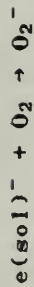
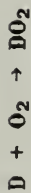
D<sub>2</sub>O<sub>3</sub>

Reference: B.H.J. Bielski, J. Phys. Chem. 74(17): 3213-6 (1970)

Transient generation: pulse radiolysis using 1.95 MeV Van de Graaff generator; pulse length 0.1 s [2]; dosimetry-ferrous sulfate

Spectral acquisition: deuterium monitoring lamp; 3-pass Suprasil quartz cell with optical path = 6.1 cm; two tandem coupled Bausch & Lomb f/3.5 monochromators [3]; 7200 RCA PMT

Transient formation:



Footnotes: [1] Extinction coefficient based on  $C(D_2O_3) = 1.86$  which was determined in a  $10^{-2}$  mol L<sup>-1</sup> DC104 solution.

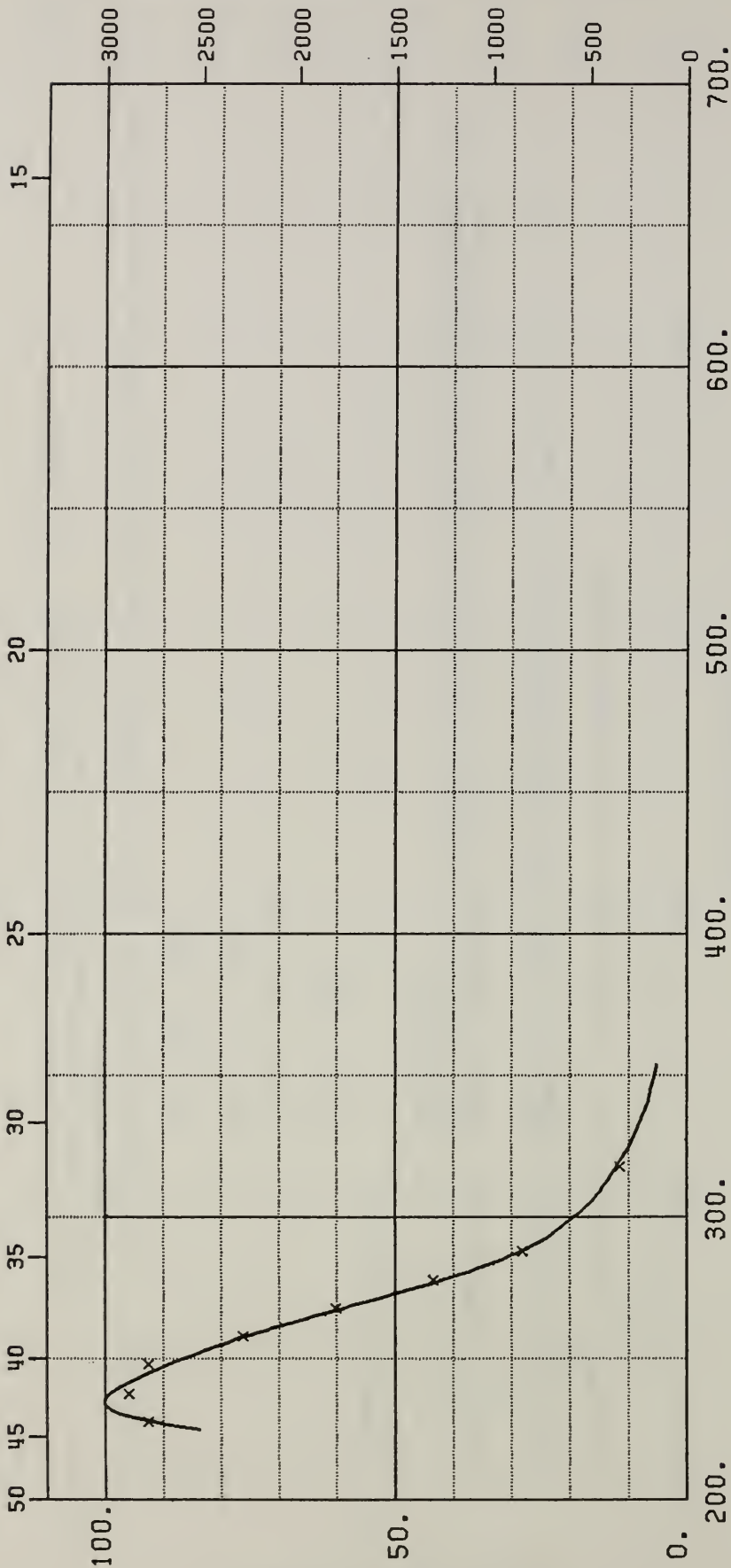
[2] Spectrum corresponds to time at end of pulse.

[3] Scattered light at 200 nm was < 0.3% of total light signal.

CO<sub>2</sub><sup>-</sup>

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



RELATIVE ABSORBANCE

WAVELENGTH (NM)

Transient [1]: CO<sub>2</sub><sup>-</sup>, carboxyl radical, λ(max) = 235 nm, ε<sub>235</sub> = 3000 L mol<sup>-1</sup> cm<sup>-1</sup> [2,3]

System: aqueous solution of 3 x 10<sup>-2</sup> mol L<sup>-1</sup> HCOO<sup>-</sup>, 1 atm N<sub>2</sub>O, pH 9

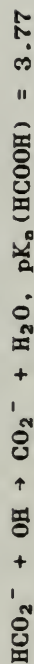
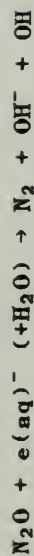
CO<sub>2</sub><sup>-</sup>

Reference: P. Neta, M. Simic, and E. Hayon, J. Phys. Chem. 73(12): 4207-13 (1969)

Transient generation: pulse radiolysis, using Febetron 705; pulse energy 2.3 MeV; pulse length ≈ 30 ns; dose per pulse 8 krad; dosimetry 0.1 mol L<sup>-1</sup> SCN<sup>-</sup> solution [4]

Spectral acquisition: Osram XB0 450 W xenon lamp (pulsed); two high-intensity Bausch & Lomb monochromators, used in series to reduce scattered light [5]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope

Transient formation:



Footnotes:

[1] Smooth curve for spectrum is from a composite spectrum.

[2] Earlier results gave  $\lambda(\text{max}) = (250 \pm 5) \text{ nm}$  and  $\epsilon_{250} = 2400 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

J.P. Keene, Y. Raef, and A.J. Swallow, Pulse Radiolysis, M. Ebert, J.P. Keene, A.J. Swallow, and J.H. Baxendale (eds.), Academic Press, London, 1965, pp.99-106.

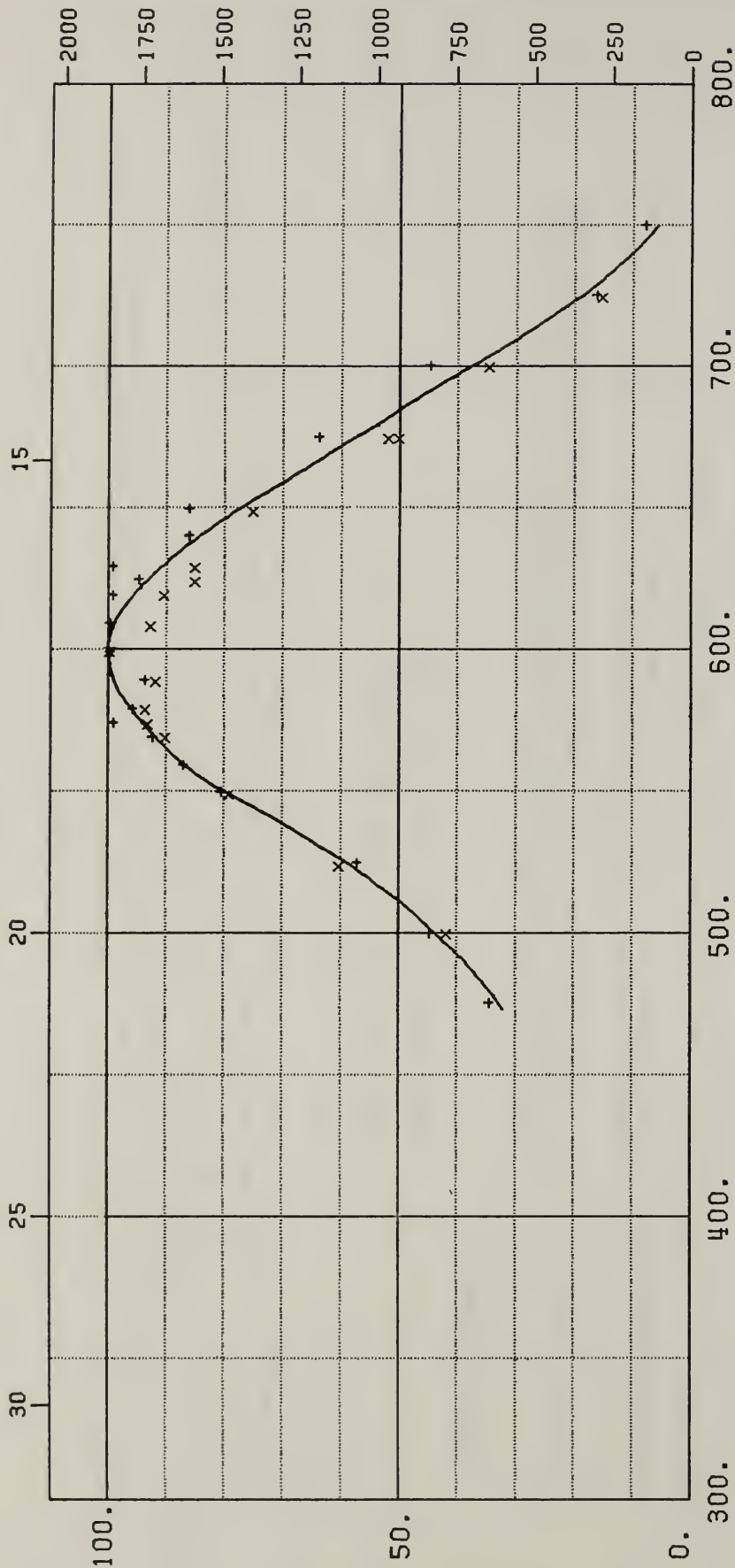
[3] Using  $G(e(\text{aq})^-) = G(\text{OH}) = 2.8$ ; deviation  $\pm 15\%$ .

[4] Using  $\epsilon_{500} = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $(\text{SCN})_2^-$ .

[5] At 230 and 210 nm the amount of scattered light was 1% and 18%, respectively. M. Simic, P. Neta, and E. Hayon, J. Phys. Chem. 73(11): 3794-800 (1969).

CO<sub>3</sub><sup>-</sup> or HCO<sub>3</sub>

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

Transient: CO<sub>3</sub><sup>-</sup> or HCO<sub>3</sub> [1], λ(max) = 600 nm, ε<sub>600</sub> = 1860 L mol<sup>-1</sup> cm<sup>-1</sup> [2]

System: the chemical system represented by the data points "x" was an aqueous solution of 1 mol L<sup>-1</sup> NaHCO<sub>3</sub>, 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>-saturated, pH 8; and the system represented by the data points "+" was an aqueous solution of 1 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>, 2 x 10<sup>-4</sup> mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>-saturated, pH 13

RELATIVE ABSORBANCE



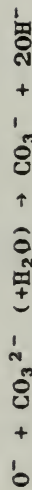
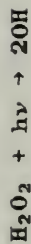
$\text{CO}_3^-$  or  $\text{HCO}_3^-$

Reference: D. Behar, G. Czapski, and I. Duchovny, *J. Phys. Chem.* 74(10): 2206-10 (1970)

Transient generation [3]: flash photolysis, four  $\text{O}_2$ -filled (5 mm Hg) Spectrosil grade quartz lamps operated at 20 kV and 2  $\mu\text{F}$  fired through a triggered spark gap

Spectral acquisition [3]: monitoring light was 120 W tungsten lamp; two 9558B EMI PMT; split beam technique; two Bausch & Lomb monochromators types 567 AB and F.D. 999

Transient formation [4]:

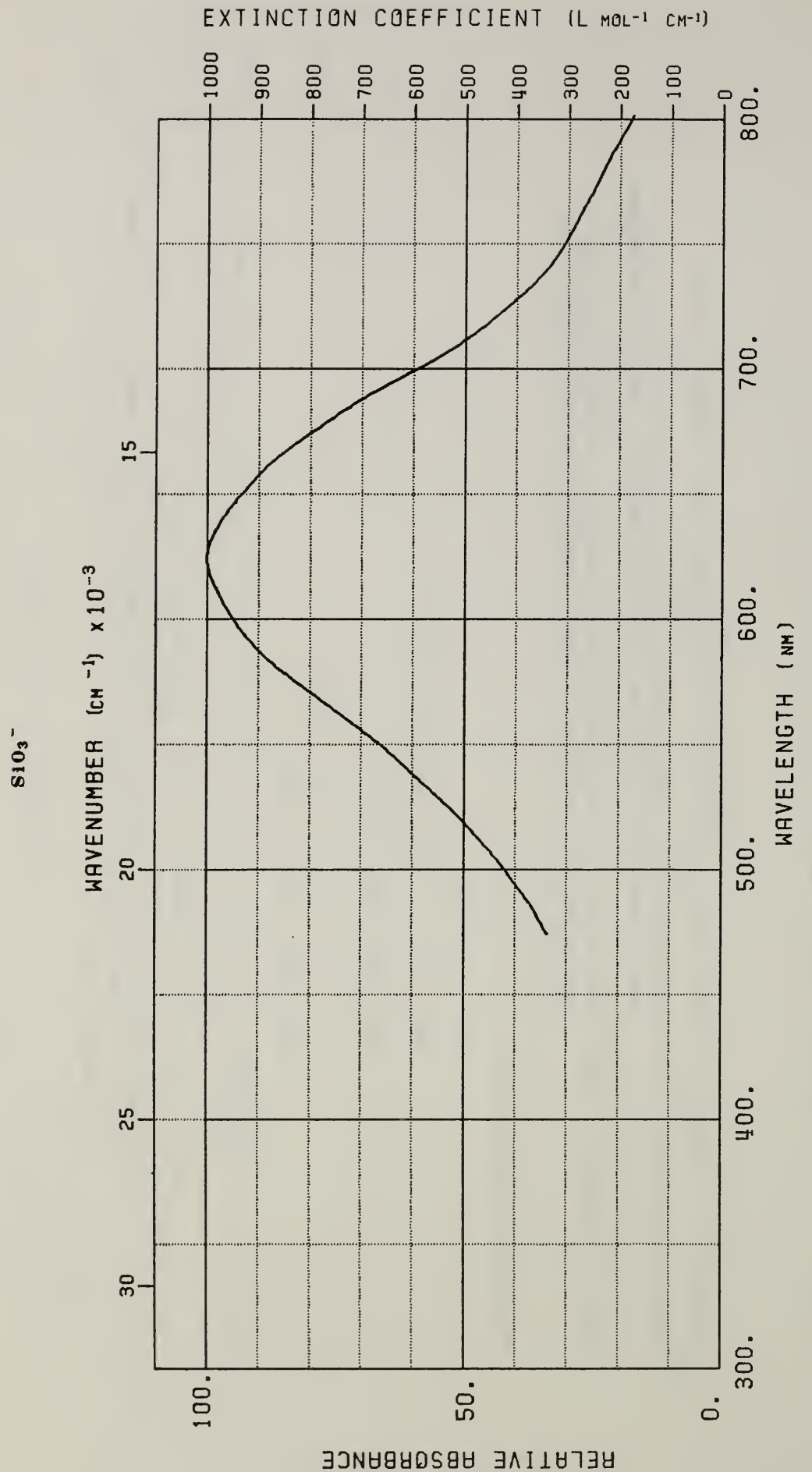


Footnotes: [1]  $\text{p}K_a(\text{HCO}_3^-) = 9.6 \pm 0.3$ ; S. Chen, V.W. Cope, and M.Z. Hoffman, *J. Phys. Chem.* 77(9): 1111-6 (1973). These authors reported no difference between the spectra of  $\text{HCO}_3^-$  and  $\text{CO}_3^-$ .

[2] J.L. Weeks and J. Rabani, *J. Phys. Chem.* 70(7): 2100-6 (1966).

[3] D. Behar and G. Czapski, *Israel J. Chem.* 6: 43-51 (1968).

[4] By measuring the rate constants in a pulse radiolysis experiment, it was found that reactions of OH with  $\text{H}_2\text{O}_2$  to form  $\text{O}_2^-$  or  $\text{HO}_2$  were negligible under the experimental conditions.



Transient: SiO<sub>3</sub><sup>-</sup>, λ(max) = 625 nm, ε = 1.0 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>

System: aqueous solution of 5 × 10<sup>-2</sup> mol L<sup>-1</sup> Na<sub>2</sub>SiO<sub>3</sub> and 1 × 10<sup>-2</sup> mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

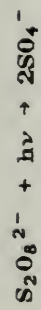
$\text{SiO}_3^-$

Reference: V.A. Kuz'min and A.K. Chibisov, High Energy Chem. 4(2): 146-7 (1970)

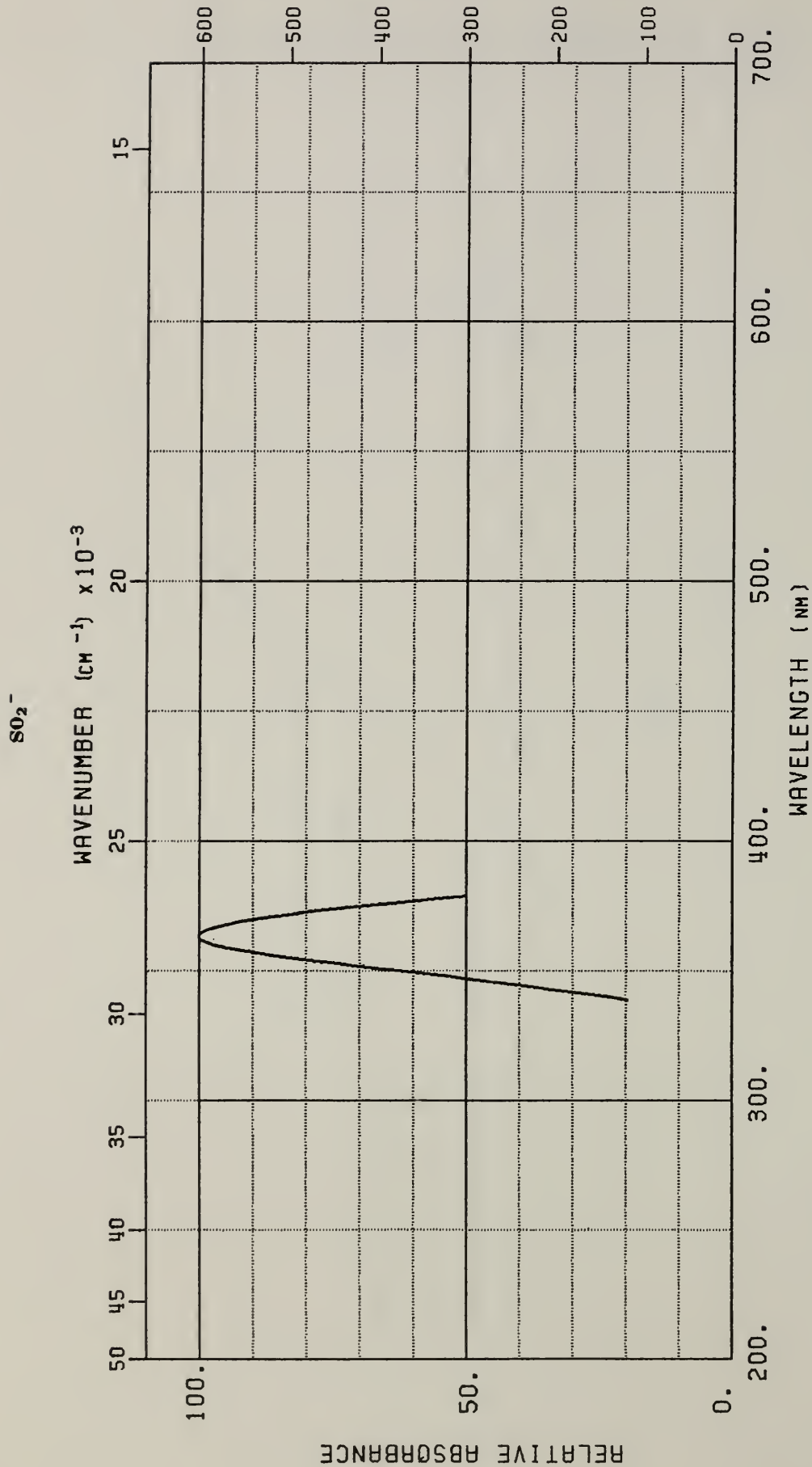
Transient generation: flash photolysis

Spectral acquisition:

Transient formation:



EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1]:  $\text{SO}_2^-$ ,  $\lambda(\text{max}) \approx 365 \text{ nm}$ ,  $\epsilon_{365} \approx 600 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2,3],  
 $2k = 1.0 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$

System: aqueous solution of  $6.0 \times 10^{-2} \text{ HSO}_3^-$ ,  $\text{N}_2$  (1 atm), pH 4.0



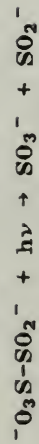
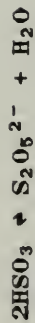
## $\text{SO}_2^-$

Reference: E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. 94(1): 47-57 (1972)

Transient generation: flash photolysis; 1800 J; duration at "1/e" time of 5  $\mu\text{s}$ ; total pulse length 70  $\mu\text{s}$ ; 240 nm cutoff filter [4]

Spectral acquisition: Bausch & Lomb grating monochromator; PMT; spectrum was obtained by a point-by-point method from oscilloscope traces; each point was average of 3 or more experiments; time delay 80  $\mu\text{s}$  after pulse

Transient formation [4]:

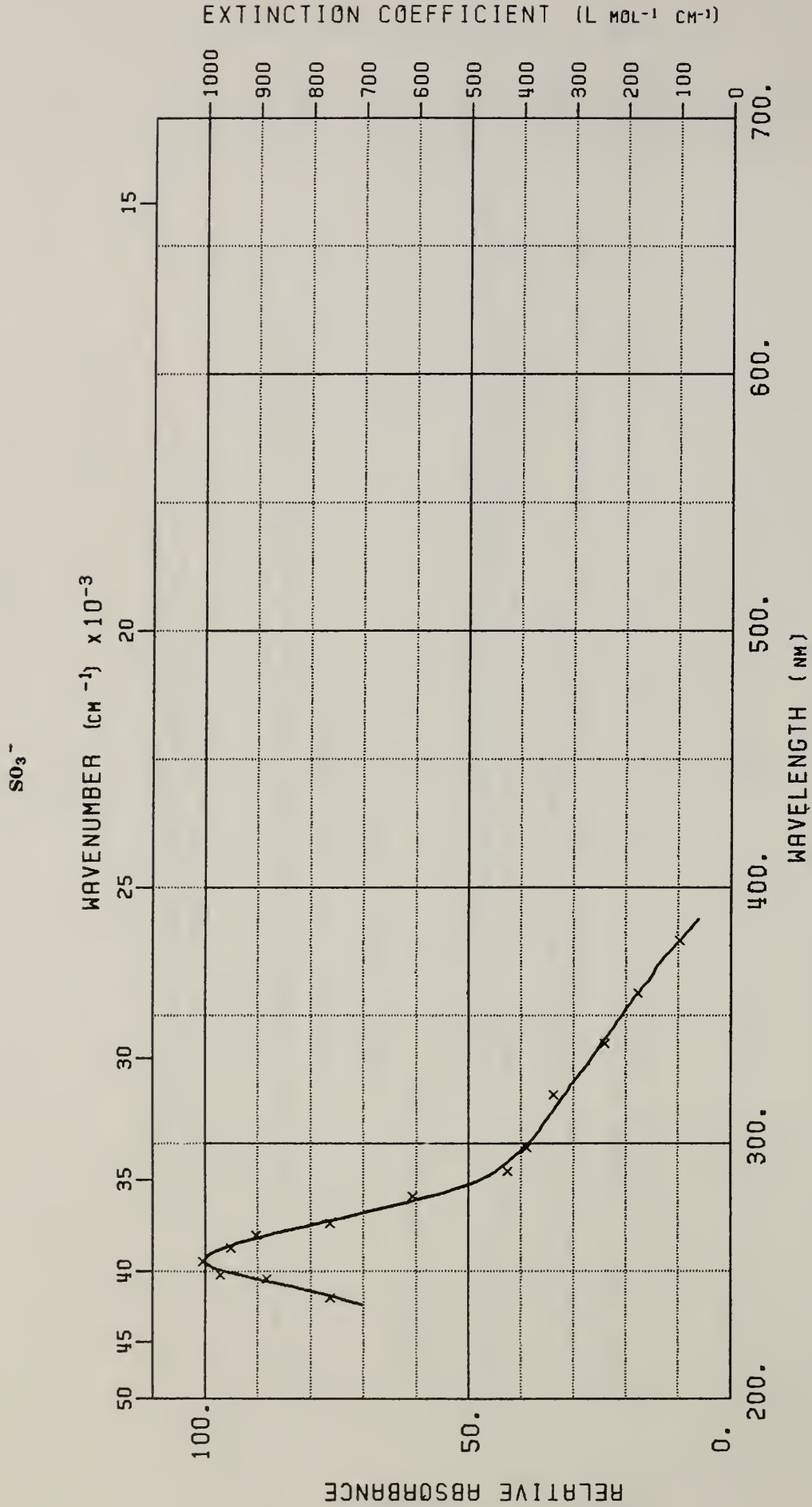


Footnotes: [1] Spectrum obtained by subtracting contribution of  $\text{S}_2\text{O}_4^{2-}$  formed from  $2\text{SO}_2^- \rightarrow \text{S}_2\text{O}_4^{2-}$ .

[2] Based on  $\epsilon(\text{max}) = 8300 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\text{S}_2\text{O}_4^{2-}$ .

[3] Displayed spectrum normalized to  $600 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 363 nm.

[4] Cutoff filter permitted only  $\text{S}_2\text{O}_5^{2-}$  to be photolyzed.



Transient [1,2]: SO<sub>3</sub><sup>-</sup>, λ(max) = 255 nm, ε<sub>255</sub> ≈ 1000 L mol<sup>-1</sup> cm<sup>-1</sup>, 2k = (1.1 ± 0.2) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of 2 × 10<sup>-3</sup> mol L<sup>-1</sup> SO<sub>3</sub><sup>2-</sup>, N<sub>2</sub>O-saturated, pH 10.3

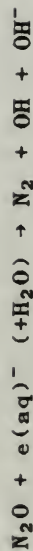
$\text{SO}_3^-$

Reference: E. Hayon, A. Treinin, and J. Wilf, *J. Am. Chem. Soc.* 94(1): 47-57 (1972)

Transient generation: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length  $\approx$  30 ns; dosimetry -  $\text{N}_2\text{O}$ -saturated, aqueous solution of  $\text{KSCN}$  [3]

Spectral acquisition: Osram XBO 450 W xenon lamp (pulsed); two high intensity Bausch & Lomb monochromators, used in series to reduce scattered light [4]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope

Transient formation:



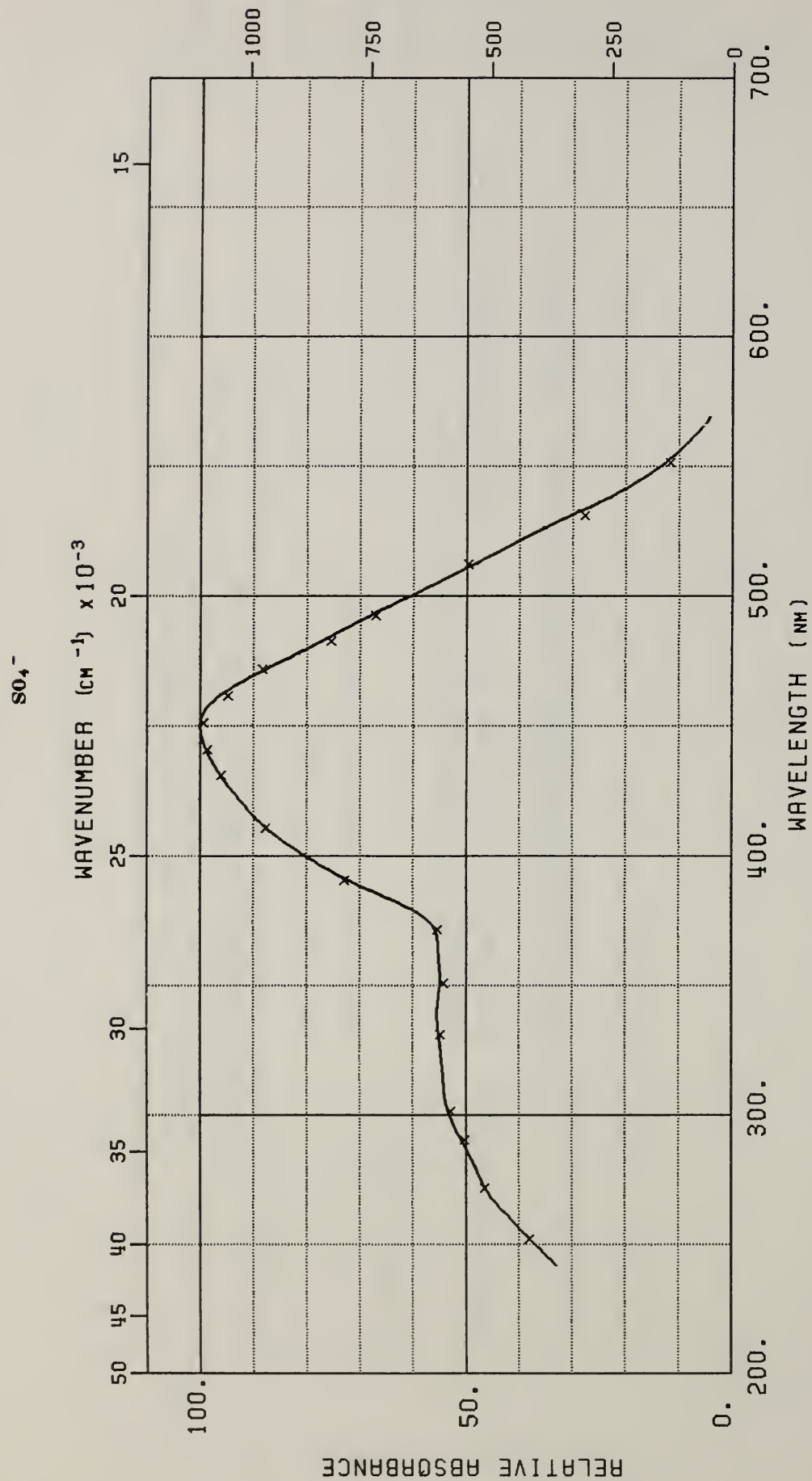
Footnotes: [1] Points in spectrum are averages of three or more experiments.

[2] Spectrum remains unchanged in pH range 4-10.

[3] Using  $\epsilon_{600}(\text{SCN})_2^- = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $10^{-1} \text{ mol L}^{-1} \text{ SCN}^-$ ,  $\text{N}_2\text{O}$ -saturated solutions at pH 5.5 and assuming  $G = G(\text{e}(\text{aq})^-) + G(\text{OH}) = 5.5$ , E. Hayon, *J. Chem. Phys.* 51(11): 4881-92 (1969).

[4] At 230 and 210 nm, the amount of scattered light was 1% and 18%, respectively.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: SO<sub>4</sub><sup>•-</sup>, sulfate radical anion, λ(max) = 450 nm [1], ε<sub>450</sub> = 1100 L mol<sup>-1</sup> cm<sup>-1</sup> [1,2]

System: aqueous solution of 2 x 10<sup>-3</sup> mol L<sup>-1</sup> S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, Ar(1 atm), pH = 5.1



Reference: E. Hayon, A. Treinin, and J. Wilf, *J. Am. Chem. Soc.* 94(1): 47-57 (1972)

Transient generation: electrons from Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length  $\approx$  30 ns; dosimetry [3] N<sub>2</sub>O-saturated aqueous solution of 0.1 mol L<sup>-1</sup> SCN<sup>-</sup> at pH 5.5

Spectral acquisition: Osram XBO W xenon lamp; two high-intensity Bausch & Lomb monochromators used in series to reduce scattered light; two EMI 9558QB PMT; dual beam Fairchild 777 oscilloscope; quartz cells with optical path lengths of 2 cm; spectrum is the average of 3 runs.

Transient formation:



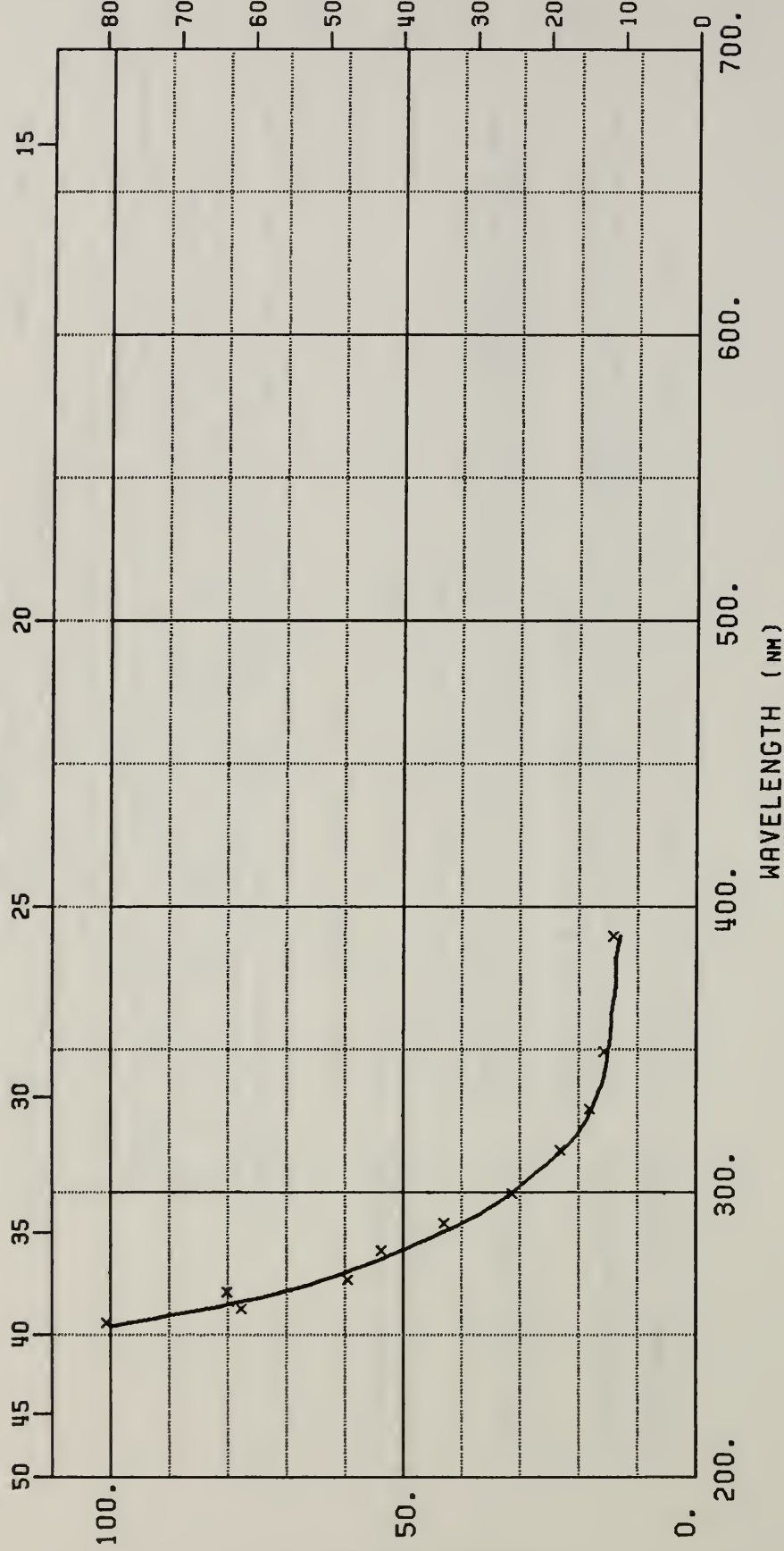
Footnotes: [1] With spectrum of SO<sub>4</sub><sup>-</sup> displayed, Hayon, Treinin, and Wilf quoted (but apparently did not measure) a value of  $\lambda(\text{max}) = 450$  nm and  $\epsilon_{450} = 1100$  L mol<sup>-1</sup> cm<sup>-1</sup>. The displayed spectrum is normalized to conform to these values.

[2] The extinction coefficient was measured by W. Roebke, M. Renz, and A. Henglein, *Int. J. Radiat. Phys. Chem.* 1(1): 39-44 (1969). They reported the maximum of the SO<sub>4</sub><sup>-</sup> spectrum to be at  $\lambda(\text{max}) = 460$  nm. Earlier values of extinction coefficients were  $\epsilon_{455} = (450 \pm 45)$  L mol<sup>-1</sup> cm<sup>-1</sup> from E. Hayon and J.J. McCarvey, *J. Phys. Chem.* 71(5): 1472-7 (1967) and  $\epsilon_{455} = (460 \pm 25)$  L mol<sup>-1</sup> cm<sup>-1</sup> from L. Dogliotti and E. Hayon, *J. Phys. Chem.* 71(8): 2511-6 (1967).

[3] In these last two references,  $\lambda(\text{max})$  was quoted at 455 nm.  
Using  $\epsilon_{500}(\text{SCN})_2^- = 7600$  L mol<sup>-1</sup> cm<sup>-1</sup> and assuming  
 $G = G(\text{e}(\text{aq})^-) + G(\text{OH}) = 5.5$ , E. Hayon, *J. Chem. Phys.* 51(11): 4881-92 (1969).

$\text{SO}_5^-$

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



Transient [1]:  $\text{SO}_5^-$ ,  $\epsilon_{265} \approx 560 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $2 \times 10^{-3} \text{ mol L}^{-1} \text{ HSO}_5^-$ ,  $\text{N}_2\text{O}$ -saturated,  $\text{pH} \approx 6$

Reference: E. Hayon, A. Treinin, and J. Willf, *J. Am. Chem. Soc.* 94(1): 47-57 (1972)

Transient generation: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length  $\approx$  30 ns; dosimetry -  $\text{N}_2\text{O}$ -saturated, aqueous solution of KSCN [3]

Spectral acquisition: Osram XBO 450 W xenon lamp (pulsed); two high intensity Bausch & Lomb monochromators, used in series to reduce scattered light [4]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope; time delay 200  $\mu\text{s}$  after pulse

Transient formation:



Footnotes:

[1] Points in spectrum are averages of three of more experiments.

[2] Quoted extinction coefficient is a lower limit.

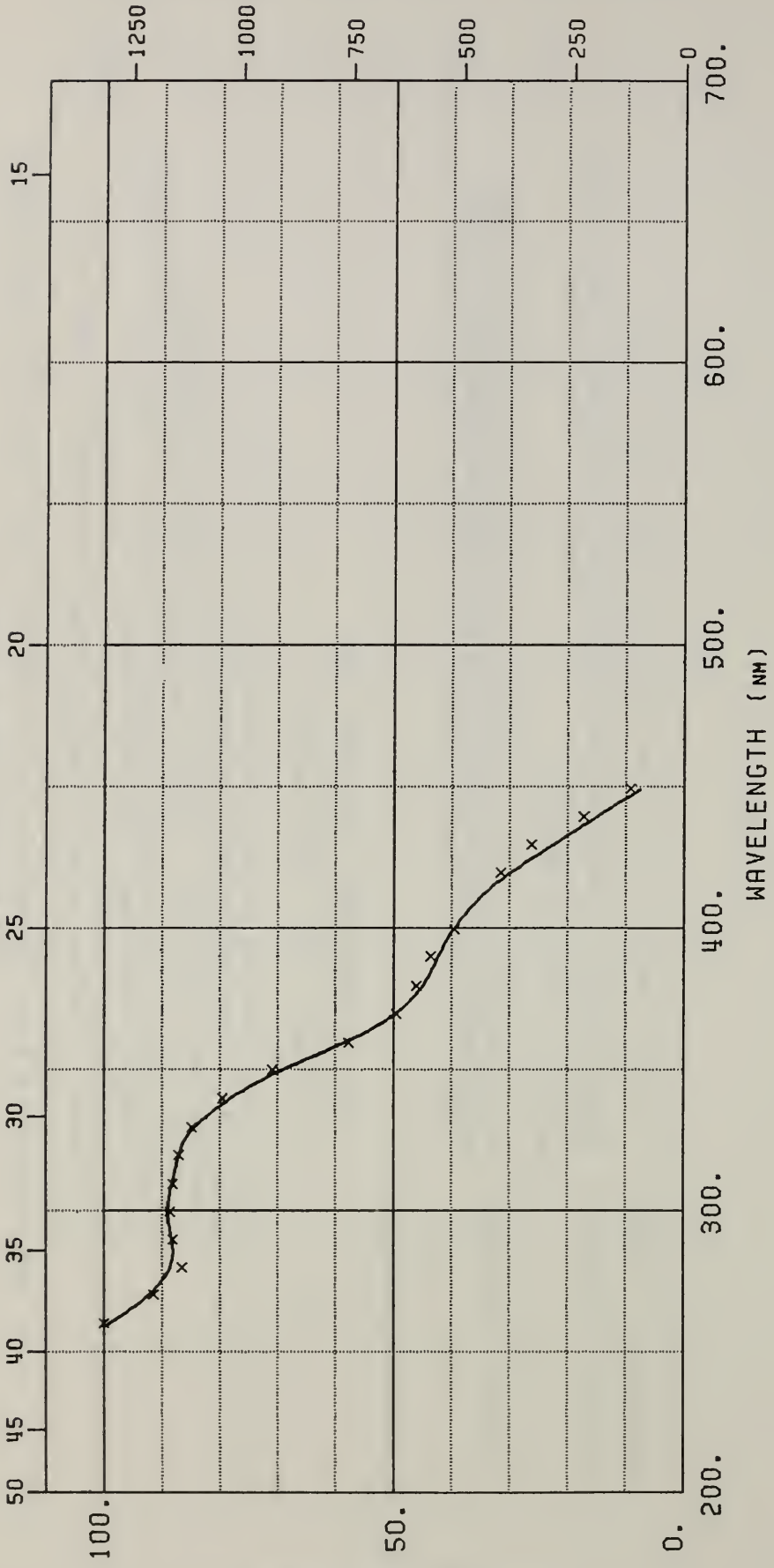
Impurities, sulfates,  $\text{H}_2\text{O}_2$ , and  $\text{S}_2\text{O}_8^{2-}$ , in the prepared salts  $\text{KHSO}_5$  and  $\text{NaHSO}_4$ , made  $\epsilon$  uncertain. Earlier values of  $\epsilon$  ( $\text{SO}_5^-$ ) and the shape of earlier spectra were somewhat different, W. Roebke, M. Renz, and A. Henglein, *Int. J. Radiat. Phys. Chem.* 1(1): 39-44 (1969).

[3] Using  $\epsilon_{500} (\text{SCN})_2^- = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $10^{-1} \text{ mol L}^{-1} \text{ SCN}^-$ ,  $\text{N}_2\text{O}$ -saturated solutions at pH 5.5 and assuming  $G = G(\text{e}(\text{aq})^-) + G(\text{OH}) = 5.5$ , E. Hayon, *J. Chem. Phys.* 51(11): 4881-92 (1969).

[4] At 230 and 210 nm, the amount of scattered light was 1% and 18%, respectively.

$S_2O_3^{2-}$

WAVENUMBER ( $cm^{-1}$ )  $\times 10^{-3}$



EXTINCTION COEFFICIENT ( $L\ mol^{-1}\ cm^{-1}$ )

100.  
50.  
0.

Transient [1]:  $S_2O_3^{2-}$  [2]

System: aqueous solution of  $10^{-4}$  mol  $L^{-1}$   $S_2O_3^{2-}$ , saturated with  $N_2O$ , pH = 4.8



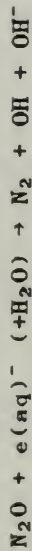
$S_2O_3^-$

Reference: M. Schoeneshoefter, *Int. J. Radiat. Phys. Chem.* 5: 375-86 (1973)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per  $\mu s$

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay immediately after pulse

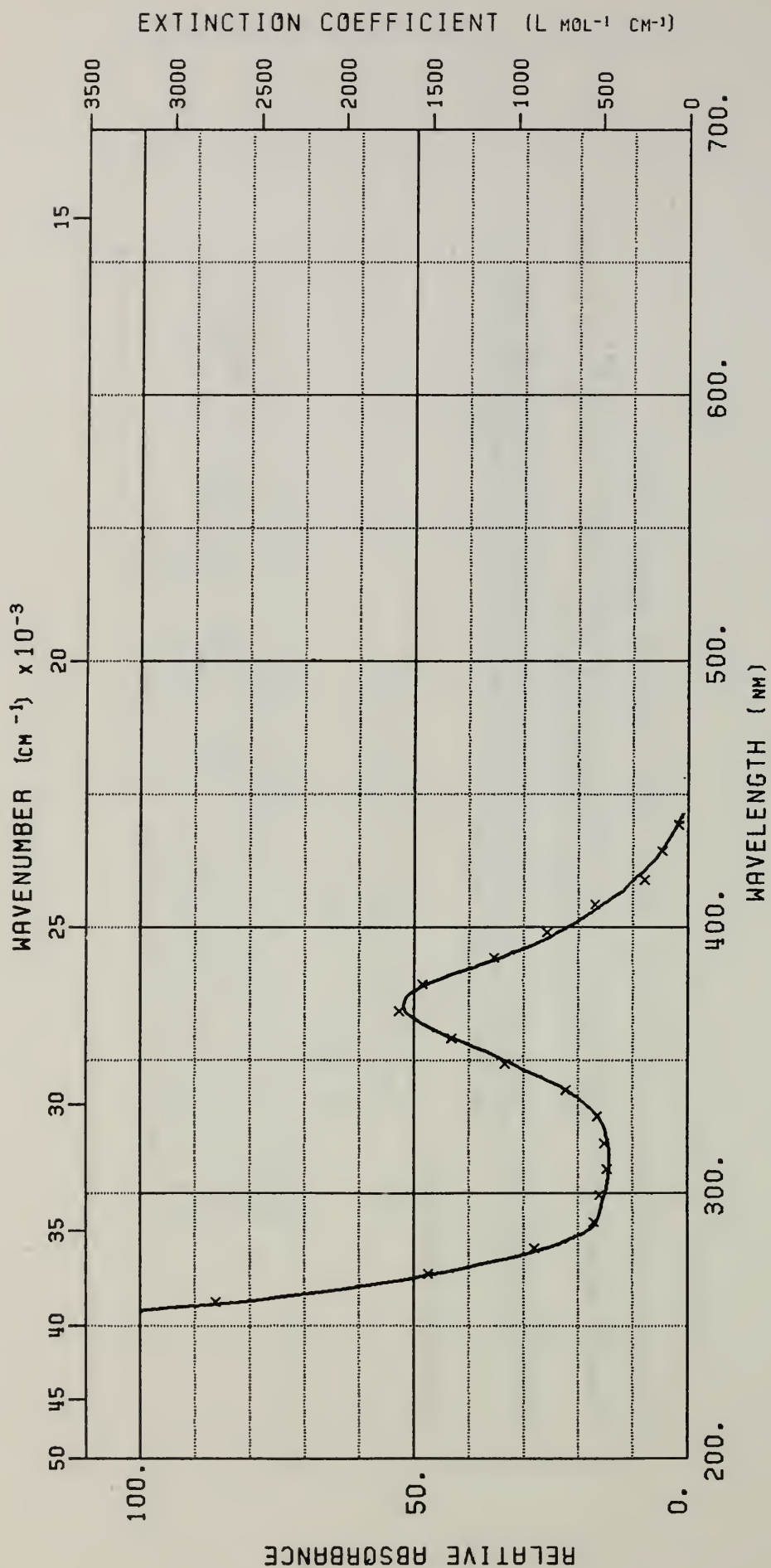
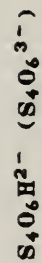
Transient formation:



Footnotes: [1] Spectrum corrected for  $S_2O_3^- + S_2O_3^{2-} \leftrightarrow S_4O_6^{3-}$  equilibrium. Extinction coefficients were based on  $G(OH) = 6$ .

[2] Another spectrum has been assigned as the  $S_2O_3^-$  spectrum: L. Dogliotti and E. Hayon, *J. Phys. Chem.* 72: 1800-7 (1968); G.E. Adams, J.W. Boag, and B.D. Michael, *Proc. Chem. Soc.* 411 (1964); G.E. Adams, J.W. Boag, and B.D. Michael, *Trans. Faraday Soc.* 61: 1674-80 (1965).

[3] A. Henglein, *Allg. Prakt. Chem.* 17(5): 295-301 (1966).



Transient:  $S_4O_6H^{2-}$  [1] ( $S_4O_6^{3-}$  [2]),  $\lambda(\max) = 370$  nm,  $\epsilon_{370} = 1650$  L mol<sup>-1</sup> cm<sup>-1</sup> [3],  
 $2k = 1.1 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of  $10^{-4}$  mol L<sup>-1</sup>  $S_2O_3^{2-}$ , saturated with  $N_2O$ , pH = 4.8

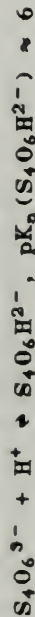
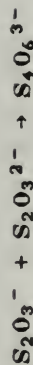
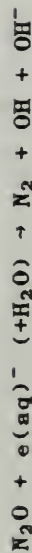


Reference: M. Schoeneshoefer, *Int. J. Radiat. Phys. Chem.* 5: 375-86 (1973)

Transient generation: pulse radiolysis [4] using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per  $\mu s$

Spectral acquisition: Osrarn XBO 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay-spectrum measured after 25  $\mu s$  and extrapolated to time zero

Transient formation [5]:



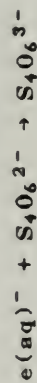
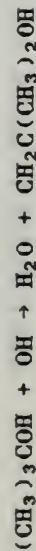
Footnotes: [1] Similar spectra have been attributed to the  $S_2O_3^-$  radical: L. Dogliotti and E. Hayon, *J. Phys. Chem.* 72: 1800-7 (1968); G.E. Adams, J.W. Boag, and B.D. Michael, *Proc. Chem. Soc.* 411 (1964); G.E. Adams, J.W. Boag, and B.D. Michael, *Trans. Faraday. Soc.* 61: 1674-80 (1965).

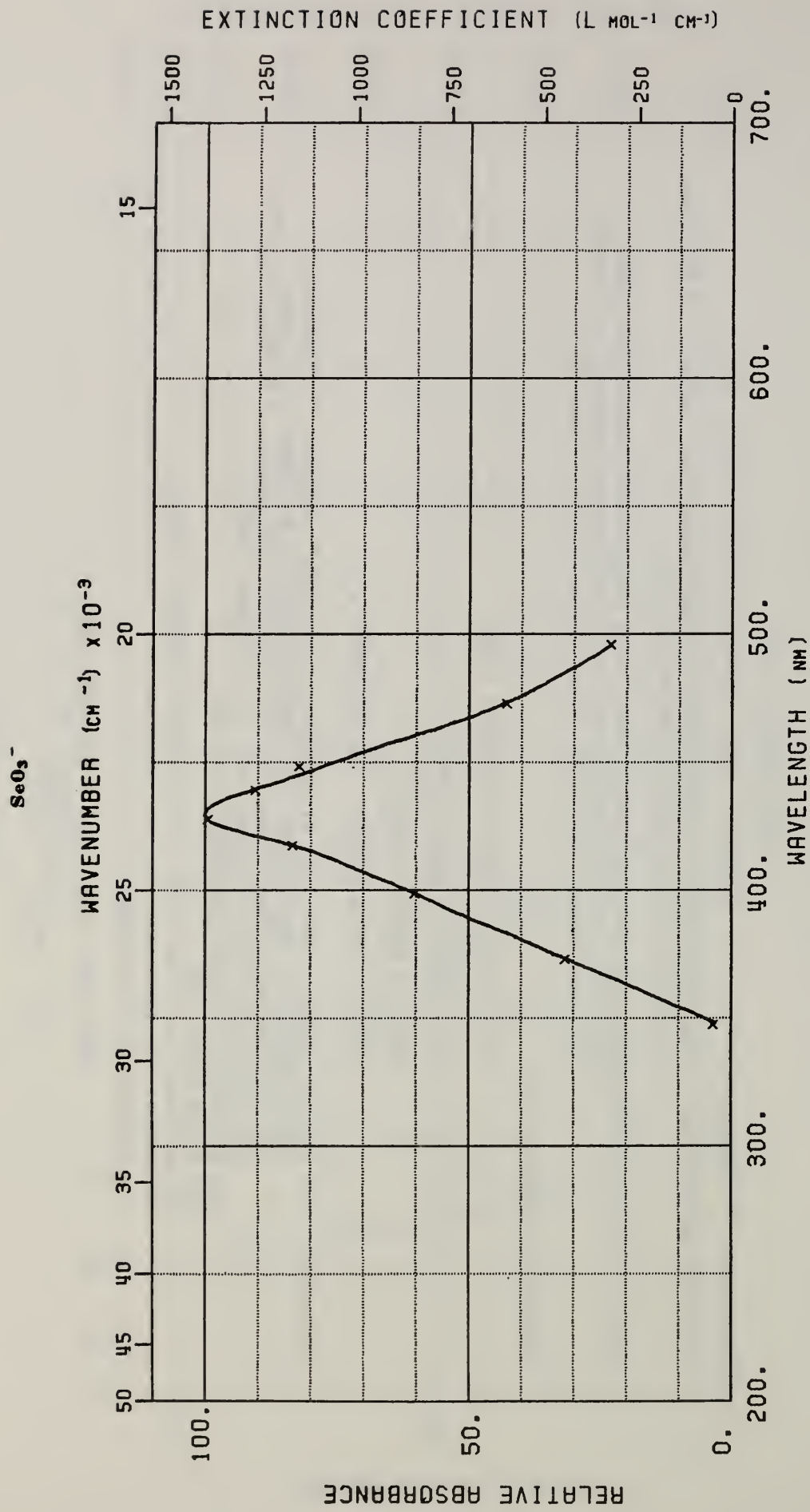
[2] Spectrum is almost independent of pH.

[3] Using  $G(OH) = 6$ .

[4] A. Henglein, *Allg. Prakt. Chem.* 17(5): 295-301 (1966).

[5] Almost identical spectrum was obtained in an alkaline, aqueous solution of  $S_4O_6^{2-}$ , containing tert-butanol.





Transient: SeO<sub>3</sub><sup>-</sup>, λ(max) = 430 nm, ε<sub>430</sub> = 1.4 x 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of 10<sup>-2</sup> mol L<sup>-1</sup> SeO<sub>3</sub><sup>2-</sup>, Ar-saturated, pH natural



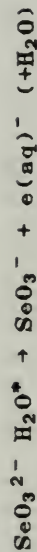
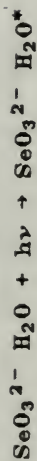
SeO<sub>3</sub><sup>-</sup>

Reference: M.S. Subhani and T. Kausar, Rev. Roum. Chim. 23(11-12): 1627-30 (1978)

Transient generation: flash photolysis, using flash tubes [2]

Spectral acquisition: monitoring lamp; monochromator; PMT; oscilloscope [3]

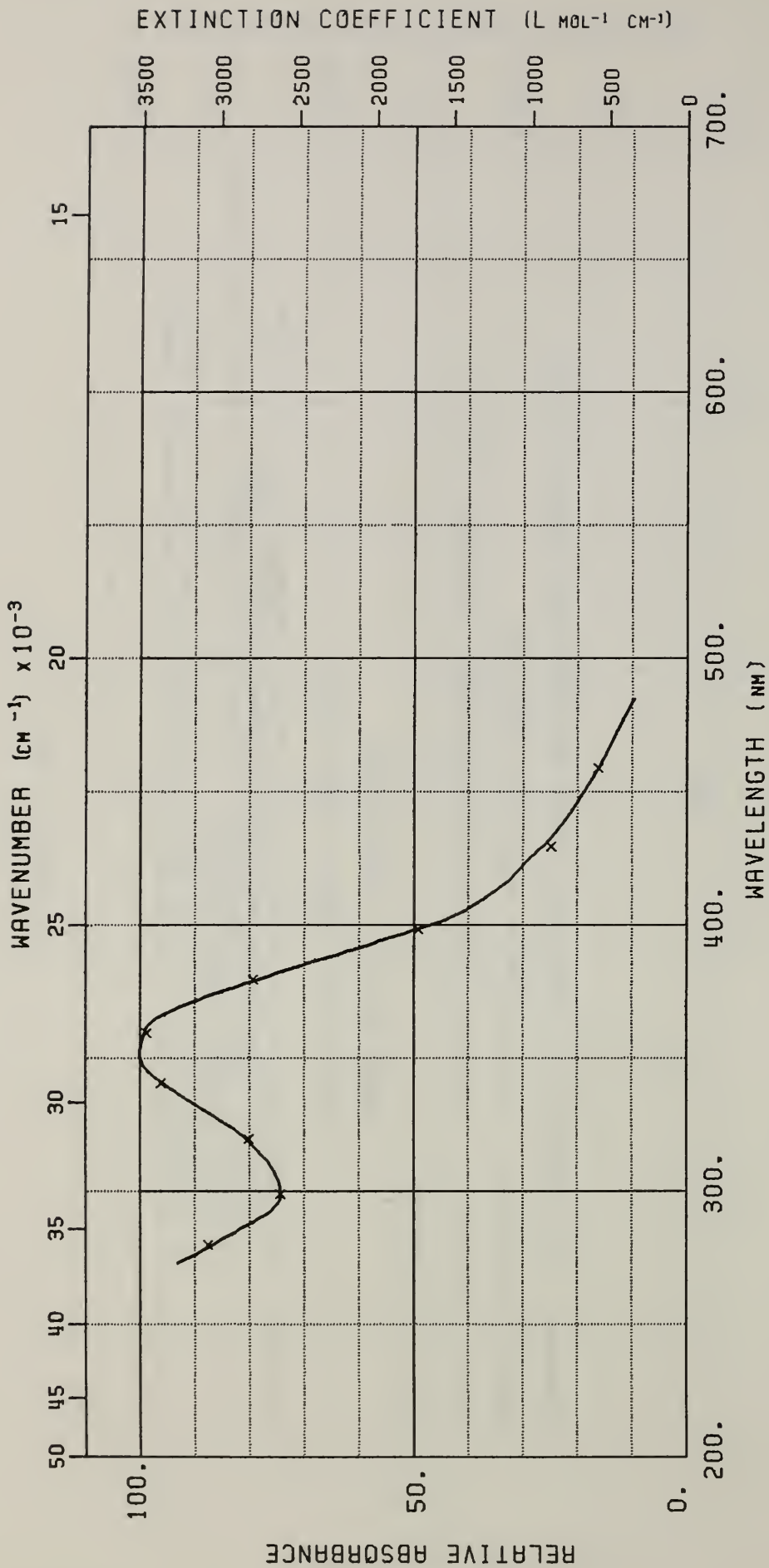
Transient formation:



Footnotes: [1] Extinction coefficient obtained by assuming amount of O<sub>2</sub><sup>-</sup>, formed from e(aq)<sup>-</sup> in O<sub>2</sub>-saturated solutions, is equal to that of SeO<sub>3</sub><sup>-</sup>.

[2] Apparatus similar to that in G.V. Buxton and M.S. Subhani, J. Chem. Soc. Faraday Trans. 1 68(5): 958-69 (1972).

[3] Apparatus similar to that in K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).



Transient:  $\text{TeO}_3^-$ ,  $\lambda(\text{max}) = 350 \text{ nm}$ ,  $\epsilon = 3500 \text{ L mol}^{-1} \text{cm}^{-1}$

System: aqueous solution of  $2 \times 10^{-2} \text{ mol L}^{-1} \text{TeO}_3^{2-}$ , air-saturated, pH neutral

TeO<sub>3</sub><sup>-</sup>

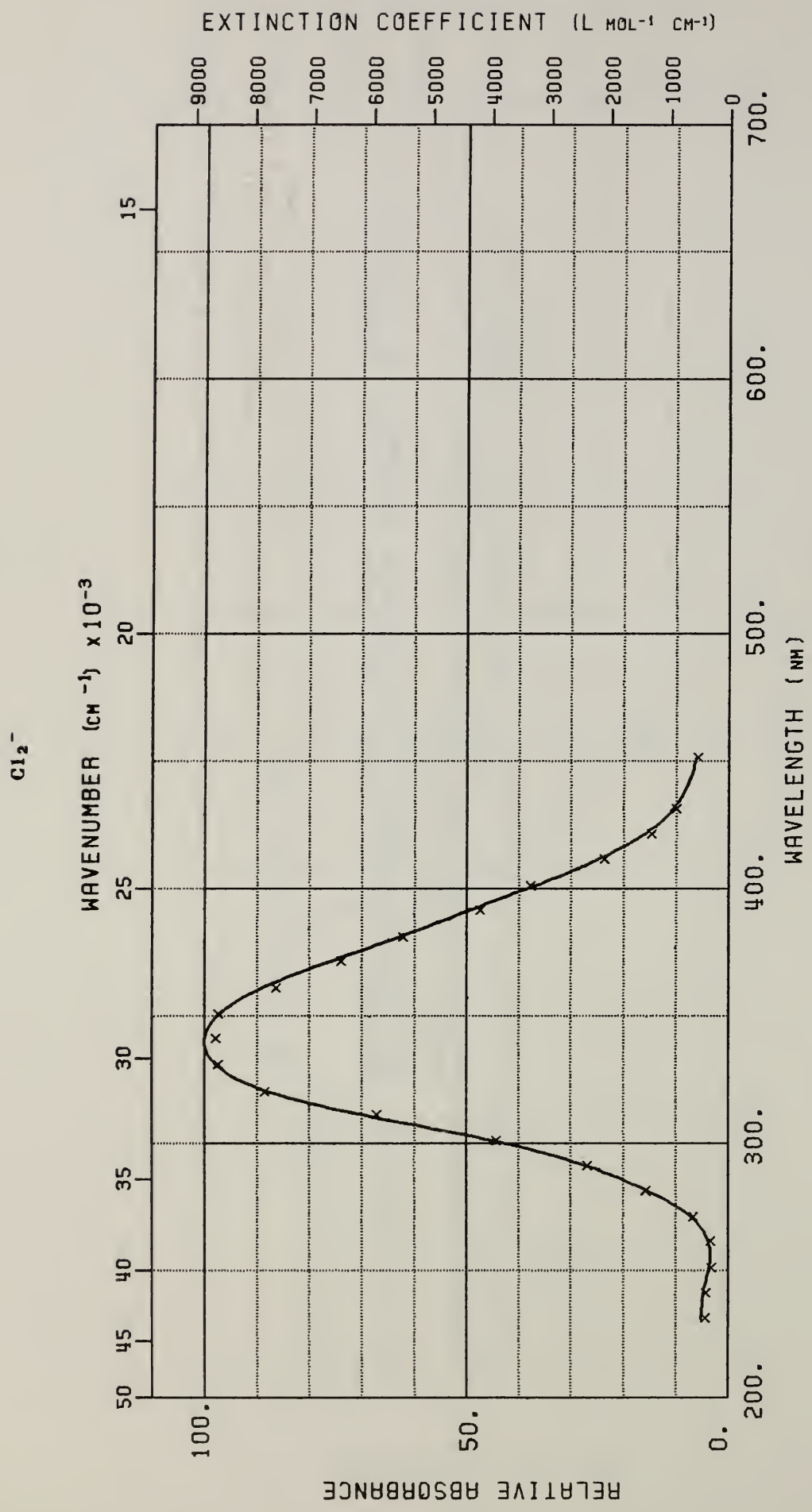
Reference: C.E. Adams, J.W. Boag, and B.D. Michael, Trans. Faraday Soc. 61: 1674-80 (1965)

Transient generation: pulse radiolysis, linear accelerator; energy 1.8 MeV;  
dosimetry, using ferrocyanide

Spectral acquisition: 450 W xenon monitoring lamp; Bausch & Lomb type 250 grating monochromator;  
EMI 9558 QC PMT; 545 Tektronix oscilloscope with 53/54L preamplifier

Transient formation:





Transient:  $\text{Cl}_2^-$ ,  $\lambda(\text{max}) = 340 \text{ nm}$ ,  $\epsilon_{340} = (8800 \pm 500) \text{ L mol}^{-1} \text{ cm}^{-1}$  [1,2]

System: aqueous solution of  $10^{-2} \text{ mol L}^{-1} \text{ Cl}_2^-$ , Ar saturated,  $10^{-1} \text{ mol L}^{-1}$  perchloric acid,  $\text{pH} \approx 1$



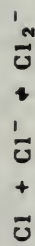
$\text{Cl}_2^-$

Reference: G.C. Jayson, B.J. Parsons, and A.J. Swallow, J. Chem. Soc., Faraday Trans. 1 69: 1597-607 (1973)

Transient generation: pulse radiolysis, electron linear accelerator; dose per pulse  $1.58 \times 10^3$  rad; dosimetry-secondary emission chamber [3]

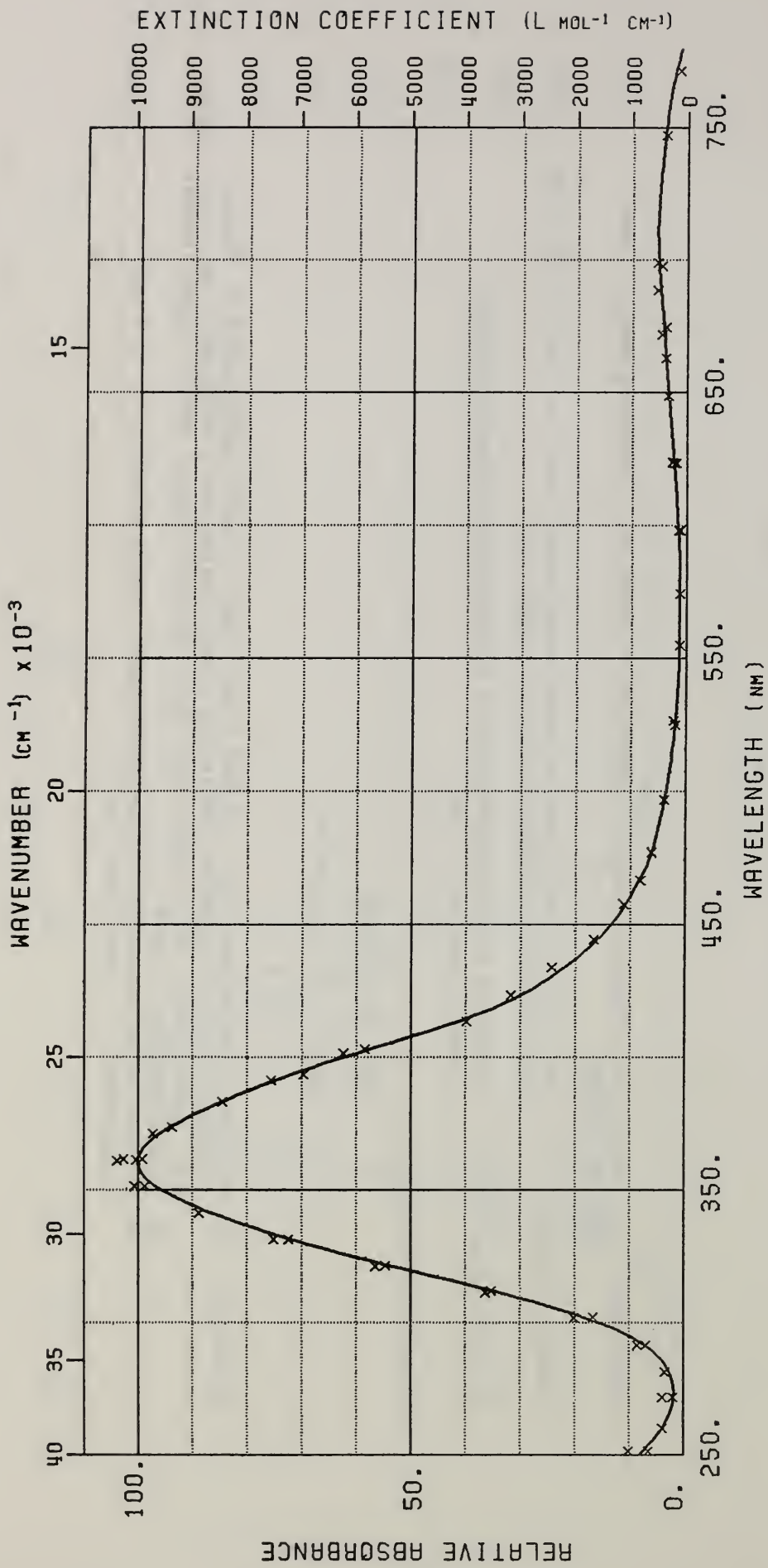
Spectral acquisition: two Bausch & Lomb high-intensity monochromators used in series to reduce scattered light.

Transient formation:



Footnotes: [1] An earlier value was  $\epsilon_{340} = 12,500 \text{ L mol}^{-1} \text{ cm}^{-1}$  from M. Anbar and J.K. Thomas, J. Phys. Chem. 68: 3829-35 (1964) and a later value was  $\epsilon = 12,400 \text{ L mol}^{-1} \text{ cm}^{-1}$  from R.K. Broszkiewicz, Bull. Acad. Pol. Sci., Ser. Sci. Chim. 24(2): 123-31 (1976).  
[2] Assuming  $G(\text{Cl}_2^-) = 2.9$ .  
[3] Calibrated by aqueous potassium thiocyanate taking  $G((\text{SCN})_2^-) = 2.9$  and  $\epsilon_{500}((\text{SCN})_2^-) = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

$\text{Br}_2^-$



Transient:  $\text{Br}_2^-$ ,  $\lambda(\text{max}) = 360 \text{ nm}$ ,  $\epsilon_{360} = (9900 \pm 600) \text{ L mol}^{-1} \text{cm}^{-1}$  [1,2]

System: aqueous solution of  $10^{-3} \text{ mol L}^{-1} \text{ Br}_2^-$ , neutral,  $\text{N}_2\text{O}$ -saturated

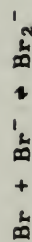
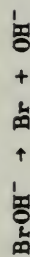
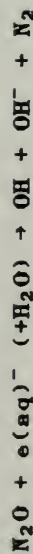
Br<sub>2</sub><sup>-</sup>

Reference: D. Zehavi and J. Rabani, *J. Phys. Chem.* 76(3): 312-9 (1972)

Transient generation: pulse radiolysis; energy 5 MeV; pulse length 0.1 μs; dosimetry-induction coil [3]

Spectral acquisition: split analyzing light beam with two monochromators; extrapolated to zero time; PMT's type R166 for 260-300 nm, 1P28 for 300-650 nm and R196 above 650 nm; dual-beam oscilloscope; filter used to prevent photolysis and second-order light; 150 W xenon lamp

Transient formation:



Footnotes:

[1] D. Behar, private communication, 1980.

[2] Value quoted by authors was (12,000 ± 1000) L mol<sup>-1</sup> cm<sup>-1</sup>. However, other values for ε<sub>360</sub> in the literature are lower. For example 9600 L mol<sup>-1</sup> cm<sup>-1</sup> [4], 8200 L mol<sup>-1</sup> cm<sup>-1</sup> [5], 8300 L mol<sup>-1</sup> cm<sup>-1</sup> [6], and 8560 L mol<sup>-1</sup> cm<sup>-1</sup> [7]. In addition ε<sub>365</sub> = 7800 L mol<sup>-1</sup> cm<sup>-1</sup> [8].

[3] Internal dosimeter using Br<sub>2</sub><sup>-</sup> absorption was also used.

[4] B. Cercek, M. Ebert, C.W. Gilbert, and A.J. Swallow, *Pulse Radiolysis*, eds. M. Ebert, J.P. Keene, A.J. Swallow, and J.H. Baxendale (Academic Press, 1965) p. 83.

[5] H.C. Sutton, G.E. Adams, J.W. Boag, and B.D. Michael, *ibid.*, p. 61.

[6] B. Cercek, *Int. J. Radiat. Phys. Chem.* 4(1): 25-30 (1972).

[7] R.K. Broszkiewicz, *Bull. Acad. Pol. Sci. Chim.* 24(2): 123-31 (1976).

[8] M.S. Matheson, W.A. Mulac, J.L. Weeks, J. Rabani, *J. Phys. Chem.* 70: 2092-9 (1966).

$I_2^-$

WAVENUMBER ( $cm^{-1}$ )  $\times 10^{-3}$

15

20

25

30

100.

50.

0.

RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT ( $L\ mol^{-1}\ cm^{-1}$ )

10000  
9000  
8000  
7000  
6000  
5000  
4000  
3000  
2000  
1000  
0

800.

700.

600.

500.

400.

300.

WAVELENGTH (NM)

Transient [1]:  $I_2^-$ ,  $\epsilon(\max) \approx 9400\ L\ mol^{-1}\ cm^{-1}$  [2,3,4]

System: aqueous solution of  $3.3 \times 10^{-4}\ mol\ L^{-1}\ I^-$ , pH neutral, oxygen-saturated



Reference: R. Devonshire and J.J. Weiss, J. Phys. Chem. 72(11): 3815-20 (1968)

Transient generation: photolysis using the 185 nm mercury line from a low-pressure Spectrosil mercury lamp; photolyzing light intensity was modulated at 50 Hz by using a leakage reactance transformer giving 120 mA and 1650 V; pure  $N_2$  was passed between the lamp and absorption cell

Spectral acquisition: absorption cell was a 50 cm Spectrosil tube of 0.5 cm inside diameter; monitoring lamp was 150 W quartz tungsten-iodine lamp using a 24 V battery; heat filter was used in monitoring beam [5]; the output from PMT was detected using phase sensitive technique using electronic components from Brookdeal Electronics Ltd. - amplifier (LA635), phase sensitive detector (PD629), phase shifter (PS946), and meter (MU947).

Transient formation:



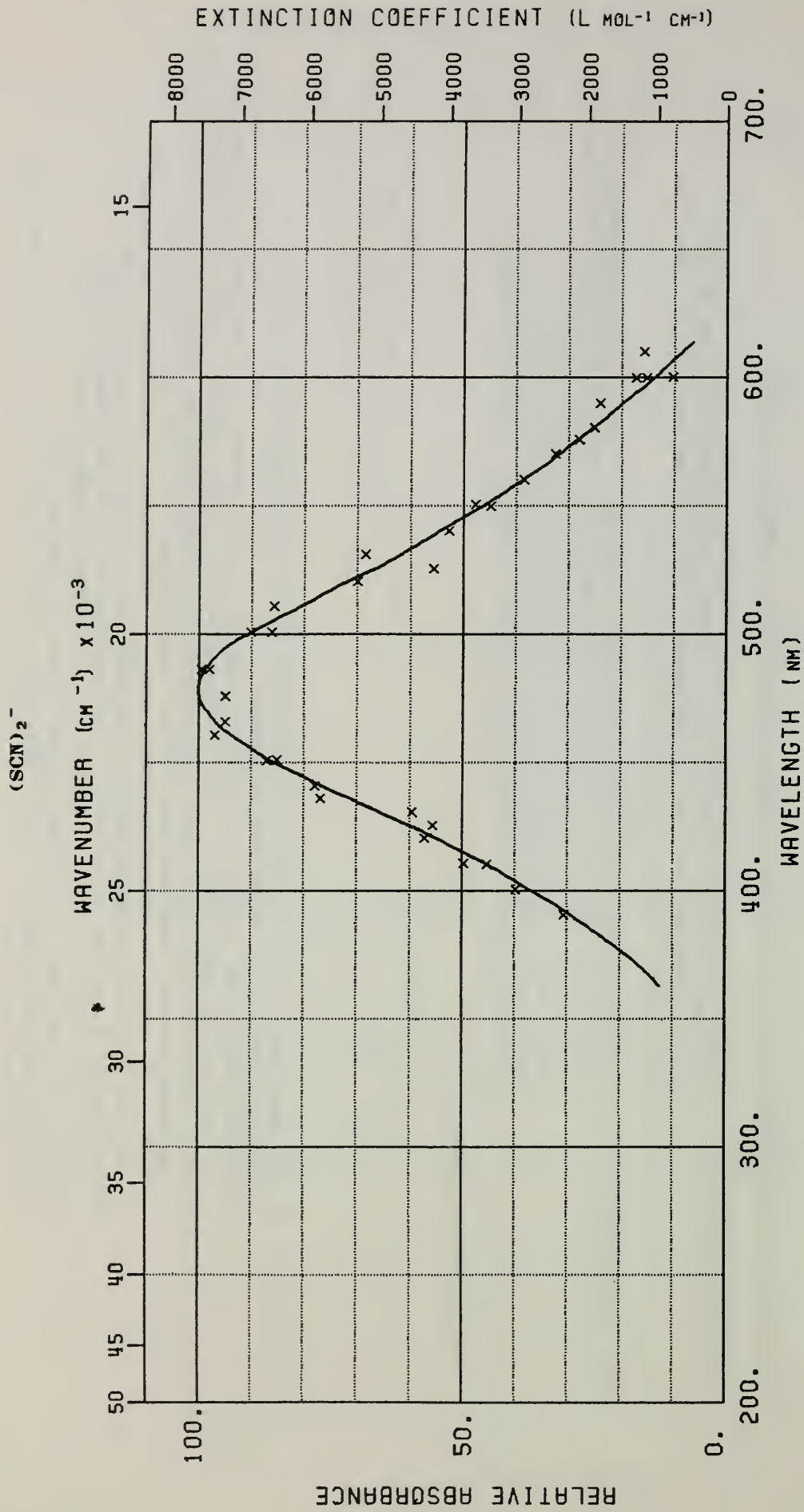
Footnotes: [1] At wavelengths shorter than about 525 nm, the spectrum has been corrected for the build-up of  $I_3^-$  from the photolysis.

[2] Listed extinction coefficient of  $9400 \text{ L mol}^{-1} \text{ cm}^{-1}$  is from a spectrum where the maximum extinction was near 380 nm. Private communication, R.H. Schuler, 1979. In contrast, the literature spectrum of  $I_2^-$ , after being digitized from the journal and smoothed, shows a maximum near 390 nm. For the purpose of this compilation, the literature spectrum is normalized to  $\epsilon(\text{max}) = 9400 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; but the original wavelength scale is used, so that the displayed spectrum has  $\lambda(\text{max}) \approx 390 \text{ nm}$ .

[3] In deaerated aqueous solution L.I. Grossweiner and M.S. Matheson, J. Phys. Chem. 61: 1089-95 (1957), measured  $\epsilon_{390} = (15,600 \pm 3000) \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[4] Ratio of absorbance at 390 nm to absorbance at 750 nm = 3.5.

[5] To further guard against large temperature fluctuations, the solutions were only irradiated for 30 s.



Transient:  $(\text{SCN})_2^-$ ,  $\lambda(\text{max}) = 480 \text{ nm}$  [1],  $\epsilon_{475} = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2,3,4]

System: aqueous  $10^{-4} \text{ mol L}^{-1} \text{ KSCN}$  (freshly prepared),  $\text{N}_2$ -saturated, pH 6.0

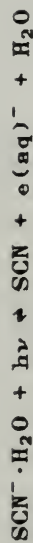
(SCN)<sub>2</sub><sup>-</sup>

Reference: L. Dogliotti and E. Hayon, *J. Phys. Chem.* 72: 1800-1807 (1968)

Transient generation: flash photolysis; energy per pulse 1800 J; duration at "1/e time" of 5 μs; pulse length 70 μs

Spectral acquisition: Bausch & Lomb grating monochromator; EMI 9558QB photomultiplier; spectra were obtained by a point-by-point method; time delay = 80 μs after start of pulse

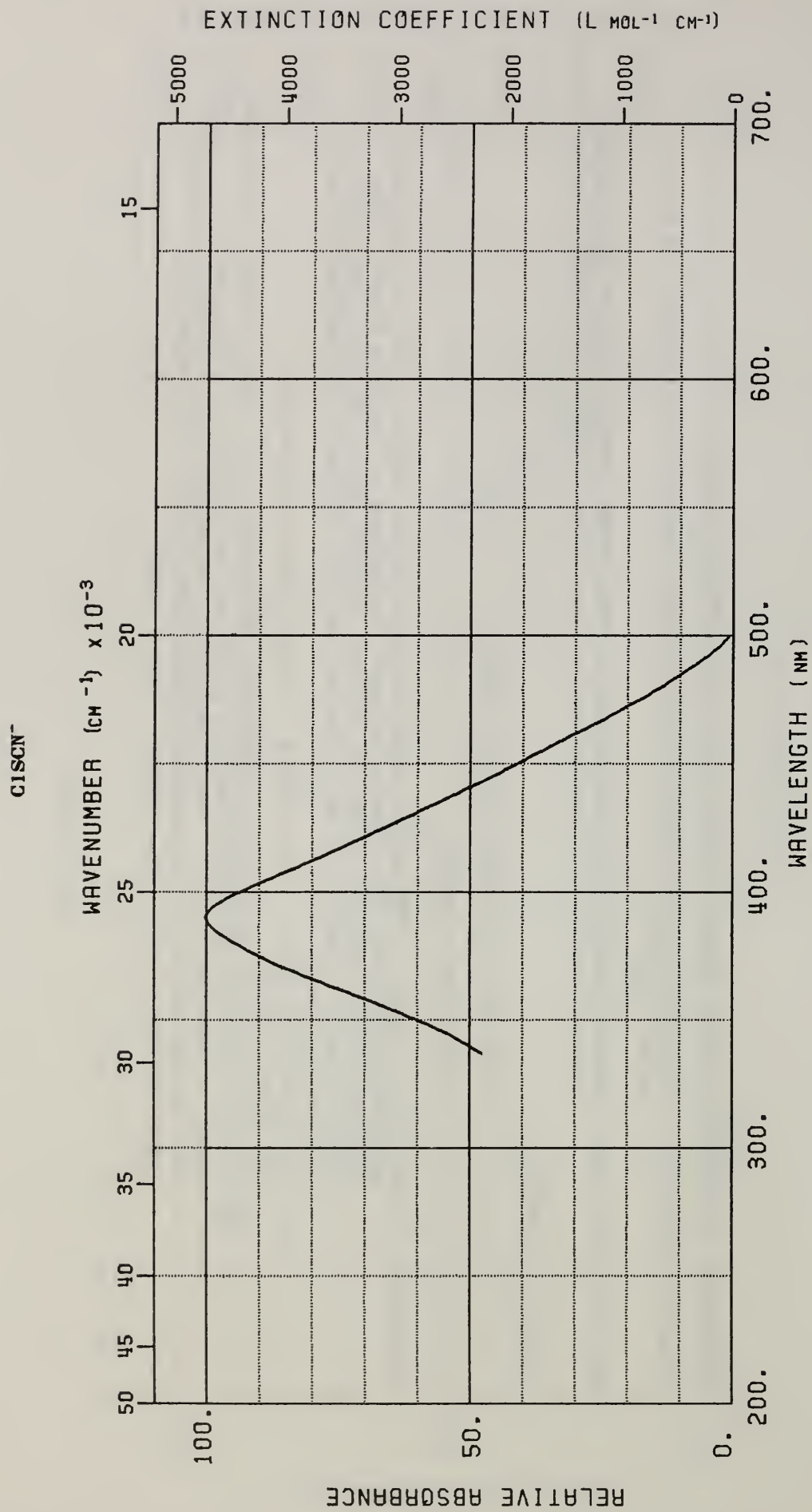
Transient formation:



Footnotes: [1] A value of λ(max) = 485 nm was quoted by the authors. However, the digitization of spectrum showed that they apparently meant the maximum of the data points. The maximum of their smoothed curve was 478 nm. For the purpose of this compilation, 478 is rounded to 480 nm in the quoted maximum, but 478 nm is the maximum of the displayed spectrum.

[2] J.H. Baxendale, P.L.T. Bevan, and D.A. Stott, *Trans. Faraday Soc.* 64: 2389-97 (1968).

[3] The spectrum displayed has been normalized to correspond to ε(max) = 7600 L mol<sup>-1</sup> cm<sup>-1</sup>.  
[4] A recent spectrum of (SCN)<sub>2</sub><sup>-</sup> has been taken and shows λ(max) = 472 nm and ε(max) = 7580 L mol<sup>-1</sup> cm<sup>-1</sup>. The G((SCN)<sub>2</sub><sup>-</sup>) was measured to be 6.13 in 10<sup>-2</sup> mol L<sup>-1</sup> SCN<sup>-</sup> aqueous solutions, saturated with N<sub>2</sub>O. R.H. Schuler, L.K. Patterson, and E. Janata, *J. Phys. Chem.* 84(16): 2088-9 (1980).



Transient [1]: ClSCN<sup>-</sup>,  $\lambda(\text{max}) = 390 \text{ nm}$ ,  $\epsilon_{390} = (4700 \pm 900) \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $3.8 \text{ mol L}^{-1} \text{ Cl}^{-}$  and  $5 \times 10^{-6} \text{ mol L}^{-1} \text{ SCN}^{-}$



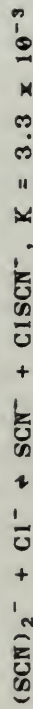
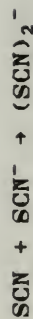
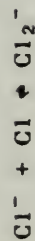
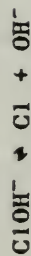
C1SCN<sup>-</sup>

Reference: M. Schoeneshoefter, Int. J. Radiat. Phys. Chem. 1: 505-13 (1969)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9538 PMT; decay curves photographed from oscilloscope display; time delay = 20  $\mu$ s [4]

Transient formation:



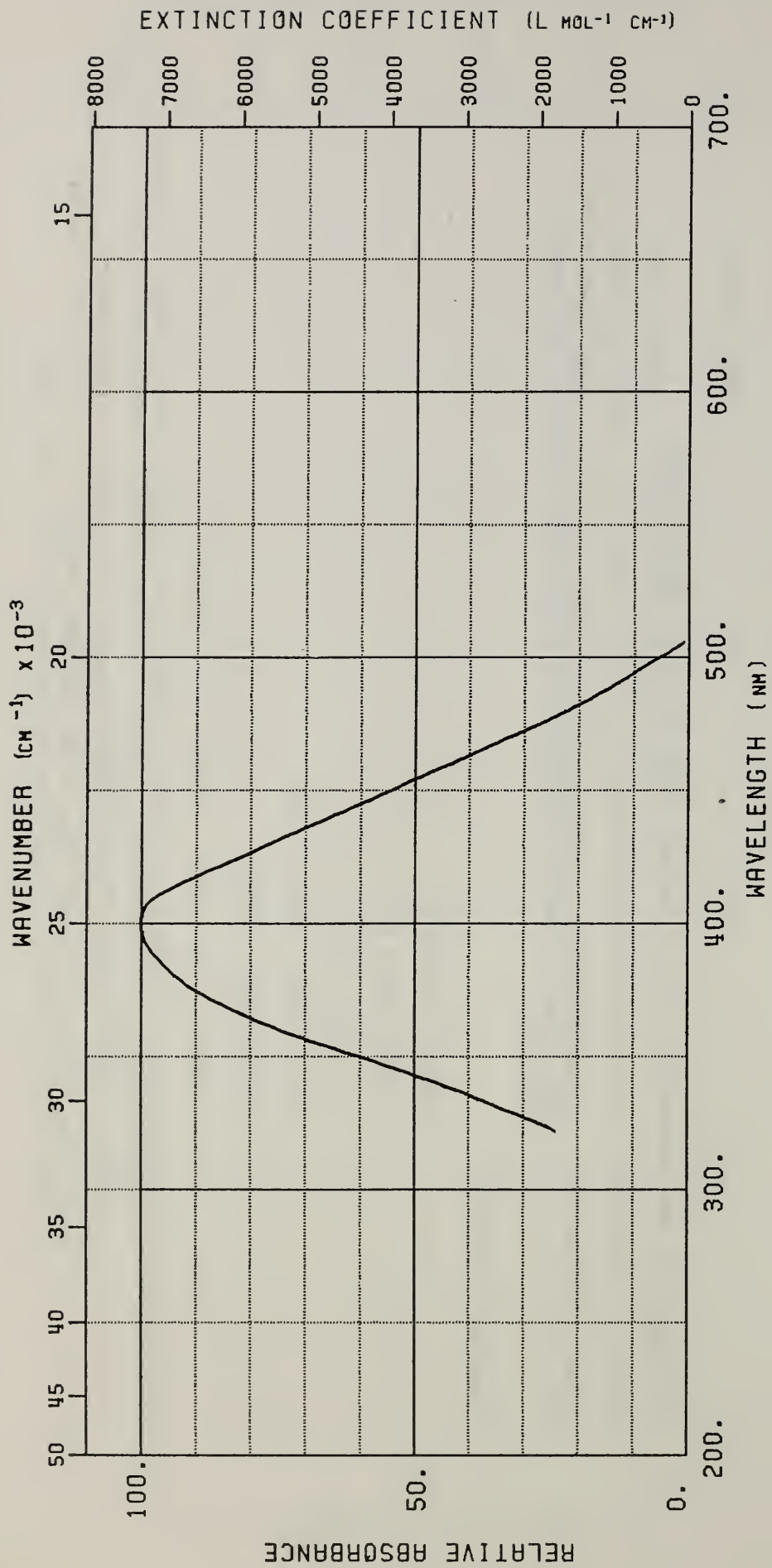
Footnotes: [1] Obtained from a mixed spectrum due to  $(\text{SCN})_2^-$  and  $\text{ClSCN}^-$ . Since  $\text{ClSCN}^-$  absorbs very little at 520 nm, the contribution of  $(\text{SCN})_2^-$  which does absorb at 520 nm could be determined.

[2] Based on  $\epsilon_{520} = 5300 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $(\text{SCN})_2^-$ .

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] Under the experimental conditions the half-life of  $\text{Cl}_2^-$  was 5  $\mu$ s.

BrSCN<sup>-</sup>



Transient [1]: BrSCN<sup>-</sup>,  $\lambda(\text{max}) = 400 \text{ nm}$ ,  $\epsilon_{400} = 7300 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $2 \times 10^{-2} \text{ mol L}^{-1} \text{ Br}^-$  and  $1 \times 10^{-4} \text{ mol L}^{-1} \text{ SCN}^-$

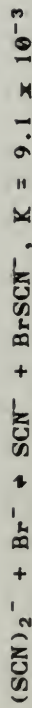
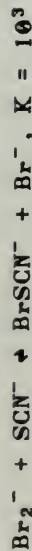
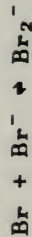
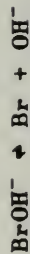
BrSCN<sup>-</sup>

Reference: M. Schoeneshoefler and A. Henglein, Ber. Bunsenges. Phys. Chem. 73(3): 289-93 (1969)

Transient generation: pulse radiolysis [3] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay greater than 10 μs [4]

Transient formation:



Footnotes: [1] Obtained from a mixed spectrum due to (SCN)<sub>2</sub><sup>-</sup> and BrSCN<sup>-</sup>. Since BrSCN<sup>-</sup> absorbs very little at 520 nm, the contribution of (SCN)<sub>2</sub><sup>-</sup> which does absorb at 520 nm could be determined.

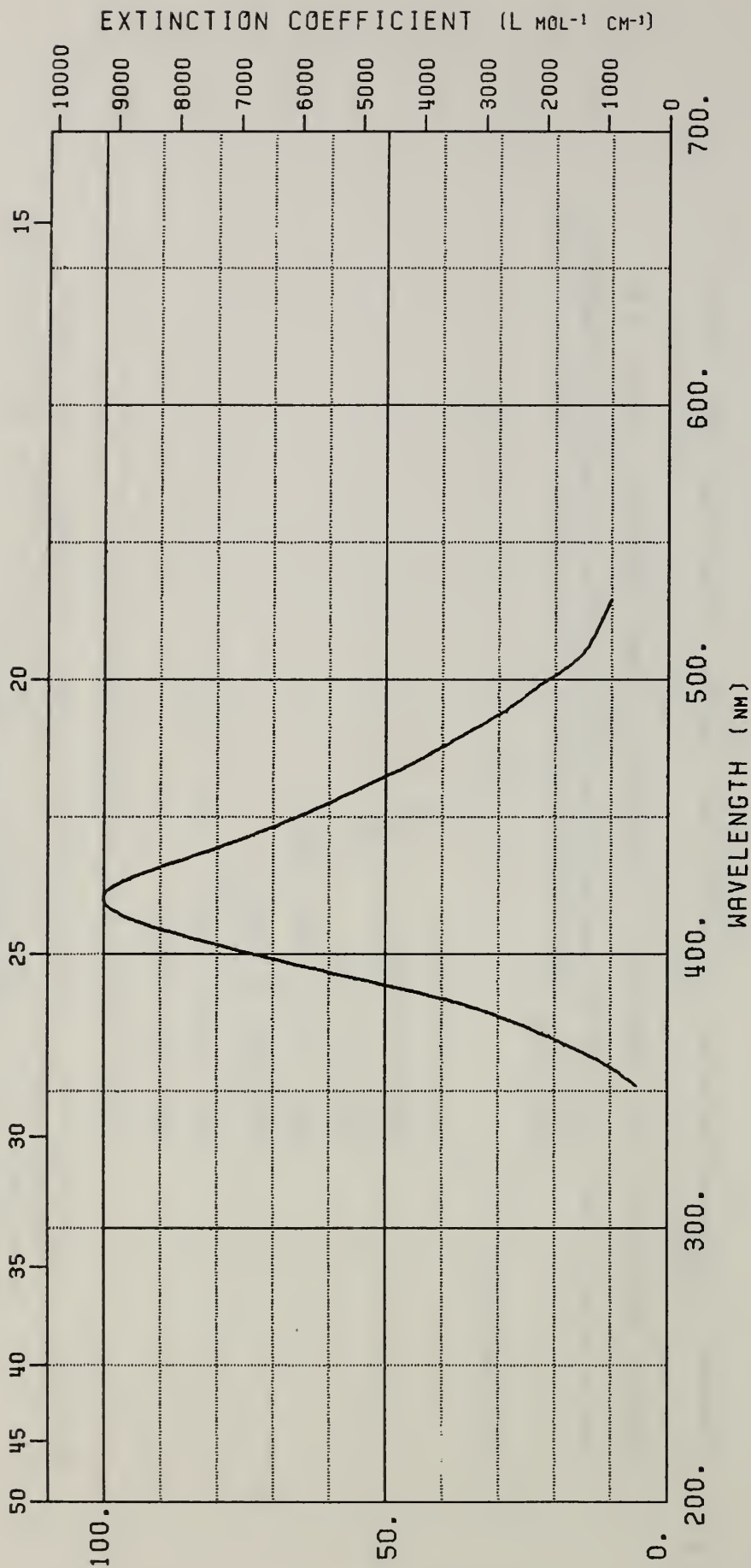
[2] Based on ε<sub>520</sub> = 5300 L mol<sup>-1</sup> cm<sup>-1</sup> for (SCN)<sub>2</sub><sup>-</sup>.

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] For ratios of [Br<sup>-</sup>]/[SCN<sup>-</sup>] ≠ 200, it was found that there was very little Br<sub>2</sub><sup>-</sup> present.

ISCN<sup>-</sup>

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



Transient [1,2]: ISCN<sup>-</sup>,  $\lambda(\text{max}) = 420 \text{ nm}$ ,  $\epsilon_{420} = 9200 \text{ L mol}^{-1} \text{ cm}^{-1}$

System: aqueous solution of  $1 \text{ mol L}^{-1}$  SCN<sup>-</sup> and  $10^{-4} \text{ mol L}^{-1}$  I<sup>-</sup>, saturated with N<sub>2</sub>O



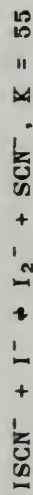
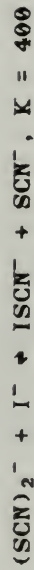
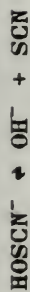
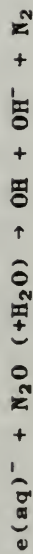
ISCN<sup>-</sup>

Reference: M. Schoeneshoefter and A. Henglein, Ber. Bunsenges. Phys. Chem. 74(4): 393-8 (1970)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.7 MeV

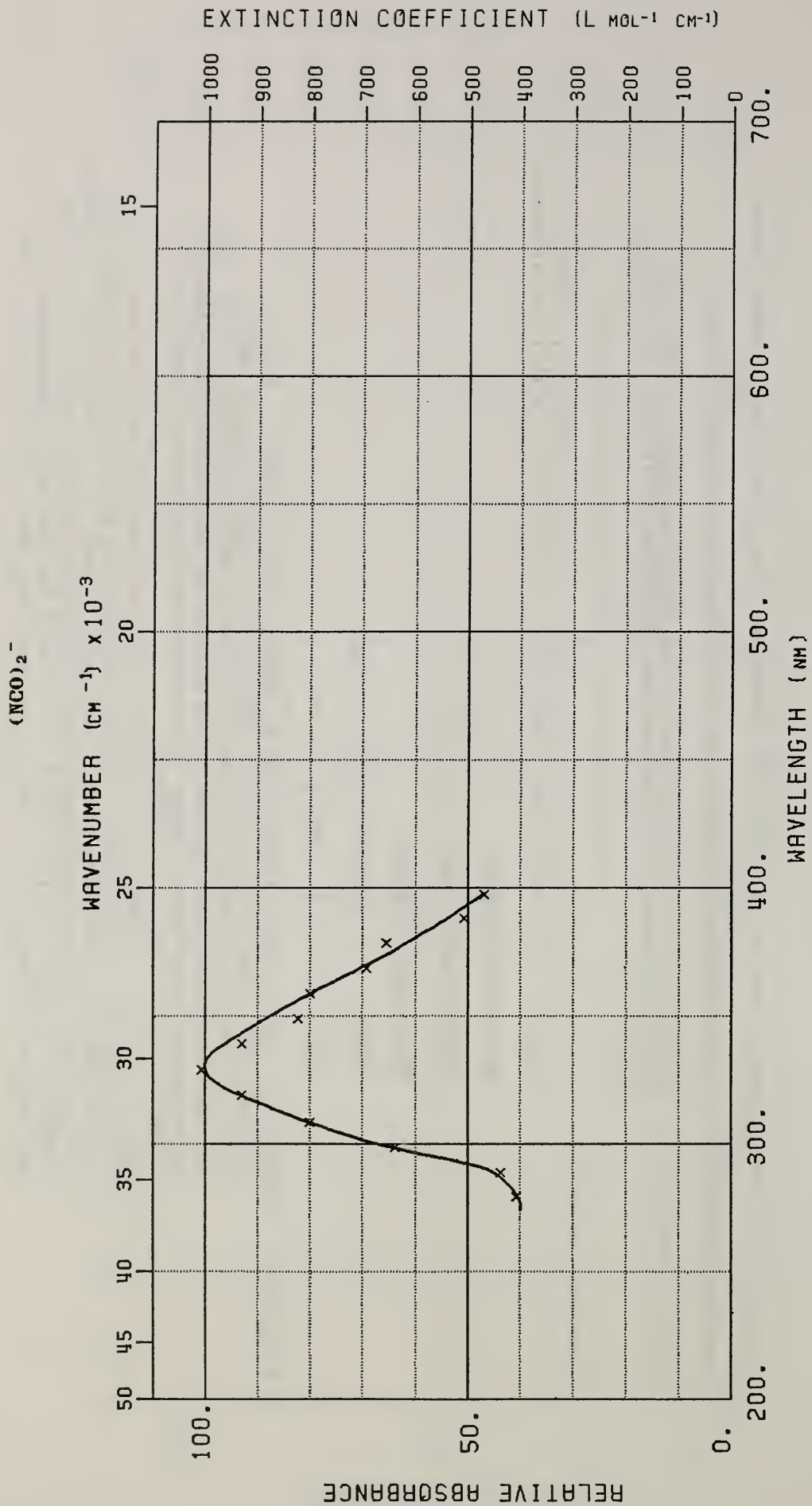
Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 20 μs

Transient formation:



Footnotes: [1] Obtained from a mixed spectrum due to (SCN)<sub>2</sub><sup>-</sup>, I<sub>2</sub><sup>-</sup> and ISCN<sup>-</sup>. Since I<sub>2</sub><sup>-</sup> and ISCN<sup>-</sup> absorb very little at 550 nm, the contribution of (SCN)<sub>2</sub><sup>-</sup> could be subtracted using the dose and yield of OH radicals of G = 5.5. I<sub>2</sub><sup>-</sup> does not contribute much because it is present in small quantities under the experimental conditions. Using the measured rate constants, [(SCN)<sub>2</sub><sup>-</sup>]: [ISCN<sup>-</sup>]: [I<sub>2</sub><sup>-</sup>] = 25 : 1 : 0.0055.

[2] Since the ratio of [(SCN)<sub>2</sub><sup>-</sup>]: [ISCN<sup>-</sup>] = 25, the shape of the spectrum is not very well established. Another spectrum was given in the reference for the initial conditions [SCN<sup>-</sup>] = 0.1 mol L<sup>-1</sup> and [I<sup>-</sup>] = 10<sup>-4</sup> mol L<sup>-1</sup>. However, in this case much more absorption was evident near 350 nm. Since the ratio of [(SCN)<sub>2</sub><sup>-</sup>]: [ISCN<sup>-</sup>]: [I<sub>2</sub><sup>-</sup>] = 2.5 : 1 : 0.055 in this latter experiment, the additional absorption at 350 nm may have been due to I<sub>2</sub><sup>-</sup> instead of ISCN<sup>-</sup>.



Transient: (NCO)<sub>2</sub><sup>-</sup>, λ(max) = 330 nm, ε<sub>330</sub> = (1000 ± 100) L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of 10<sup>-1</sup> mol L<sup>-1</sup> NCO<sup>-</sup>, N<sub>2</sub>O-saturated, pH = 5.0 ± 0.2 [2]



Reference: J.C. Leopold and M. Faraggi, J. Phys. Chem. 81(8): 803-6 (1977)

Transient generation: pulse radiolysis [3]; energy 5 MeV; dosimetry-electron coil [4]

Spectral acquisition: 150 W xenon lamp; Bausch & Lomb high-intensity monochromator; 1P28A or R136 PMT; Type 556 Tektronix double beam oscilloscope with Polaroid camera

Transient formation:



Footnotes:

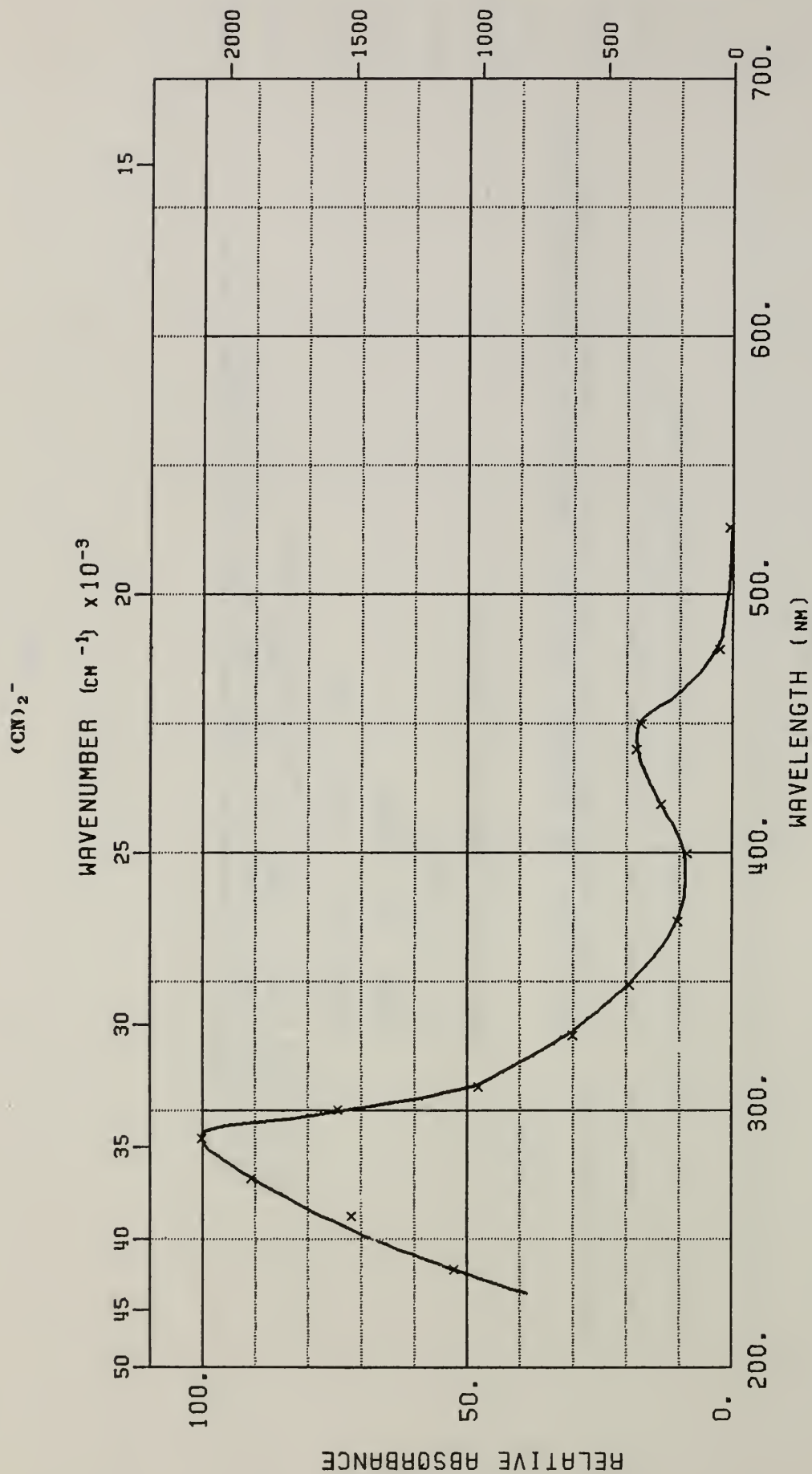
[1] Based on  $\text{C}(\text{OH}) = 5.6$  for  $\text{N}_2\text{O}$ -saturated solutions.

[2] Dose was such that  $[\text{OH}] = 9.7 \times 10^{-6}$  mol  $\text{L}^{-1}$ .

[3] M. Faraggi and Y. Tendler, J. Chem. Phys. 56(7): 3287-93 (1972).

[4] Dosimetry used  $\text{N}_2\text{O}$  saturated solutions of  $10^{-2}$  mol  $\text{L}^{-1}$   $\text{Fe}(\text{CN})_6^{4-}$ , using  $\text{G}(\text{Fe}(\text{CN})_6^{3-}) = 6.1$

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: (CN)<sub>2</sub><sup>-</sup>, cyanogen radical ion, λ(max) = 290 nm, ε<sub>290</sub> = 2100 L mol<sup>-1</sup> cm<sup>-1</sup>,  
and λ(max) = 440 nm, ε<sub>440</sub> = 360 L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of 3.7 × 10<sup>-4</sup> mol L<sup>-1</sup> (CN)<sub>2</sub>, He-purged, at natural pH ≈ 6



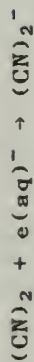


Reference: I.G. Draganic, Z.D. Draganic, and R.A. Holroyd, *J. Phys. Chem.* 75(5): 608-12 (1971)

Transient generation: pulse radiolysis using Febetron 705 system; energy 2 MeV; pulse length  $< 0.1 \mu\text{s}$ ; dose 4.72 krad/pulse; two dosimetry methods were used [2]; syringe technique

Spectral acquisition: 450 W xenon analyzing lamp with an arc booster [3]; path length 4.0 cm; high-intensity Bausch & Lomb grating monochromators; AmpereX XP 1003 PMT; Tektronix 434 oscilloscope

Transient formation [4]:

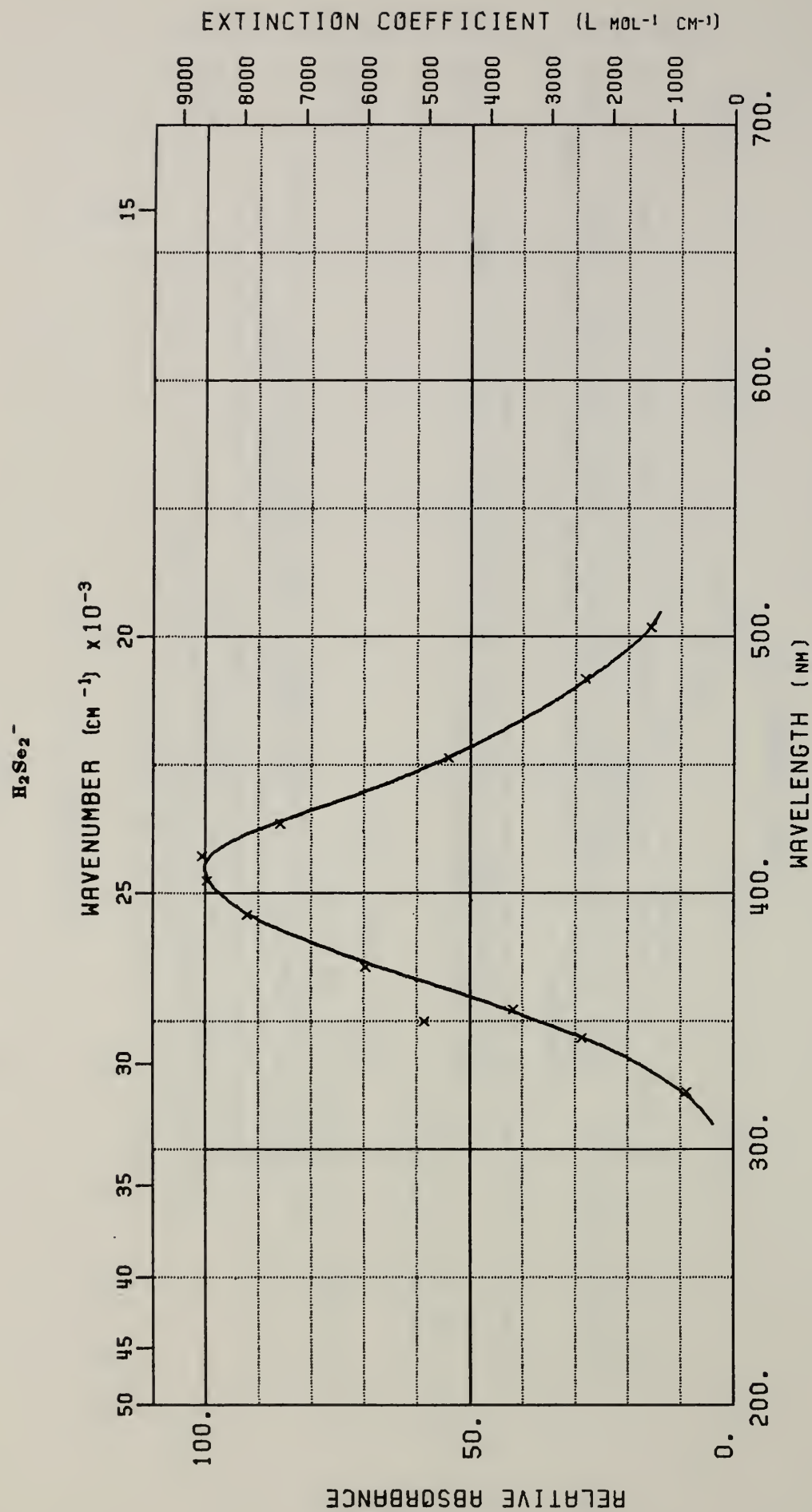


Footnotes: [1] Corrected for OH absorption.

[2] The first method used  $\text{N}_2\text{O}$ -saturated aqueous solutions of  $0.1 \text{ mol L}^{-1}$  thiocyanate using  $\epsilon_{600} = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $(\text{SCN})_2^-$ . The second method used  $\text{N}_2\text{O}$ -saturated aqueous solutions of  $10^{-3} \text{ mol L}^{-1}$  ferrocyanide containing a small amount of air. In this system  $\epsilon_{420} = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the ferricyanide formed. Both methods assumed  $G(\text{product}) = 5.4$ .

[3] Increased lamp intensity in ultraviolet by 60-fold.

[4] The reaction of  $(\text{CN})_2$  with OH was too slow ( $k \approx 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ) for the product to interfere with the spectrum.



Transient:  $\text{H}_2\text{Se}_2^-$ ,  $\lambda(\text{max}) = 410 \text{ nm}$ ,  $\epsilon_{410} = 8600 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: aqueous solution [2] of  $10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{Se}$ , Ar-saturated,  $\text{pH} = 3.7$

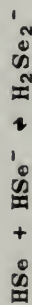
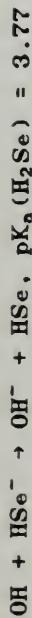
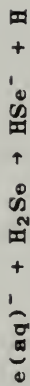
$$\text{H}_2\text{Se}_2^-$$

Reference: M. Schoeneshoefler, W. Karmann, and A. Henglein, *Int. J. Radiat. Phys. Chem.* 1: 407-23 (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per  $\mu\text{s}$ ; dosimetry based on  $\text{SCN}^-$  [3]

Spectral acquisition [4]: Osram XB0 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay immediately after pulse

Transient formation:



Footnotes:

[1] Based on  $C(\text{H}_2\text{Se}_2^-) = 6$ .

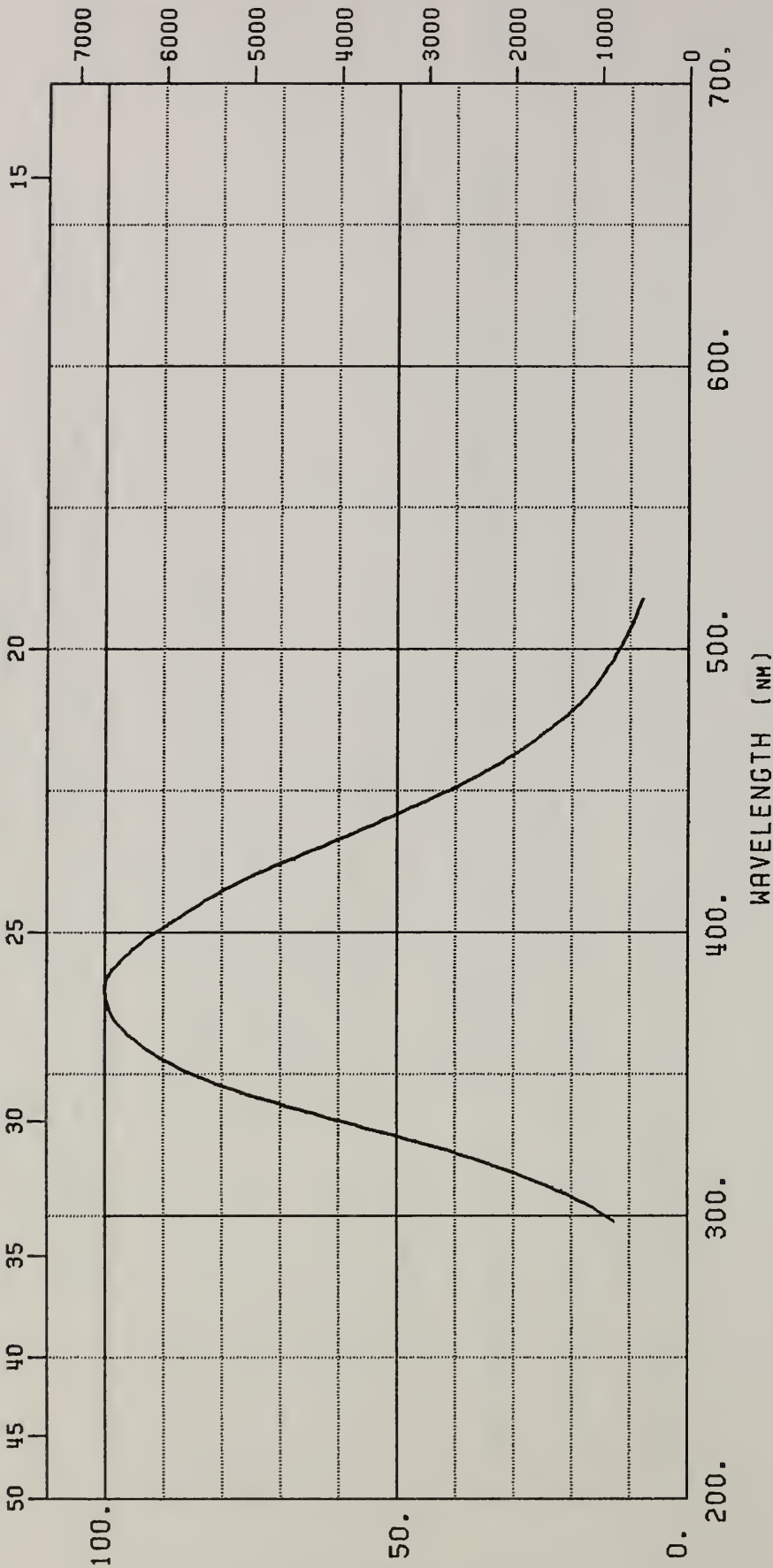
[2] Oxygen was removed from water before  $\text{H}_2\text{Se}$  was added to make solution.

[3] Based on the measurement of  $\text{SCN}^-$  solutions under equivalent conditions, using  $\epsilon_{500} = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[4] A. Henglein, *Allg. Prakt. Chem.* 17(5): 295-301 (1966).

(SH)<sub>2</sub><sup>-</sup> or S<sub>2</sub>H<sup>2-</sup>

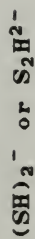
WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



Transient [I]: (SH)<sub>2</sub><sup>-</sup> or S<sub>2</sub>H<sup>2-</sup>, λ(max) = 380 nm

System: aqueous solution of 10<sup>-3</sup> mol L<sup>-1</sup> H<sub>2</sub>S, pH = 6.6



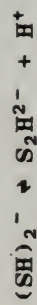
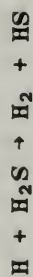


Reference: W. Karmann, G. Meissner, and A. Henglein, Z. Naturforsch. Pt. B 22(3): 273-82 (1967)

Transient generation: pulse radiolysis [2] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 955B PMT; decay curves photographed from oscilloscope display

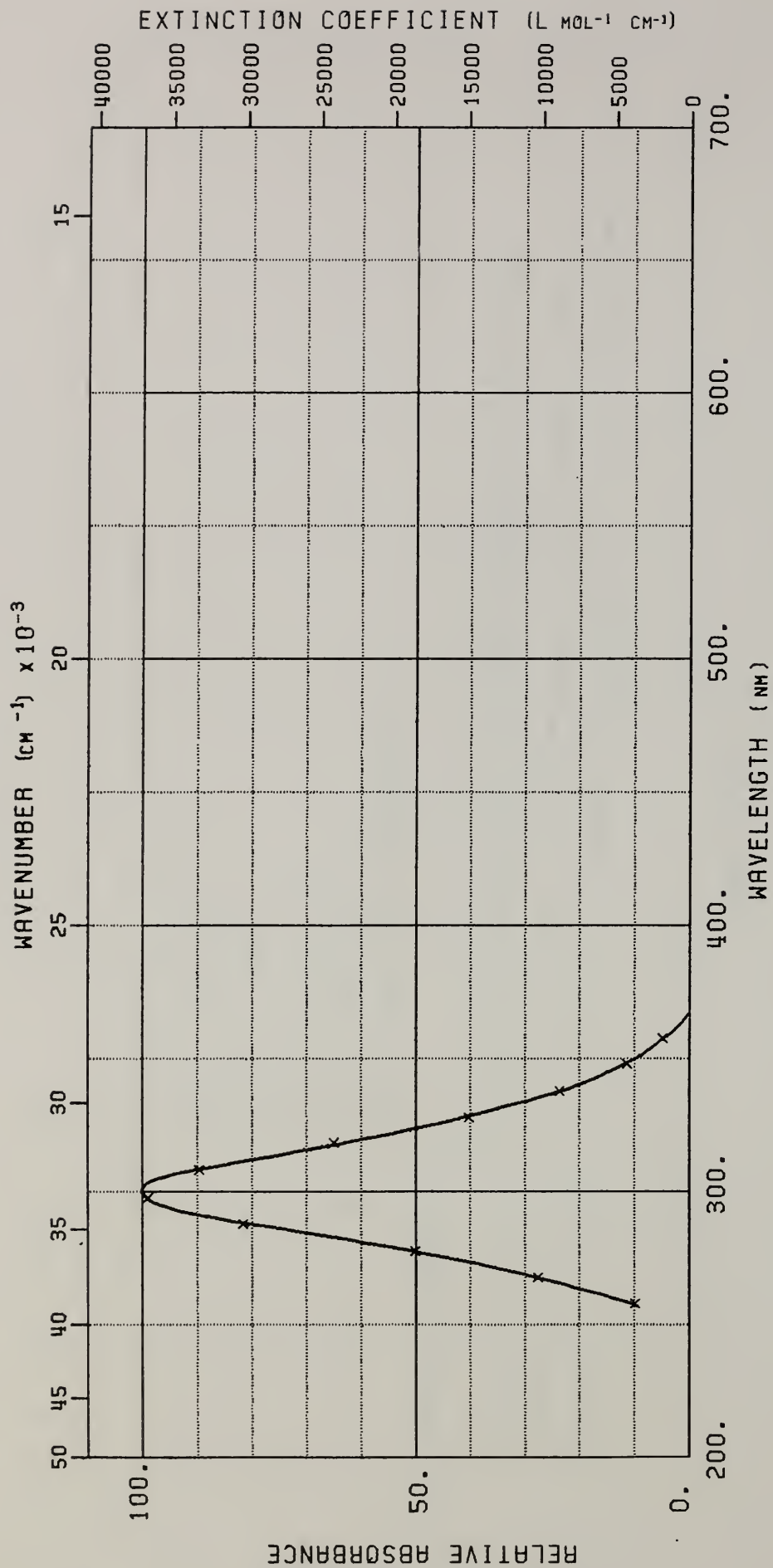
Transient formation:



Footnotes: [1] Extinction coefficient based on C = 6.

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

$I_2SCN^-$



Transient [1]:  $I_2SCN^-$ ,  $\lambda_{(max)} = 300\ nm$ ,  $\epsilon_{300} = 37,000\ L\ mol^{-1}\ cm^{-1}$  [2]

System: aqueous solution of  $10^{-1}\ mol\ L^{-1}\ SCN^-$  and  $2 \times 10^{-4}\ mol\ L^{-1}\ I^-$ , saturated with  $N_2O$

$I_2SCN^-$ 

Reference: M. Schoeneshoefer and A. Henglein, Ber. Bunsenges. Phys. Chem. 74(4): 393-8 (1970)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.7 MeV

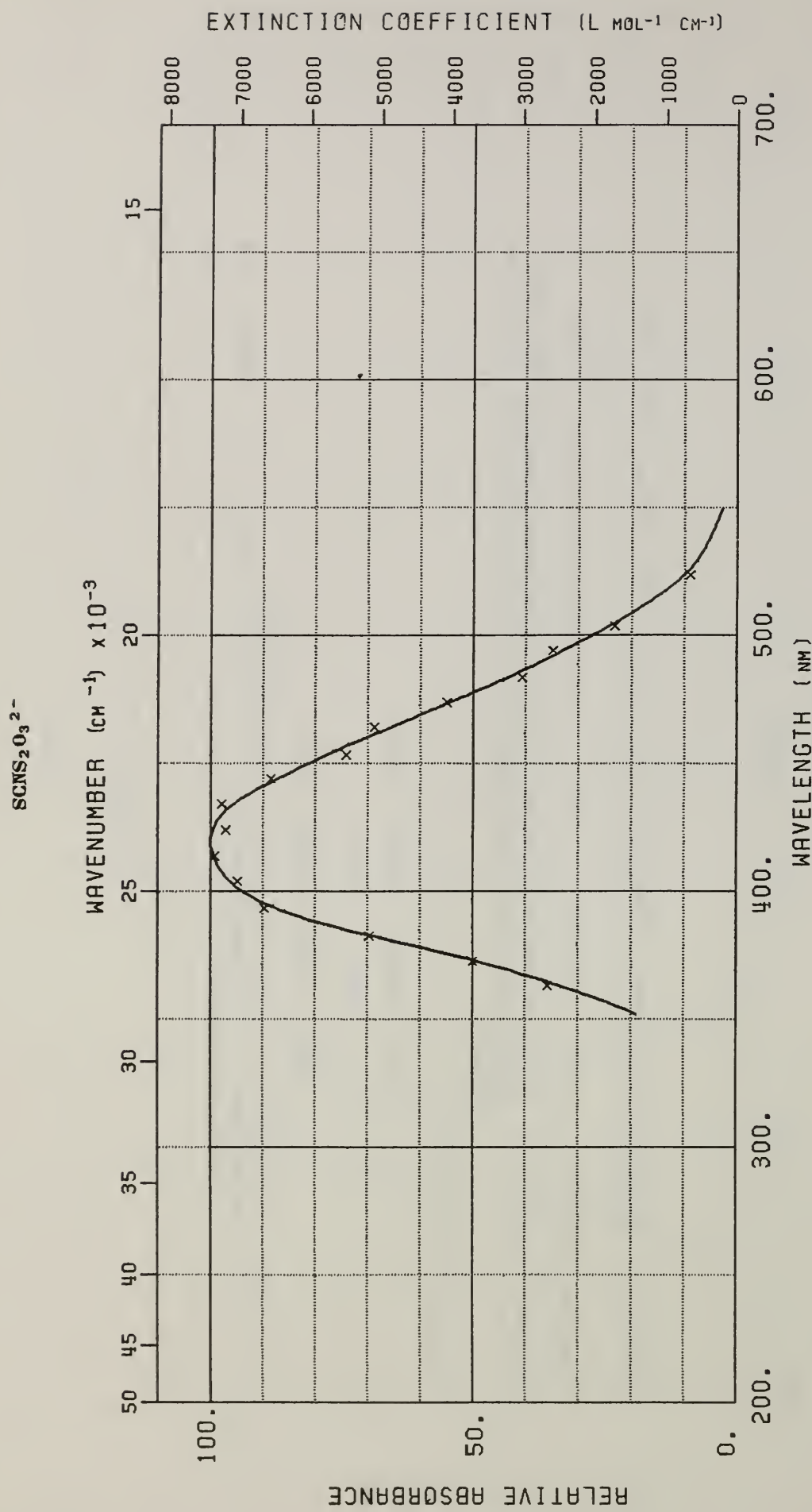
Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 200  $\mu s$

Transient formation :



Footnotes: [1] Compound is relatively stable in acid solutions.

[2] Assuming  $G = 2.75$  and assuming  $G$  for the three complexes,  $I_2^-$ ,  $(SCN)_2^-$ , and  $ISCN^-$ , was collectively 5.5.



Transient [1]: SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup>, λ(max) = 420 nm, ε<sub>420</sub> = 7400 L mol<sup>-1</sup> cm<sup>-1</sup> [2]

System: aqueous solution of 5 × 10<sup>-2</sup> mol L<sup>-1</sup> SCN<sup>-</sup> and 4 × 10<sup>-4</sup> mol L<sup>-1</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, saturated with N<sub>2</sub>O [3]



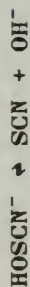
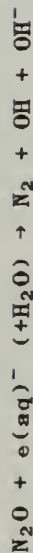
SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup>

Reference: M. Schoeneshoefer, Ber. Bunsenges. Phys. Chem. 77(4): 257-62 (1973)

Transient generation: pulse radiolysis [4] using Van de Graaff generator; energy 1.7 MeV

Spectral acquisition: Osrarn XBO 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

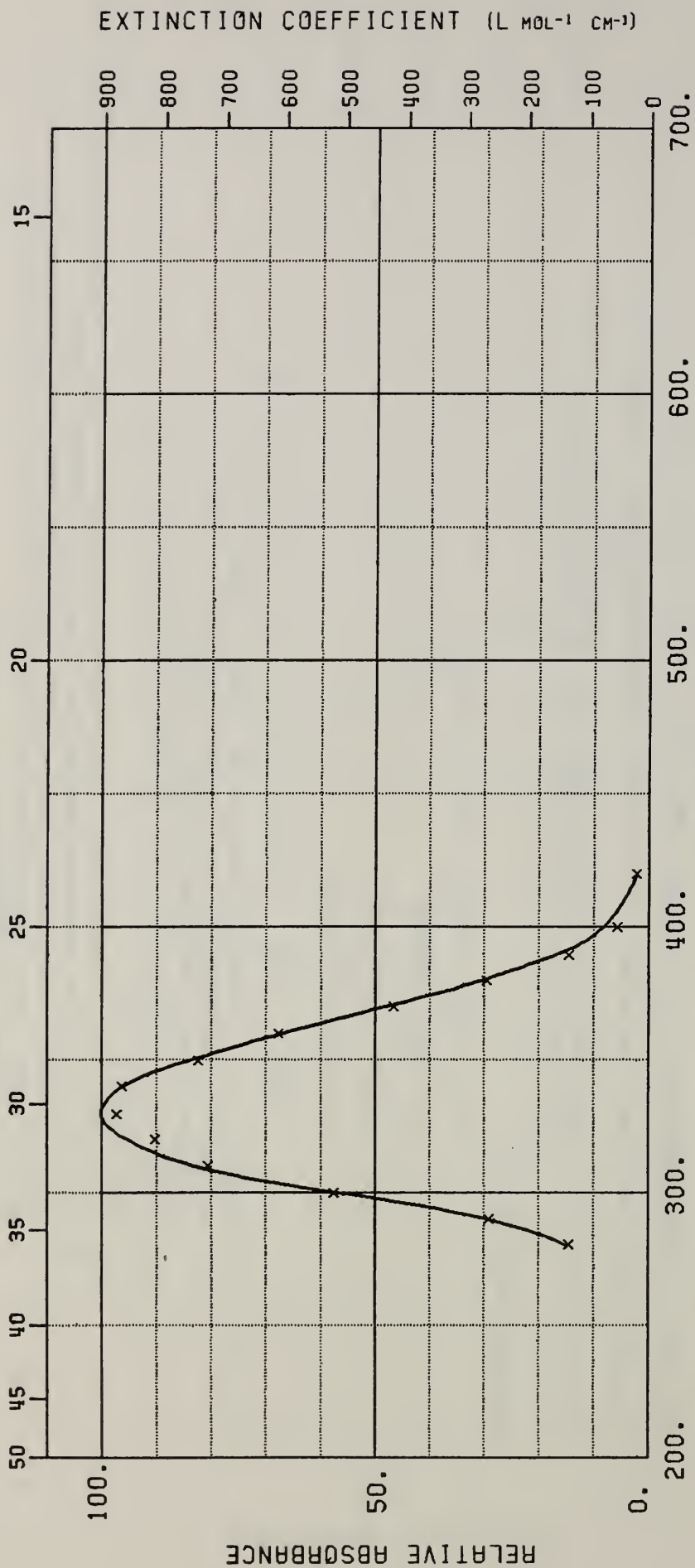
Transient formation [5]:



- Footnotes: [1] Obtained from a mixed spectrum due to (SCN)<sub>2</sub><sup>-</sup>, S<sub>4</sub>O<sub>6</sub><sup>3-</sup>, and SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup>. The SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup> spectrum was obtained from the experimental spectrum using a kinetic analysis.
- [2] Based on  $\epsilon = 1600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for S<sub>4</sub>O<sub>6</sub><sup>3-</sup> and  $7100 \text{ L mol}^{-1} \text{ cm}^{-1}$  for the  $\epsilon$  of (SCN)<sub>2</sub><sup>-</sup>.
- [3] C(OH) taken to be 6.
- [4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).
- [5] Shows only the most prominent pathway for formation of SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup> under the experimental conditions. Several other equilibria complicate the analysis. In particular, there are two important mechanisms that lead to formation of S<sub>4</sub>O<sub>6</sub><sup>3-</sup> starting from SCNS<sub>2</sub>O<sub>3</sub><sup>2-</sup>.

SCN

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



EXTINCTION COEFFICIENT ( $\text{L MOL}^{-1} \text{CM}^{-1}$ )

Transient [1]: SCN,  $\lambda(\text{max}) = 330 \text{ nm}$ ,  $\epsilon_{330} = 900 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $10^{-4} \text{ mol L}^{-1}$  SCN<sup>-</sup>, saturated with N<sub>2</sub>O, natural pH

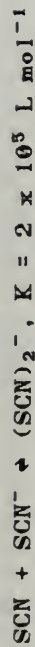
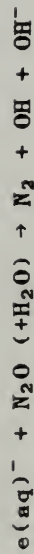
SCN

Reference: D. Behar, P.L.T. Bevan, and G. Scholes, J. Phys. Chem. 76(11): 1537-42 (1972)

Transient generation: pulse radiolysis, linear accelerator; pulse length 0.1  $\mu$ s; doses 0.1 to 1.0 krad

Spectral acquisition: kinetic spectroscopy; time delay 1  $\mu$ s

Transient formation [3]:

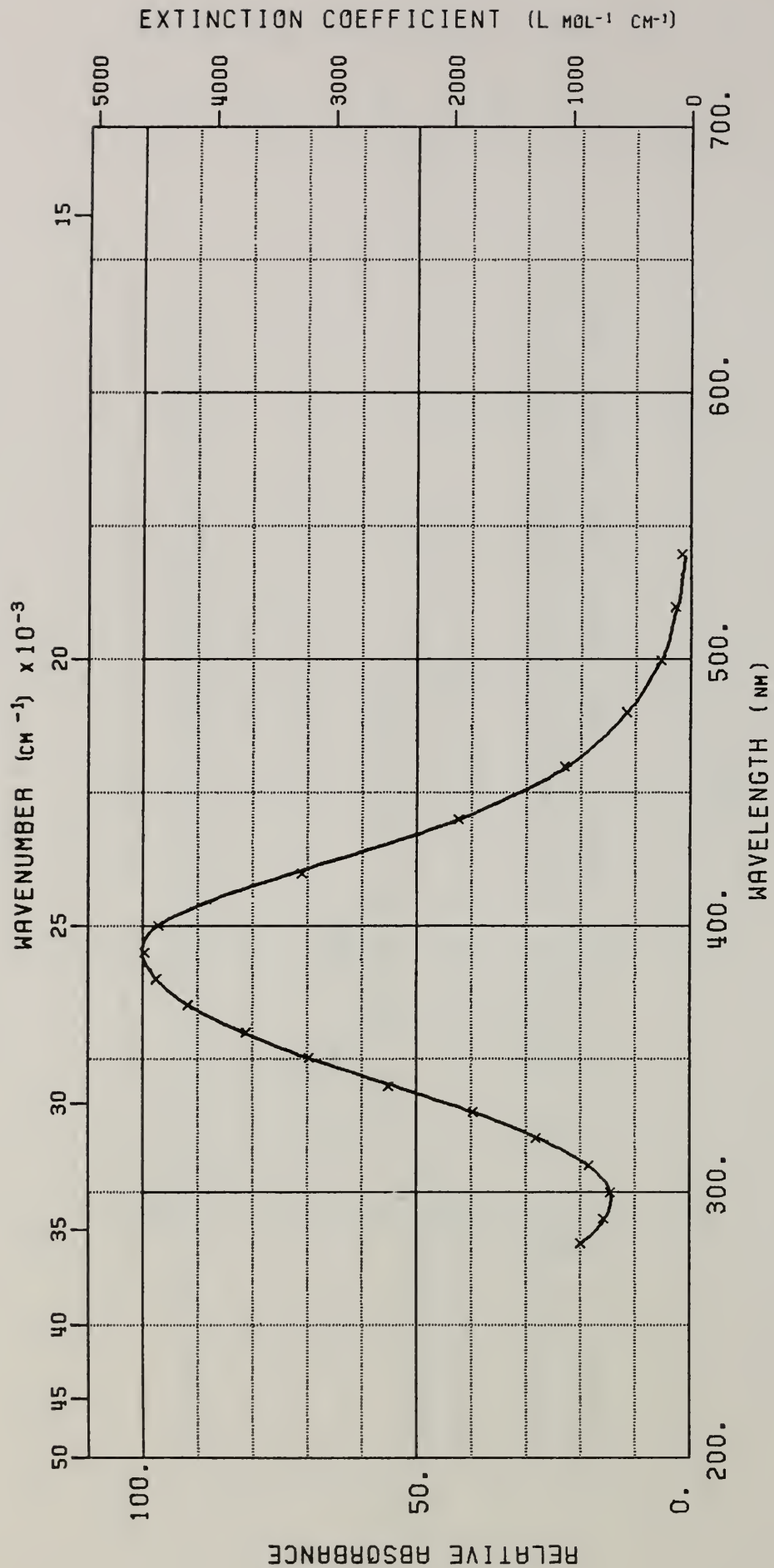


Footnotes: [1] Obtained from a composite spectrum by subtracting  $(\text{SCN})_2^-$  contribution.

[2] Based on the kinetic analysis and the value  $7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  for  $\epsilon_{475}$  of  $(\text{SCN})_2^-$ .

[3] Mechanism involving  $\text{SCNO}_2^-$  was eliminated by considering  $[\text{OH}^-]$  dependence.

HOSCN<sup>-</sup>



Transient [1]: HOSCN<sup>-</sup>,  $\lambda(\text{max}) = 390 \text{ nm}$ ,  $\epsilon_{390} = 4600 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of  $10^{-4} \text{ mol L}^{-1} \text{ SCN}^{-}$  and  $10^{-1} \text{ mol L}^{-1} \text{ OH}^{-}$ , saturated with N<sub>2</sub>O



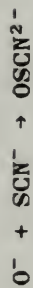
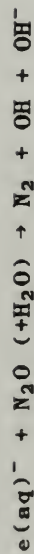
HOSCN<sup>-</sup>

Reference: D. Behar, P.L.T. Bevan, and G. Scholes, J. Phys. Chem. 76(11): 1537-42 (1972)

Transient generation: pulse radiolysis, linear accelerator; pulse length 0.1 μs; doses 0.1 to 1.0 krad

Spectral acquisition: kinetic spectroscopy; time delay 3.5 μs

Transient formation [3]:

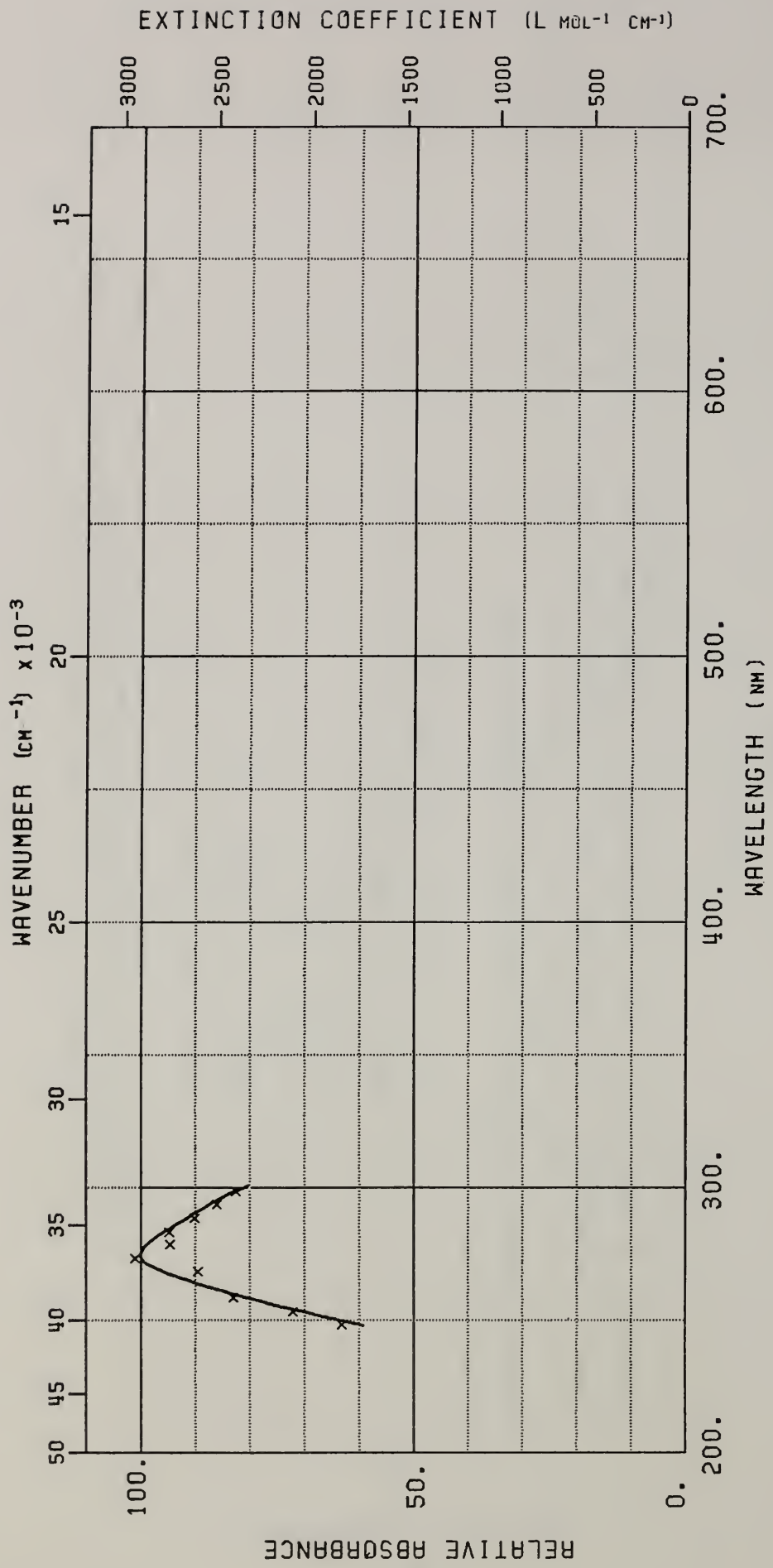


Footnotes: [1] Obtained from a composite spectrum by subtracting (SCN)<sub>2</sub><sup>-</sup> contribution.

[2] Based on extinction coefficients at 390 nm and 475 nm.

[3] The transient OSCN<sup>2-</sup> was shown to have a negligible concentration by a study of the dependence of the spectrum on OH<sup>-</sup> concentration.

Br



Transient [1]: Br [2], bromine atom,  $\lambda(\text{max}) = 275 \text{ nm}$ ,  $\epsilon(\text{max}) = 2900 \text{ L mol}^{-1} \text{ cm}^{-1}$  [3,4]  
System: aqueous solution of  $2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ Br}_2$  and  $1.4 \text{ mol L}^{-1} \text{ HClO}_4$ , argon saturated before  $\text{Br}_2$  was added

Reference: A. Treinin and E. Hayon, J. Am. Chem. Soc. 97(7): 1716-21 (1975)

Transient generation: laser flash photolysis, frequency-quadrupled neodymium laser, excitation wavelength 265 nm; pulse length  $\approx 15$  ns; energy per pulse  $\approx 2 \times 10^{-2}$  J

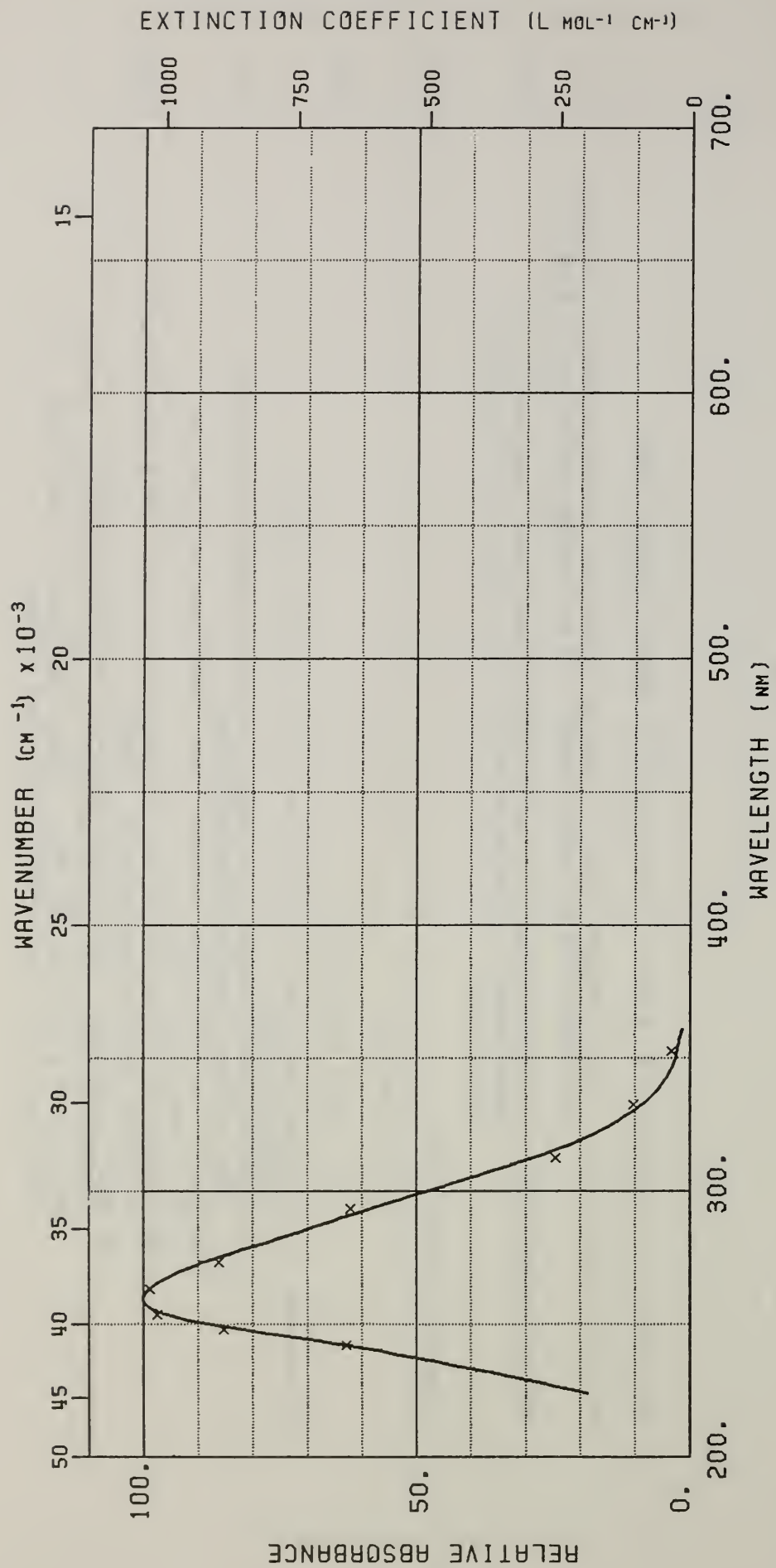
Spectral acquisition: monitoring lamp was a pulsed 250 W Osram xenon lamp; monitoring beam formed a right angle to the laser beam; time delay 20 ns after pulse

Transient formation [5]:



- Footnotes: [1] Spectrum corrected for depletion of  $\text{Br}_2$  and  $\text{Br}_3^-$  and for formation of  $\text{Br}_2^-$ .  
 [2] Spectrum is attributed to a complex with the transition being due to an electron transfer from  $\text{H}_2\text{O}$  to  $\text{Br}$ .  
 [3] Extinction coefficient measured under conditions such that all  $\text{Br}$  is converted to  $\text{Br}_2^-$ .  
 [4] Extinction coefficient of  $\text{Br}_2^-$  is taken to be  $\epsilon_{360} = 9900 \text{ L mol}^{-1} \text{ cm}^{-1}$ , D. Behar, private communication, 1980.  
 [5] Under conditions where no  $\text{Br}^-$  was added initially, authors calculated that their solutions contained  $5$  to  $15 \times 10^{-6} \text{ mol L}^{-1} \text{ Br}^-$  and  $2$  to  $7 \times 10^{-7} \text{ mol L}^{-1} \text{ Br}_3^-$ . Under experimental conditions absorbance due to  $\text{Br}_3^-$  was  $0.1$  to  $0.2$  at  $265 \text{ nm}$ .

I



Transient: I, iodine atom,  $\lambda(\text{max}) = 260 \text{ nm}$ ,  $\epsilon(\text{max}) = 1040 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: aqueous solution of  $3 \times 10^{-4} \text{ mol L}^{-1} \text{ I}_2$

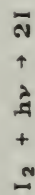


Reference: P. Fournier de Violet, R. Bonneau, and J. Jousot-Dubien, Chem. Phys. Lett. 19(2): 251-3 (1973)

Transient generation: laser flash photolysis; excitation wavelength 529 nm; pulse energy 1 J

Spectral acquisition: pulsed xenon monitoring lamp; rise time of detection system < 10 ns; accuracy  $\approx$  0.5 % on transmission measurements

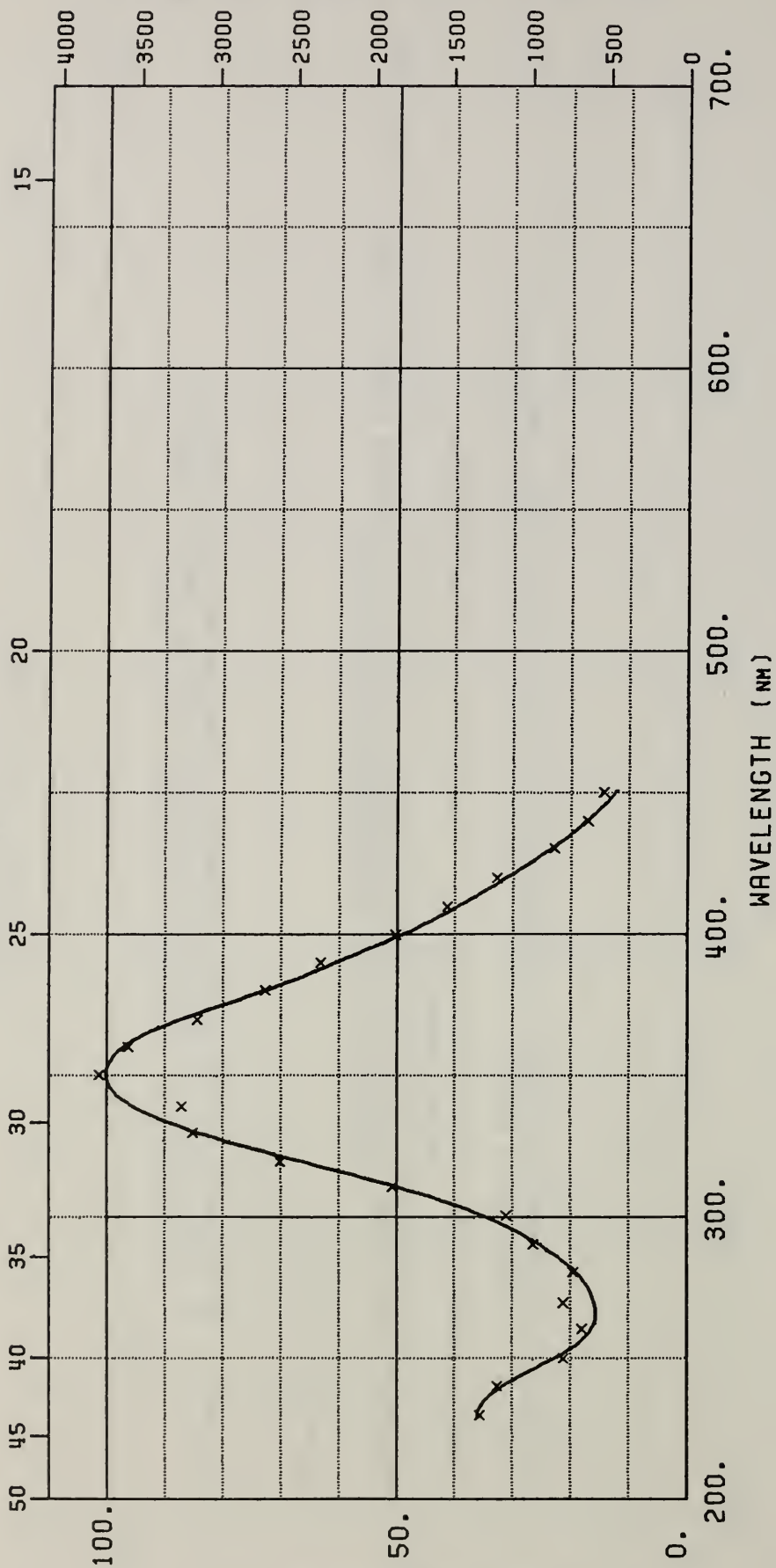
Transient formation:



Footnote: [1] Extinction coefficient attributed to these authors by A. Treinin and E. Hayon, J. Am. Chem. Soc. 97(7): 1716-21 (1975). Basis for extinction coefficient measurement is not known.

$\text{ClOH}^-$

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



Transient [1]:  $\text{ClOH}^-$ ,  $\lambda(\text{max}) = 350 \text{ nm}$ ,  $\epsilon_{350} = (3700 \pm 400) \text{ L mol}^{-1} \text{ cm}^{-1}$  [2,3]

System: aqueous solution of  $3 \text{ mol L}^{-1} \text{ NaCl}$ , neutral pH,  $\text{N}_2\text{O}$  or  $\text{O}_2$  saturated [1]

ClOH<sup>-</sup>

Reference: C.G. Jayson, B.J. Parsons, and A.J. Swallow, J. Chem. Soc., Faraday Trans. 1 69: 1597-607 (1973)

Transient generation: pulse radiolysis, electron linear accelerator; dose per pulse  $1.63 \times 10^3$  rad; dosimetry-secondary emission chamber [4]

Spectral acquisition: two Bausch & Lomb high-intensity monochromators used in series to reduce scattered light

Transient formation:



Footnotes: [1] The resulting spectrum was obtained from the spectra obtained from N<sub>2</sub>O-saturated and from O<sub>2</sub>-saturated solutions. The absorption in O<sub>2</sub>-saturated solutions was thought to be due to both ClOH<sup>-</sup> and Cl<sub>2</sub><sup>-</sup>. The Cl<sub>2</sub><sup>-</sup> was thought to be formed in the spurs by hole scavenging with Cl<sup>-</sup> or by ClOH<sup>-</sup> + H<sup>+</sup>  $\rightleftharpoons$  H<sub>2</sub>O + Cl and Cl + Cl<sup>-</sup>  $\rightleftharpoons$  Cl<sub>2</sub><sup>-</sup>. The N<sub>2</sub>O-saturated solutions had these reactions in addition to the extra ClOH<sup>-</sup> formed by OH formed from



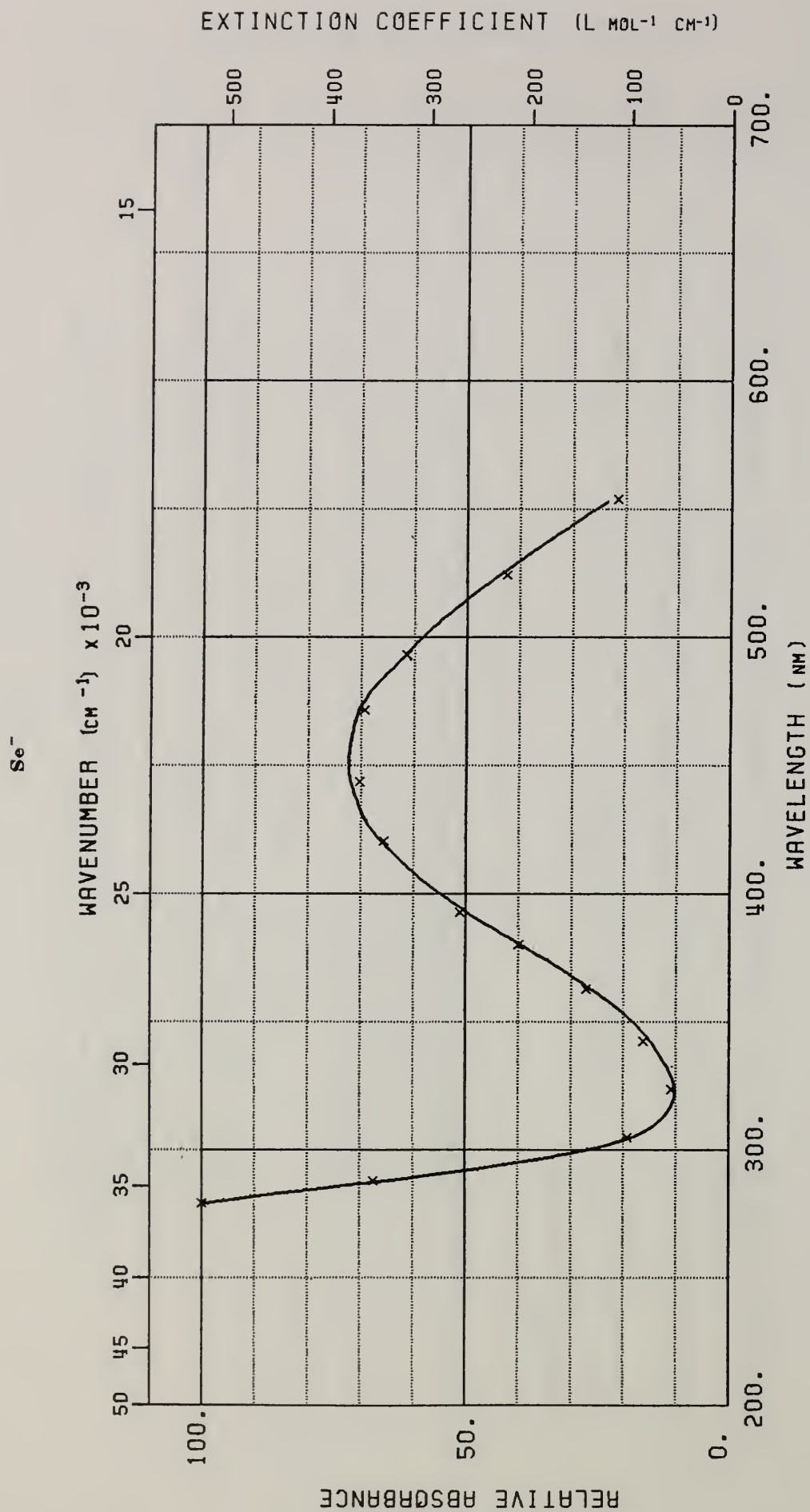
Spectra from O<sub>2</sub>-saturated solutions were corrected for O<sub>2</sub><sup>-</sup> absorption, using  $\epsilon_{240} \approx 1720 \text{ L mol}^{-1} \text{ cm}^{-1}$  for O<sub>2</sub><sup>-</sup>.

[2] Assumed excess yield of OH in N<sub>2</sub>O solutions was  $G(\text{e}(\text{aq})^-) = 2.75$  for OH formed from N<sub>2</sub>O reaction with hydrated electron.

[3] A more recent report gave a value for  $\epsilon(\text{max})$  of ClOH<sup>-</sup> that was much lower,  $\epsilon(\text{max}) = 1200 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

R.W. Fessenden, private communication, 1980.

[4] Calibrated by aqueous potassium thiocyanate taking  $G((\text{SCN})_2^-) = 2.9$  and  $\epsilon_{500}((\text{SCN})_2^-) = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$ .



Transient: Se<sup>-</sup>, λ(max) = 450 nm, ε<sub>450</sub> = 380 L mol<sup>-1</sup> cm<sup>-1</sup> [1], 2k = (4.6 ± 1.5) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution [2] of HSe<sup>-</sup>, N<sub>2</sub>O-saturated, pH = 11



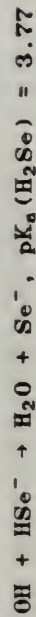
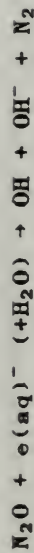
Se<sup>-</sup>

Reference: M. Schoeneshoefter, W. Karmann, and A. Henglein, Int. J. Radiat. Phys. Chem. 1: 407-23 (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per  $\mu$ s; dosimetry based on SCN<sup>-</sup> [3]

Spectral acquisition [4]: Osram XBO 450 monitoring lamp; Zeiss M403 monochromator; EMI 9538 PMT; decay curves photographed from oscilloscope display; time delay 20  $\mu$ s

Transient formation:



Footnotes: [1] Based on  $\text{C}(\text{OH}) = 6$ .

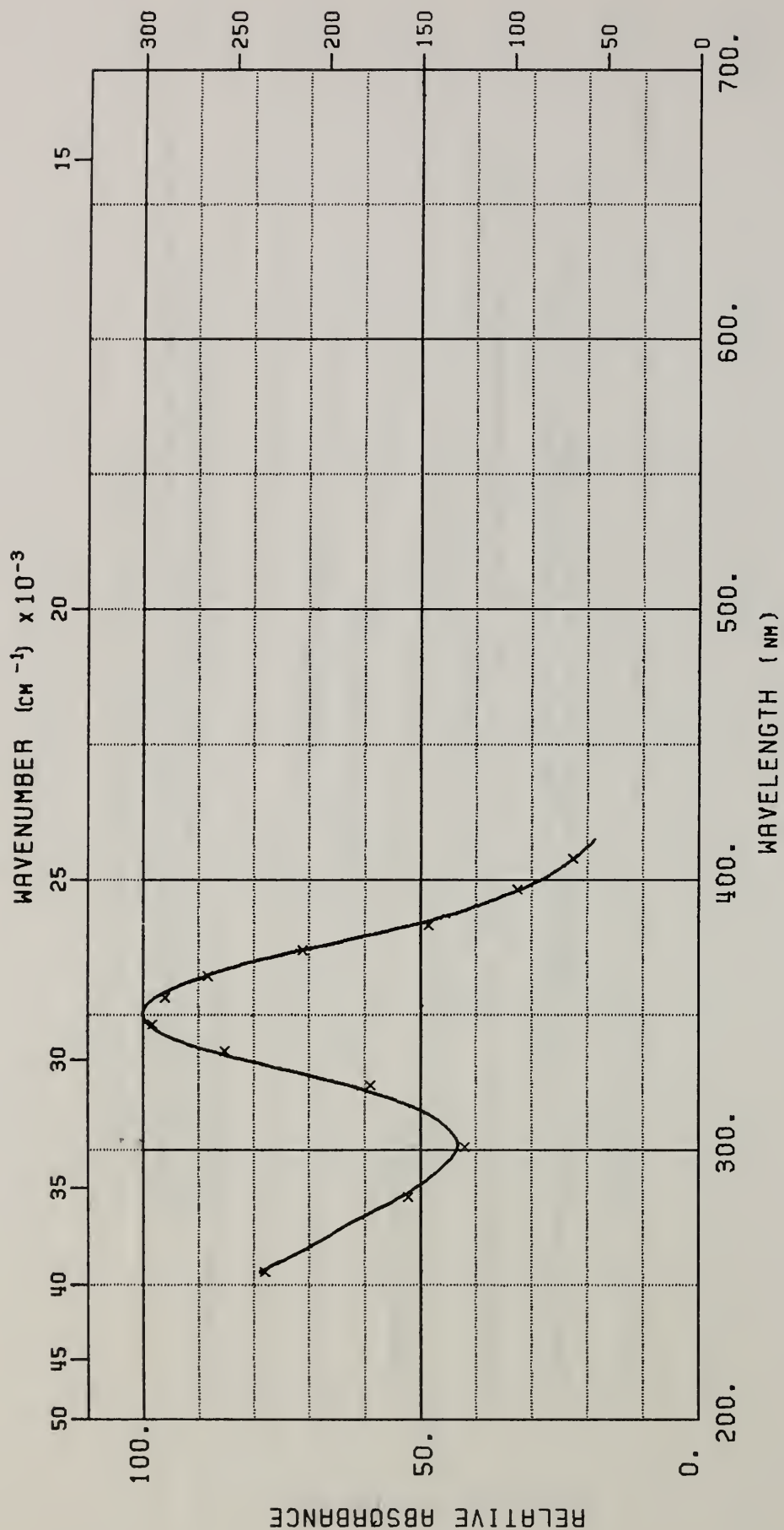
[2] Oxygen was removed from water before H<sub>2</sub>Se was added to make solution.

[3] Based on the measurement of SCN<sup>-</sup> solutions under equivalent conditions, using  $\epsilon_{500} = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[4] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

HSe



Transient: HSe,  $\lambda(\text{max}) = 350 \text{ nm}$ ,  $\epsilon_{350} = 300 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1],  $2k = (8.1 \pm 2.0) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$

System: aqueous solution [2] of H<sub>2</sub>Se, N<sub>2</sub>O-saturated, pH = 0.8

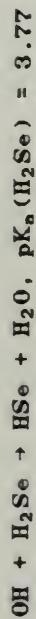
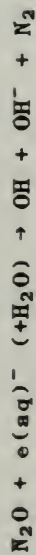
## HSe

Reference: M. Schoeneshoefter, W. Karmann, and A. Henglein, *Int. J. Radiat. Phys. Chem.* 1: 407-23 (1969)

Transient generation: pulse radiolysis, Van de Graaff generator; energy 1.6 MeV; dose rate during the pulse was 700 rad per  $\mu$ s; dosimetry based on  $\text{SCN}^-$  [3]

Spectral acquisition [4]: Osram 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 5  $\mu$ s after pulse

Transient formation:



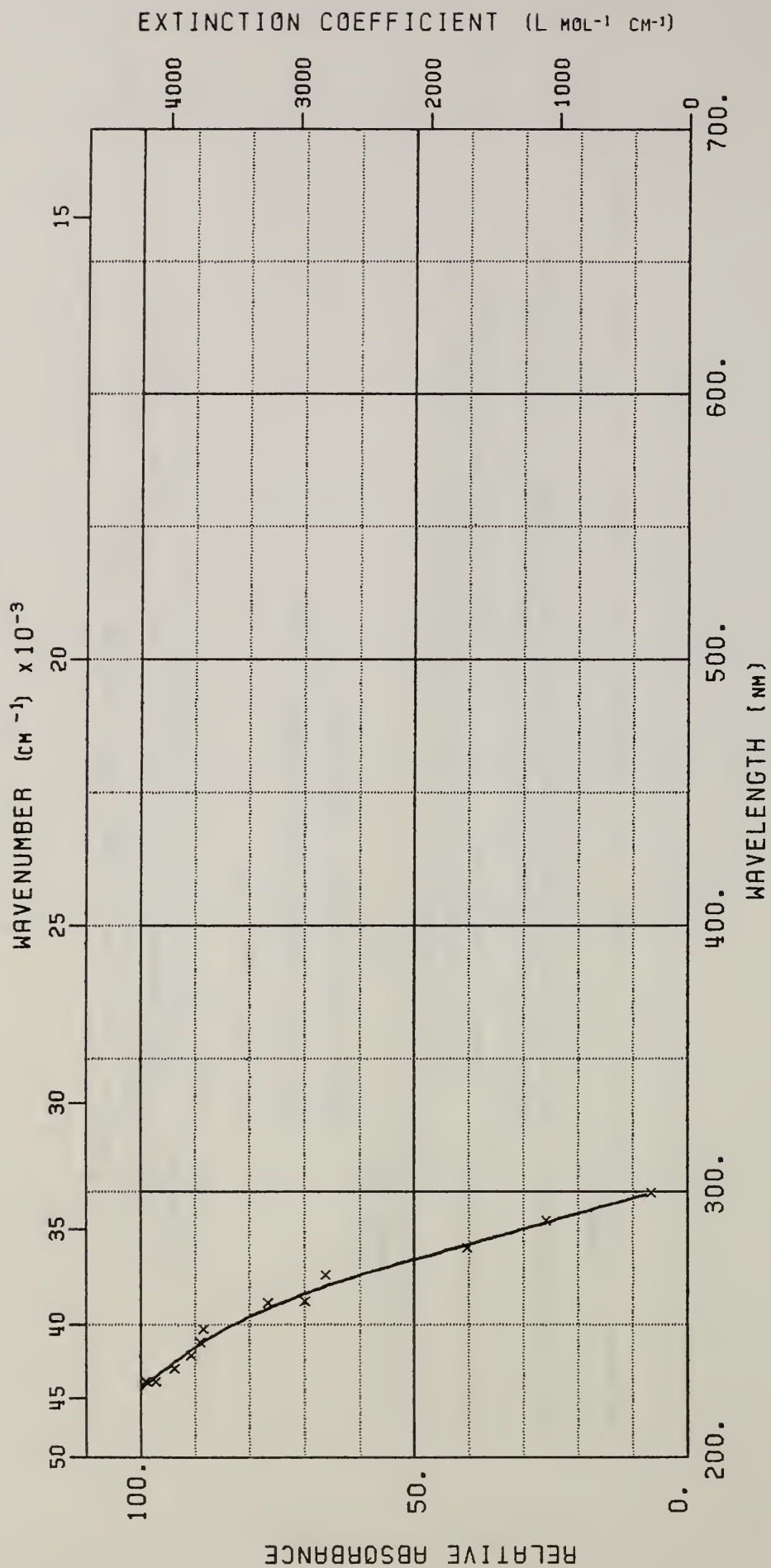
Footnotes:

[1] Based on  $G(\text{OH}) = 6$ .

[2] Oxygen was removed from water before  $\text{H}_2\text{Se}$  was added to make solution.

[3] Based on the measurement of  $\text{SCN}^-$  solutions under equivalent conditions, using  $\epsilon_{600} = 7100 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[4] A. Henglein, *Allg. Prakt. Chem.* 17(5): 295-301 (1966).



Transient:  $\text{PO}_3^{2-}$ , phosphite radical anion,  $\epsilon_{256} = 3500 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: aqueous solution of  $2 \times 10^{-3} \text{ mol L}^{-1}$  phosphorous acid, saturated with  $\text{N}_2\text{O}$ , pH 9



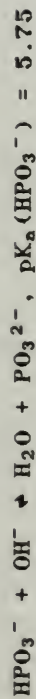
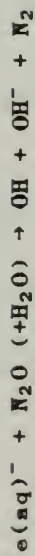
$\text{PO}_3^{2-}$

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV;  
dose rate during pulse was 700 rad per  $\mu\text{s}$

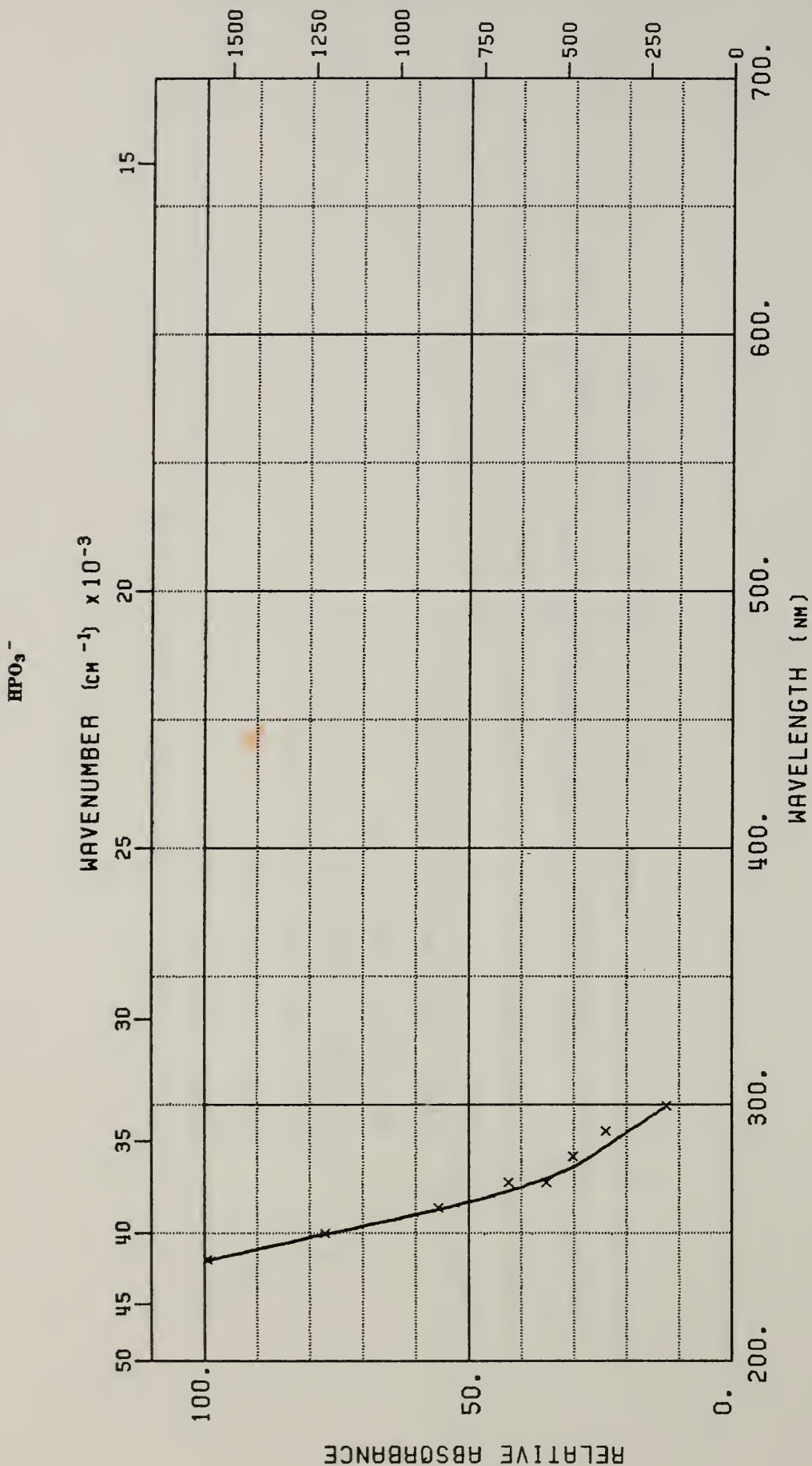
Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M4Q3 monochromator; EMI 9558 QB PMT

Transient formation:



Footnote: [1] Assuming  $\text{C}(\text{PO}_3^{2-}) = \text{C}(\text{OH}^-) + \text{C}(\text{H}) + \text{C}(\text{e}(\text{aq})^-) = 6.2$

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: HPO<sub>3</sub><sup>-</sup>, protonated phosphite radical anion, ε<sub>250</sub> = 1200 L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of 2 x 10<sup>-3</sup> mol L<sup>-1</sup> phosphorous acid, saturated with N<sub>2</sub>O, pH 4

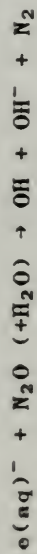
$\text{HPO}_3^-$

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

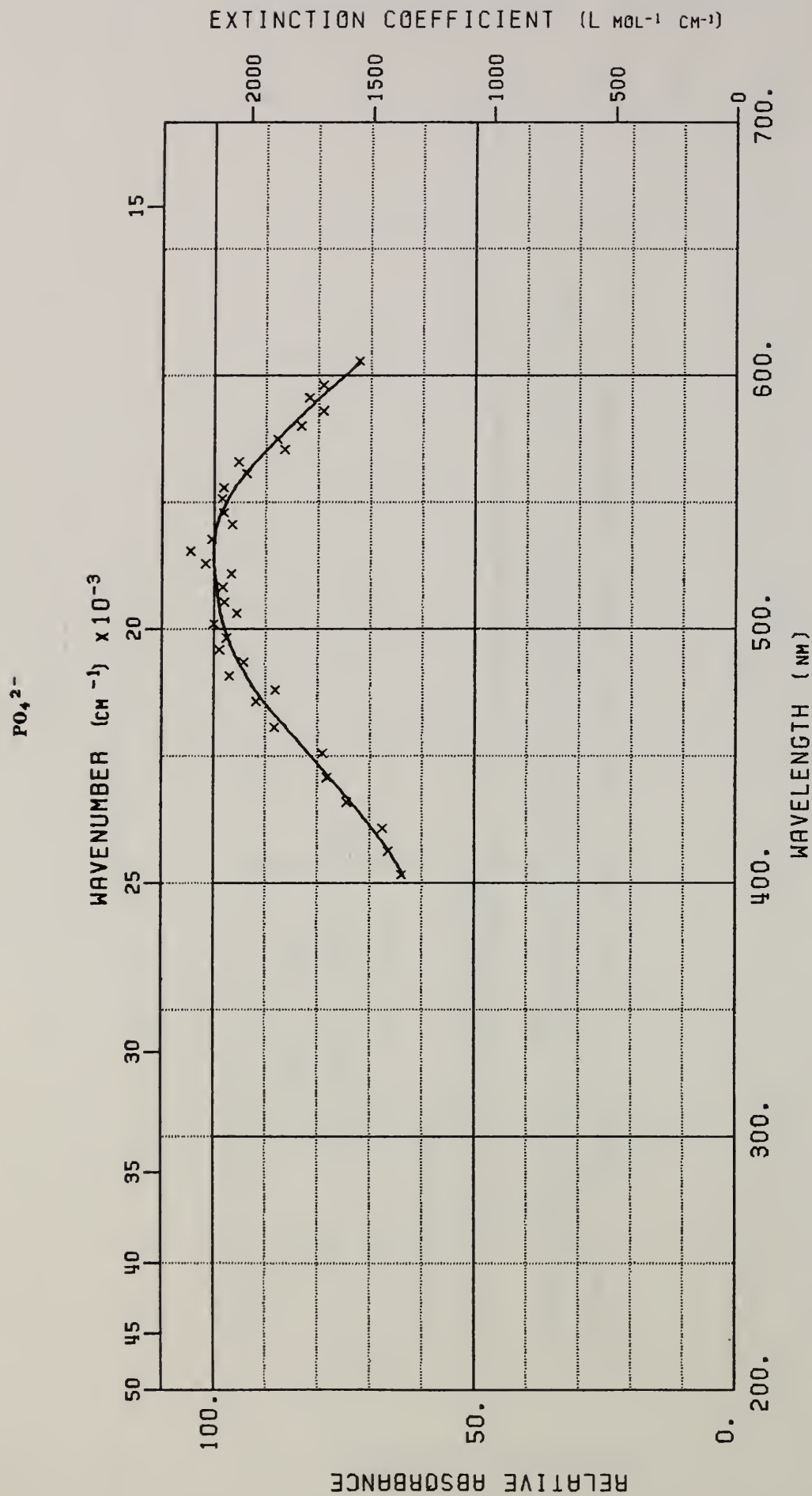
Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV;  
dose rate during pulse was 700 rad per  $\mu\text{s}$

Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M403 monochromator;  
EMI 9558 QB PMT

Transient formation:



Footnote: (1) Assuming  $G(\text{HPO}_3^-) = G(\text{OH}) + G(\text{H}) + G(\text{e}(\text{aq})^-) = 6.2$



Transient [1]: PO<sub>4</sub><sup>2-</sup>, λ(max) = 530 nm, ε<sub>530</sub> = 2150 L mol<sup>-1</sup> cm<sup>-1</sup>

System: aqueous solution of 2.5 x 10<sup>-2</sup> mol L<sup>-1</sup> peroxodiphosphate at pH 11



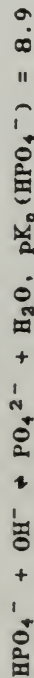
$\text{PO}_4^{2-}$

Reference: P. Maruthamuthu and P. Neta, *J. Phys. Chem.* 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Biomation 8100 recorder; signal averaging with PDP-8 computer; time delay 2-10  $\mu\text{s}$  after pulse-formation was complete after this delay

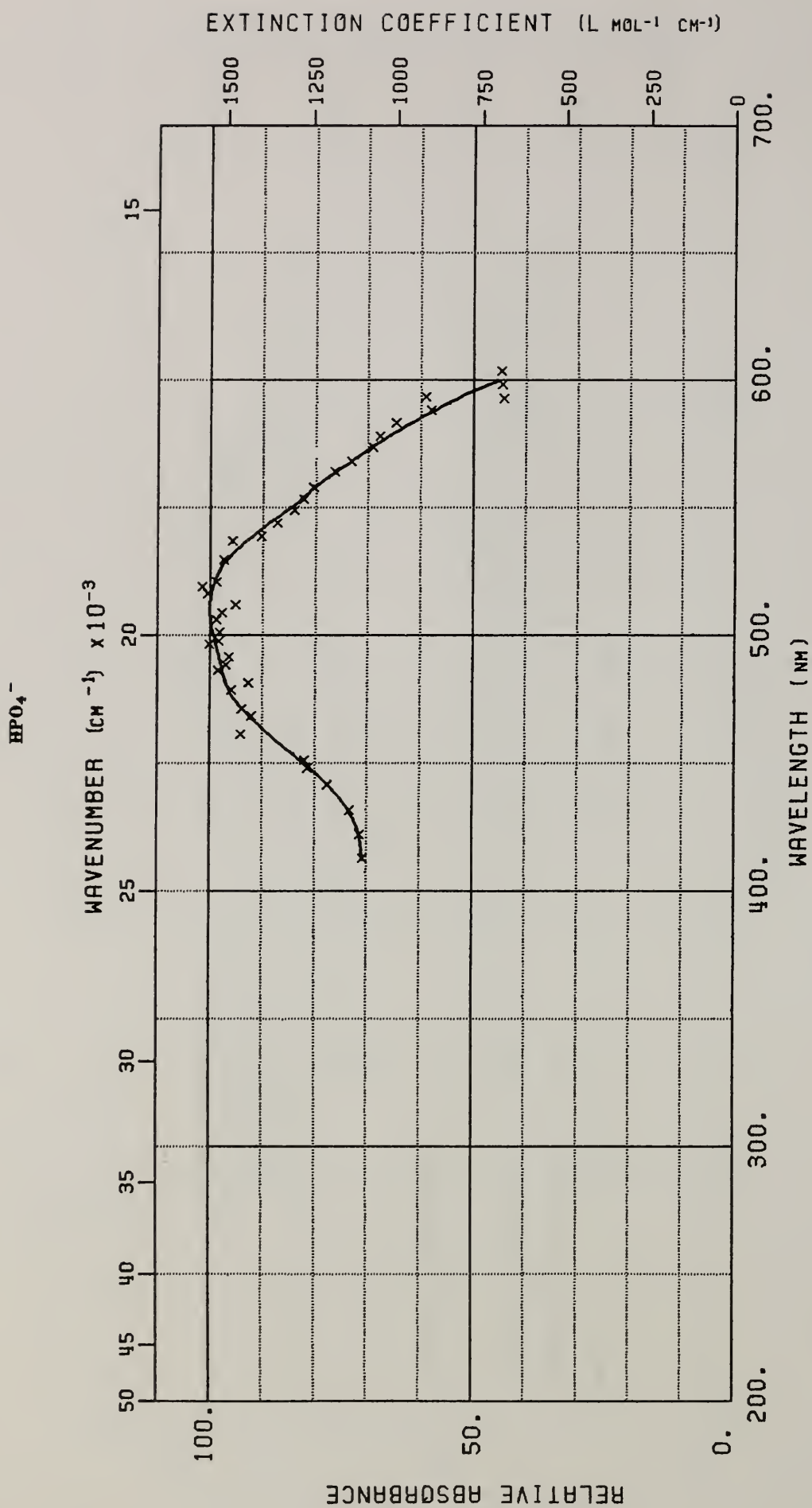
Transient formation:



Footnotes: [1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For examples see references in footnotes 2 and 3.

[2] C. Levey and E.J. Hart, *J. Phys. Chem.* 79(16): 1642-6 (1975).

[3] E.D. Black and E. Hayon, *J. Phys. Chem.* 74(17): 3199-203 (1970).



**Transient [1]: HPO<sub>4</sub><sup>-</sup>, λ(max) = 510 nm, ε<sub>510</sub> = 1550 L mol<sup>-1</sup> cm<sup>-1</sup>**

**System: aqueous solution of 2.5 × 10<sup>-2</sup> mol L<sup>-1</sup> HP<sub>2</sub>O<sub>6</sub><sup>3-</sup> at pH 7**

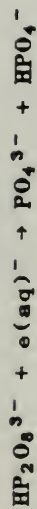


Reference: P. Maruthamuthu and P. Neta, *J. Phys. Chem.* 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Biomation 8100 recorder; signal averaging with PDP-8 computer; time delay 2-10  $\mu\text{s}$  after pulse-formation was complete after this delay.

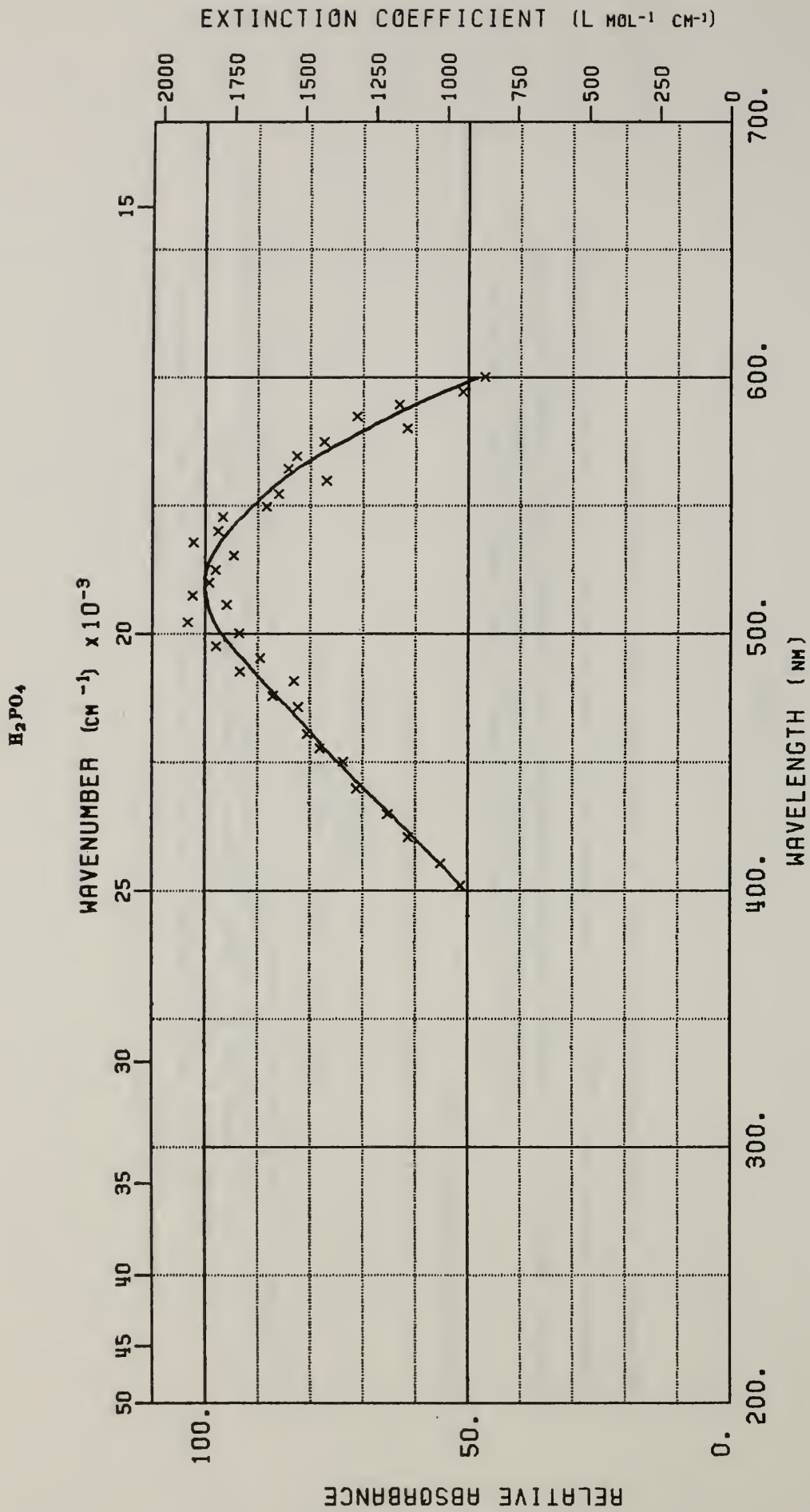
Transient formation [3]:



Footnotes: [1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For example see reference in footnote [2].

[2] G. Levey and E.J. Hart, *J. Phys. Chem.* 79(16): 1642-6 (1975).

[3] At pH = 7,  $\text{HP}_2\text{O}_8^{3-}$  is in equilibrium with  $\text{P}_2\text{O}_8^{4-}$  which is about 18% of total peroxophosphate concentration, see p. 392, *Topics in Phosphorus Chemistry*, Vol. 7 edited by E.J. Griffith and M. Grayson. I.I. Creaser and J.O. Edwards. "Peroxyphosphates".



Transient [1]: H<sub>2</sub>PO<sub>4</sub>, λ(max) = 520 nm, ε<sub>520</sub> = 1850 L mol<sup>-1</sup> cm<sup>-1</sup>

System: aqueous solution of 2.5 × 10<sup>-2</sup> mol L<sup>-1</sup> H<sub>2</sub>P<sub>2</sub>O<sub>6</sub><sup>2-</sup> ions at pH 4



## H<sub>2</sub>PO<sub>4</sub>

Reference: P. Maruthamuthu and P. Neta, J. Phys. Chem. 82(6): 710-13 (1978)

Transient generation: ARCO LP-7 linear accelerator; pulse length 5 ns; dosimetry thiocyanate

Spectral acquisition: Bausch & Lomb monochromator 0.5 m; photomultiplier signals digitized by Blomation 8100 recorder; signal averaging with PDP-8 computer; spectrum extrapolated to time zero.

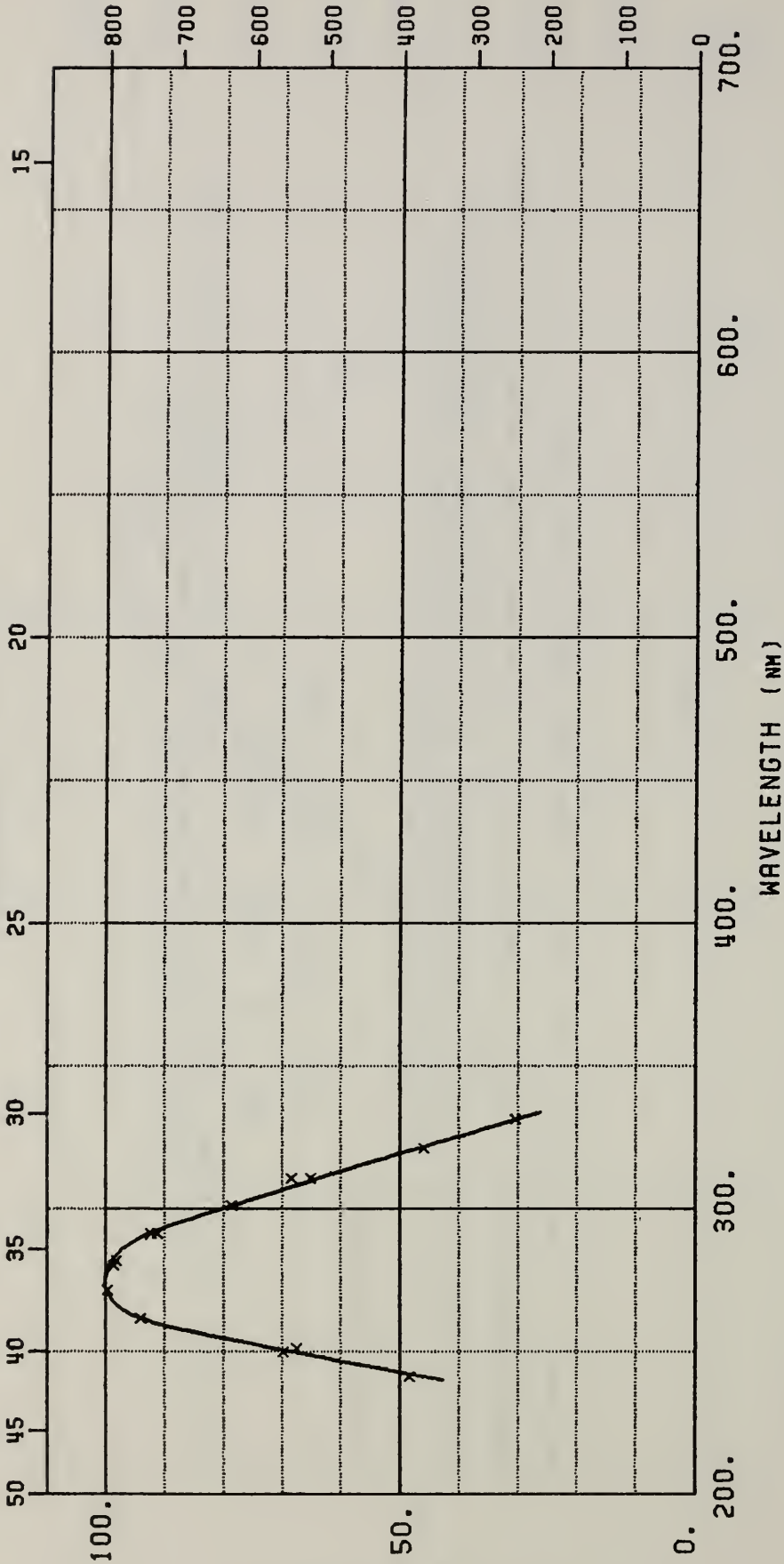
Transient formation:



Footnotes: [1] In other works where spectra were taken at shorter wavelengths, another peak was observed in the 300-400 nm region. For example see reference in footnote [2].  
[2] G. Levey and E.J. Hart, J. Phys. Chem. 79(16): 1642-6 (1975).

$\text{PO}_5^{2-}$

HAVENUMBER ( $\text{CM}^{-1}$ )  $\times 10^{-3}$



Transient:  $\text{PO}_5^{2-}$ , peroxy phosphite radical anion,  $\lambda(\text{max}) = 275 \text{ nm}$ ,  $\epsilon_{275} = 800 \text{ L mol}^{-1} \text{ cm}^{-1}$

System: aqueous solution of phosphite ions, containing oxygen, pH 9

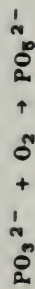
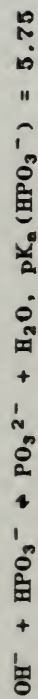
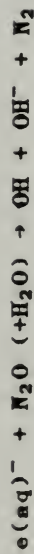


Reference: K. Schaefer and K.-D. Assmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graaff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per  $\mu\text{s}$ .

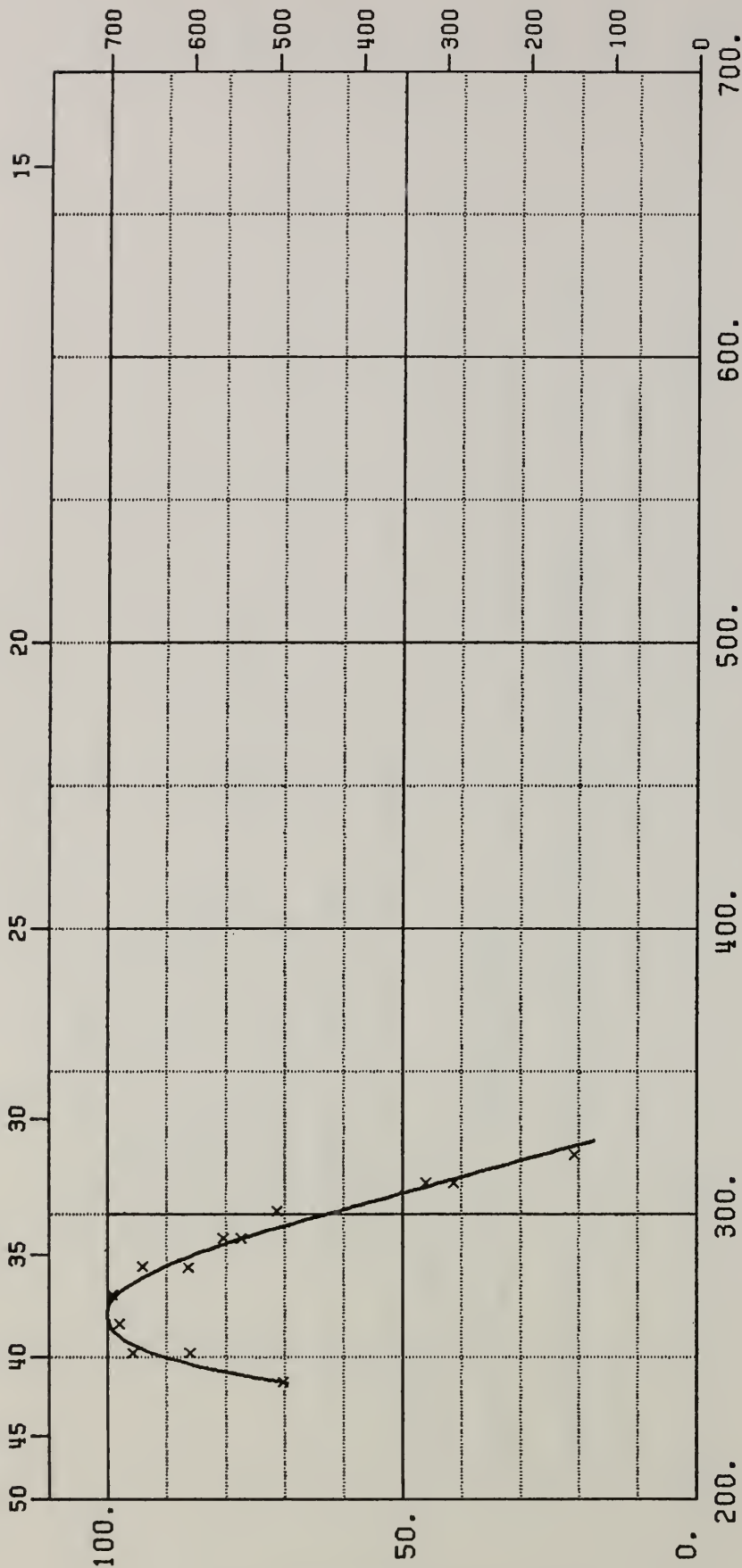
Spectral acquisition: Osram XBO 450 monitoring lamp; Zeiss M403 monochromator; EMI 9658 QB PMT

Transient formation:





WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



RELATIVE ABSORBANCE

WAVELENGTH (NM)

Transient:  $\text{HPO}_3^-$ , protonated peroxy phosphite radical anion,  $\lambda(\text{max}) = 265 \text{ nm}$ ,  
 $\epsilon_{265} = 700 \text{ L mol}^{-1} \text{ cm}^{-1}$

System: aqueous solution of phosphite ions, containing oxygen, pH 2.5



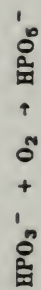
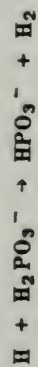
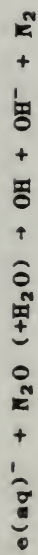
$\text{HPO}_3^-$

Reference: K. Schaefer and K.-D. Asmus, J. Phys. Chem. 84(17): 2156-60 (1980)

Transient generation: pulse radiolysis using Van de Graff generator; energy 1.6 MeV; dose rate during pulse was 700 rad per  $\mu\text{s}$

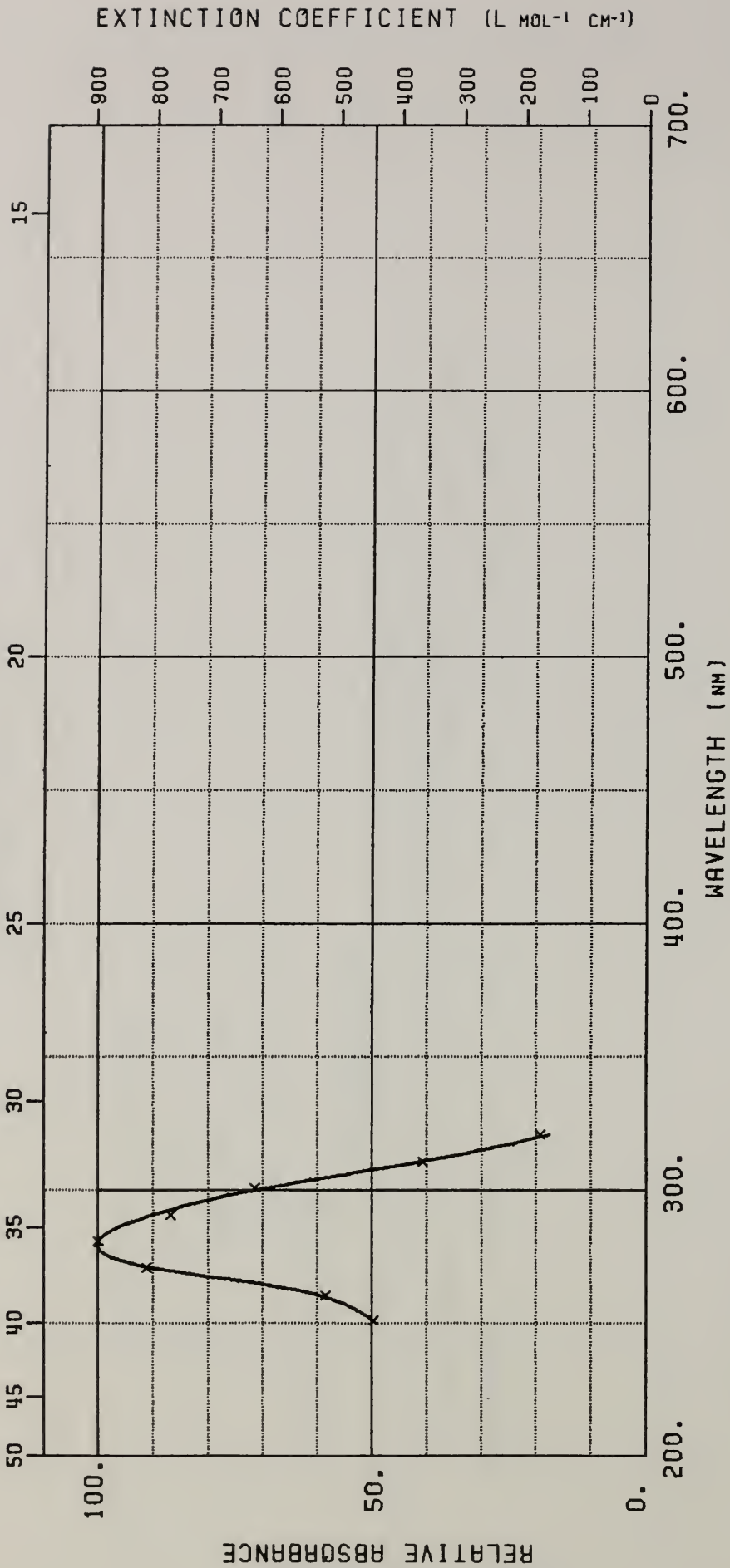
Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 QB PMT

Transient formation:



C10

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



Transient [1]: C10,  $\lambda(\text{max}) \approx 280 \text{ nm}$ ,  $\epsilon_{280} \approx 890 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2,3]

System: aqueous solution of  $10^{-3} \text{ mol L}^{-1} \text{ C10}^-$ , Ar-saturated, pH 11.4

Reference: G.V. Buxton and M.S. Subhani, J. Chem. Soc., Faraday 1 68: 947-57 (1972)

Transient generation [4]: pulse radiolysis, Van de Graaff accelerator; dosimetry-secondary emission chamber [5]

Spectral acquisition [4]: monitoring lamp - Philips 150 W CSX xenon lamp; Bausch & Lomb f/3.5 high intensity, grating monochromator; EMI 9558 BQ PMT; Tektronix 545 oscilloscope with type B input preamplifier; bandwidth 10 nm

Transient formation:



Footnotes: [1] Spectrum was corrected for depletion of  $ClO^{\cdot -}$  which absorbs in the region of  $ClO$  absorption.

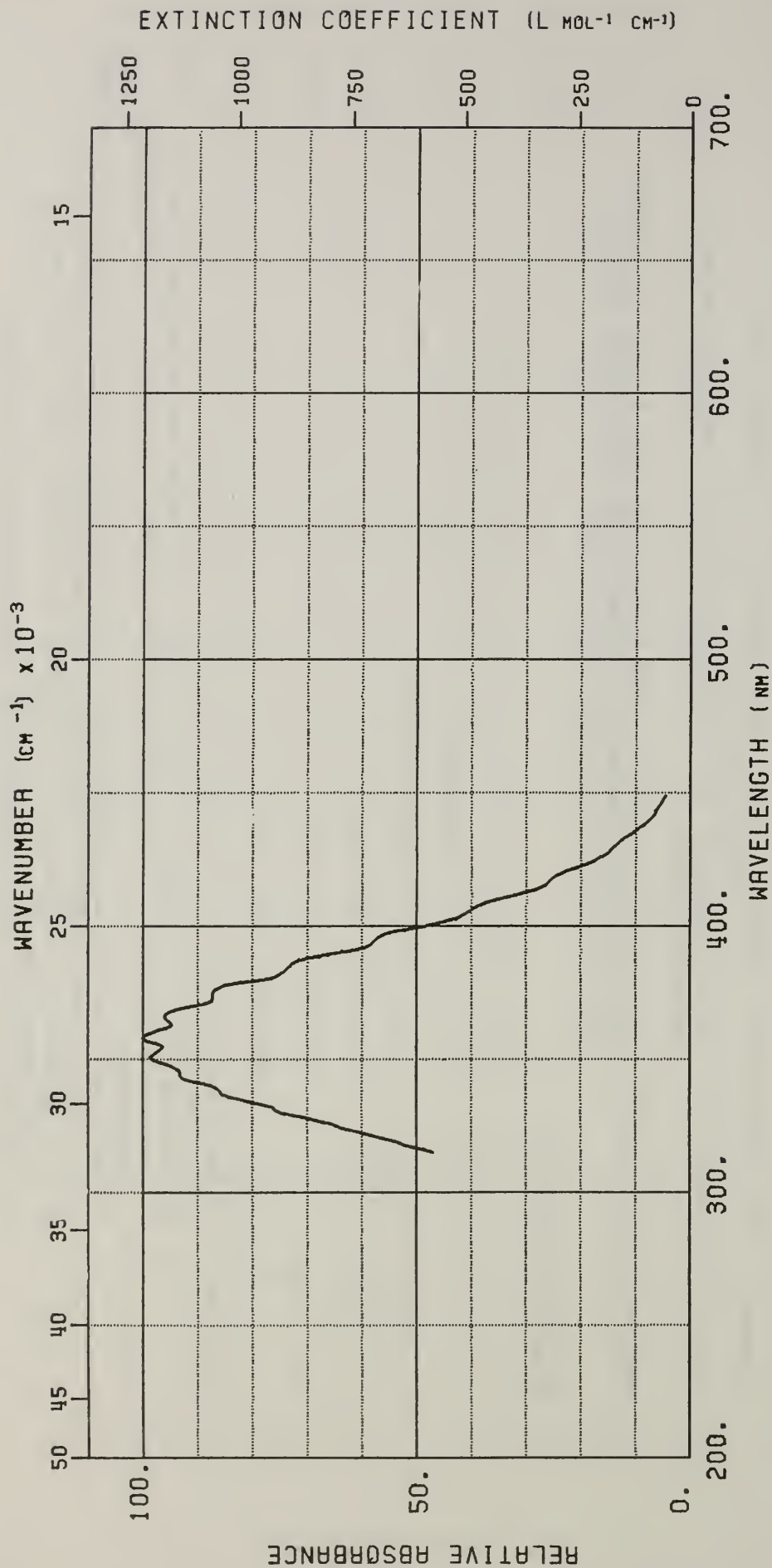
[2] Assuming  $G(ClO) = G(e(aq)^{\cdot -}) + G(OH) + G(H)$ . This value was calculated from the reaction mechanism by using measured product yields in a steady state radiolysis experiment.

[3]  $890 \text{ L mol}^{-1} \text{ cm}^{-1}$  is the average of two extinction coefficients measured by the authors. The average was rounded to the nearest  $10 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[4] K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).

[5] Calibrated by ferrocyanide dosimeter, using  $G(Fe(CN)_6^{3-}) = 3.2$  and  $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

ClO<sub>2</sub>



Radical: ClO<sub>2</sub>,  $\lambda(\text{max}) \approx 360$ ,  $\epsilon_{360} \approx 1000$  L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of  $1.5 \times 10^{-3}$  mol L<sup>-1</sup> ClO<sub>2</sub>



**ClO<sub>2</sub>**

Reference: F. Stitt, S. Friedlander, H.J. Lewis, and F.E. Young, Anal. Chem. 26(9): 1478-84 (1954)

Transient generation: radical is stable

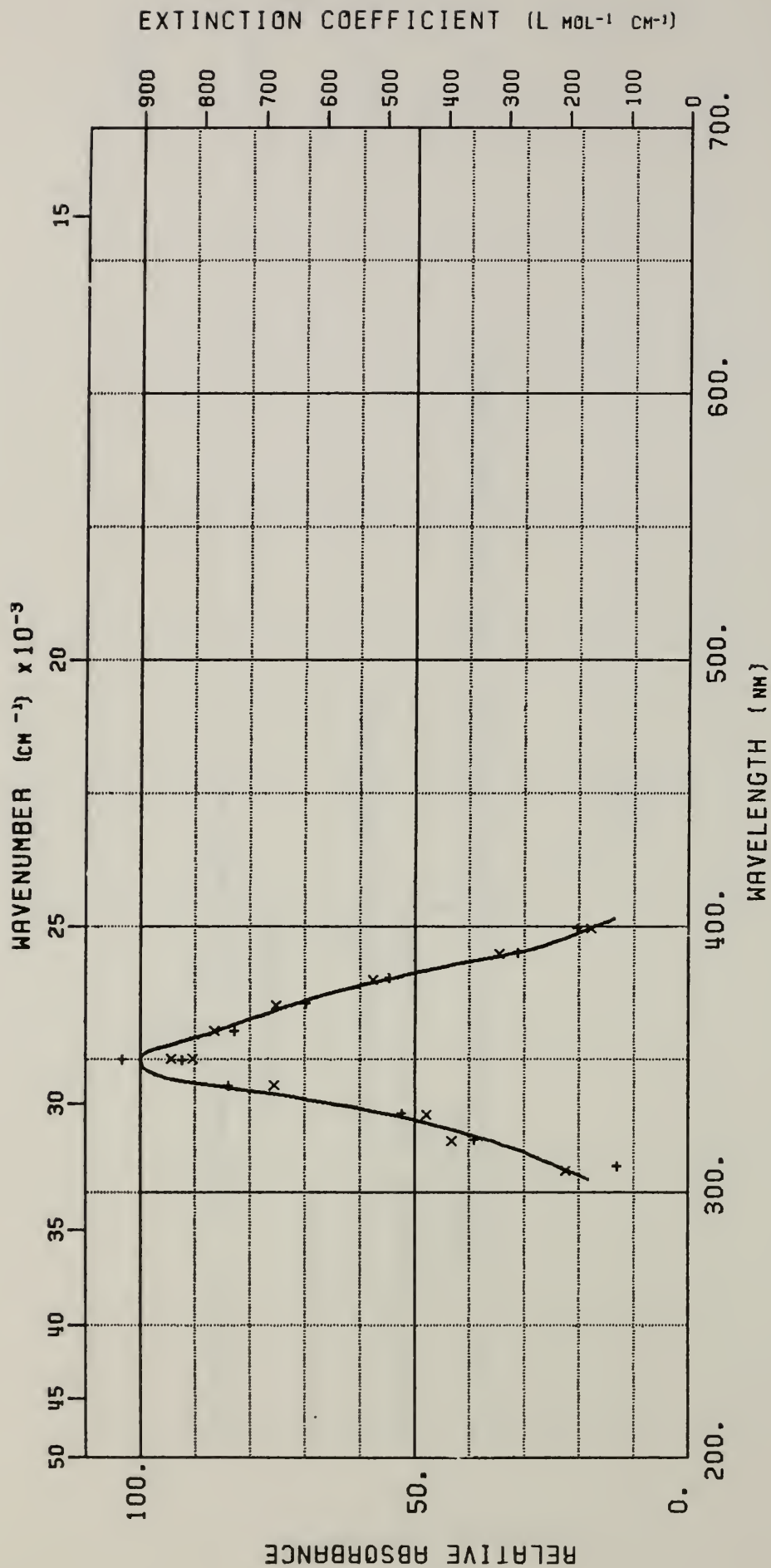
Spectral acquisition: Beckman Model DU spectrophotometer

Transient formation:

radical is stable

Footnote: [1]  $\epsilon = 495 \text{ L}\cdot\text{mol}^{-1} \text{ cm}^{-1}$  at  $\lambda = 404.7 \text{ nm}$ .

BrO



Transient: BrO,  $\lambda(\text{max}) = 350 \text{ nm}$ ,  $\epsilon_{350} \approx 900 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: aqueous  $1.5 \times 10^{-3} \text{ mol L}^{-1}$  hypobromite [2]; data points represented by "x" are for  $0.1 \text{ mol L}^{-1} \text{ NaOH}$ , and data points represented by "+" are for  $10^{-3} \text{ mol L}^{-1} \text{ NaOH}$

BrO

Reference: C.V. Buxton, F.S. Dainton, and F. Wilkinson, Chem. Commun. (11): 320-321 (1966)

Transient generation: pulse radiolysis; pulse energy 3 MeV

Spectral acquisition:

Transient formation [3]:

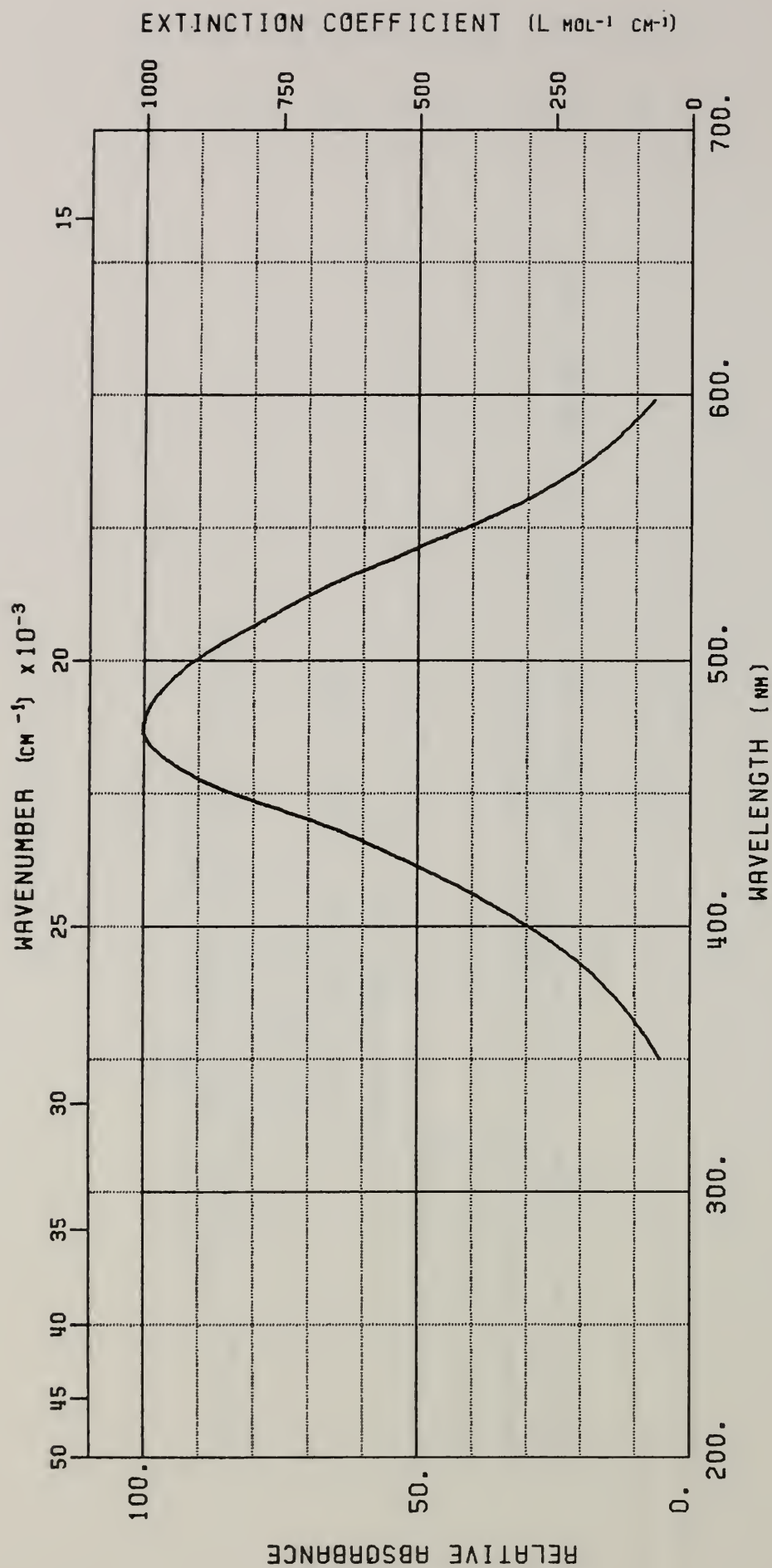


Footnotes: [1] Using  $G(e(\text{aq})^-) + G(\text{OH}) \approx 6$ .

[2]  $\text{Br}^-$  was removed from the solution by adding  $\text{Ag}^+$ .

[3] Written for  $10^{-3}$  mol  $\text{L}^{-1}$  NaOH system.

BrO<sub>2</sub>



Transient: BrO<sub>2</sub>, λ(max) = 475 nm, ε<sub>475</sub> = (1000 ± 100) L mol<sup>-1</sup> cm<sup>-1</sup> [1]

System: aqueous solution of BrO<sub>3</sub><sup>-</sup>, saturated with Ar, pH neutral or alkaline



BrO<sub>2</sub>

Reference: G.V. Buxton and F.S. Dainton, Proc. Roy. Soc. (London) Ser. A 304: 427-39 (1968)

Transient generation: pulse radiolysis, Van de Graaff accelerator; energy 2.9 MeV; syringe technique; dosimetry-secondary emission chamber [2]

Spectral acquisition [3]: monitoring lamp - Phillips 150 W CSX xenon lamp; Bausch & Lomb f/3.5 high intensity, grating monochromator; EMI 9558 BQ PMT; Tektronix 545 oscilloscope with type B input preamplifier; bandwidth 10 nm

Transient formation:

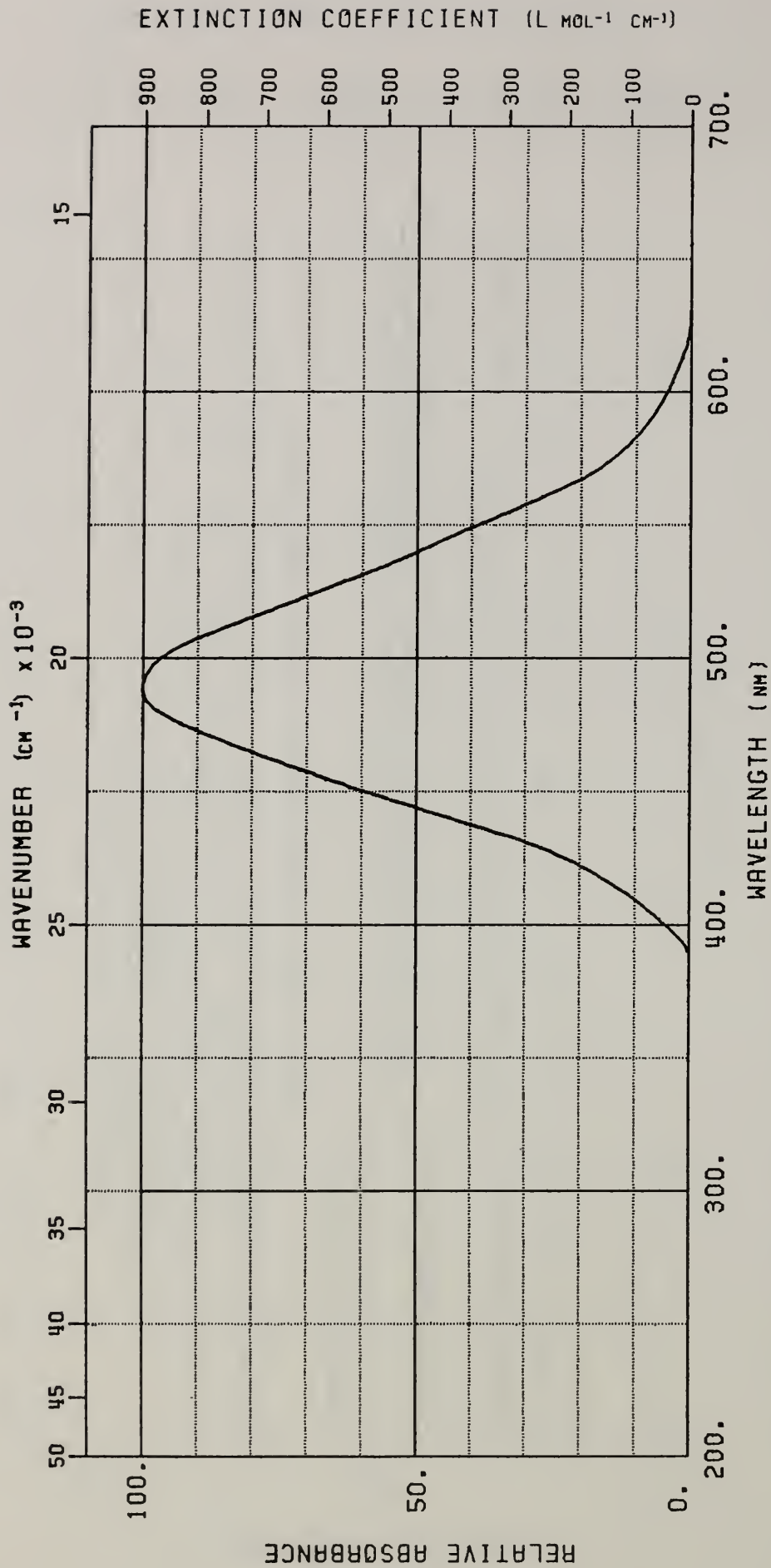


Footnotes: [1] Based on assuming  $G(\text{BrO}_2) = G(e(\text{aq})^-) + G(\text{H}) + G(\text{OH})$  for alkaline solutions of  $\text{BrO}_2^-$  and  $\text{BrO}_3^-$ . In these systems  $\text{OH}^- + \text{BrO}_2^- \rightarrow \text{BrO}_2 + \text{OH}^-$  can occur in addition to the reduction of  $\text{BrO}_3^-$ .

[2] Calibrated by ferrocyanide dosimeter, using  $G(\text{Fe}(\text{CN})_6^{3-}) = 3.2$  and  $\epsilon_{420}(\text{Fe}(\text{CN})_6^{3-}) = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[3] K.W. Chambers, E. Collinson, F.S. Dainton, W.A. Seddon, and F. Wilkinson, Trans. Faraday Soc. 63: 1699-711 (1967).

10



Transient: 10,  $\lambda(\text{max}) = 490 \text{ nm}$ ,  $\epsilon_{490} = 900 \pm 130 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

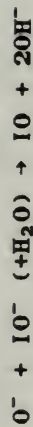
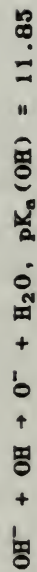
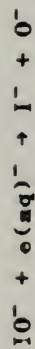
System: aqueous solution of  $1.2 \times 10^{-3} \text{ mol L}^{-1} \text{ IO}^-$ ,  $\text{pH} = 13.6$

Reference: O. Amichai and A. Treinin, J. Phys. Chem. 74(4): 830-5 (1970)

Transient generation: pulse radiolysis (Varian linear accelerator); energy 5 MeV; pulse length 1.5  $\mu$ s; dosimetry  $K_4Fe(CN)_6$  [2]

Spectral acquisition: two Bausch & Lomb monochromators, type 567 AB; R136 and 1P28 PMT; split monitoring beam; spectrum was recorded at 5 nm intervals [3]; multiple reflections through cell, optical path 6 cm; time delay, 20  $\mu$ s

Transient formation:



Footnotes:

- [1] Assuming  $G(IO) = G(OH) + G(e(aq)^-)$   
 [2] Dosimeter consisted of air-saturated  $K_4Fe(CN)_6$  solution, taking  $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $G(Fe(CN)_6^{3-}) = 2.7$ .  
 [3] Experimental points were within 5% of smoothed curve.

$\text{IO}_2$

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$

15

20

25

100.

50.

0.

RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT ( $\text{L MOL}^{-1} \text{CM}^{-1}$ )

200

150

100

50

0

850.

750.

650.

550.

450.

WAVELENGTH (NM)

Transient [1]:  $\text{IO}_2$  [2],  $\lambda(\text{max}) = 715 \text{ nm}$ ,  $\epsilon_{715} = (220 \pm 30) \text{ L mol}^{-1} \text{ cm}^{-1}$  [3]

System: aqueous solution of  $1.1 \times 10^{-2} \text{ mol L}^{-1} \text{ IO}_3^-$



Reference: O. Amichai and A. Treinin, J. Phys. Chem. 74(4): 830-5 (1970)

Transient generation: pulse radiolysis (Varian linear accelerator); energy 5 MeV; pulse length 1.5  $\mu$ s; dosimetry  $K_4Fe(CN)_6$  [4]

Spectral acquisition: two Bausch & Lomb monochromators, type 567 AB; R136 and 1P28 PMT; split monitoring beam; spectrum was recorded at 5 nm intervals [5]; multiple reflections through cell, optical path 6 cm; time delay - 23  $\mu$ s after pulse

Transient formation [6]:



Footnotes: [1] In the flash photolysis of aqueous solutions of  $KIO_3$ , F. Barat, L. Gilles, B. Hickel, and J. Sutton, Chem. Commun. (24): 1485 (1969) assigned a

spectrum having  $\lambda(max) = 480$  nm to the  $IO_2$  radical.

[2] The spectrum was a composite spectrum due to  $IO_3$ ,  $IO$ , and  $IO_2$ . The  $IO_2$  component was resolved by Gaussian fit on a wavenumber scale.

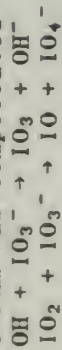
[3] From ratio of optical densities at zero time,  $A(IO_2)/A(IO_3)$ , the authors obtained  $\epsilon(max)IO_2/\epsilon(max)IO_3 = 0.53 \pm 0.08$ . For  $IO_3$ ,

$\epsilon(max) = (400 \pm 60) L mol^{-1} cm^{-1}$ , assuming  $G(IO_3) = G(OH)$ , see footnote 6.

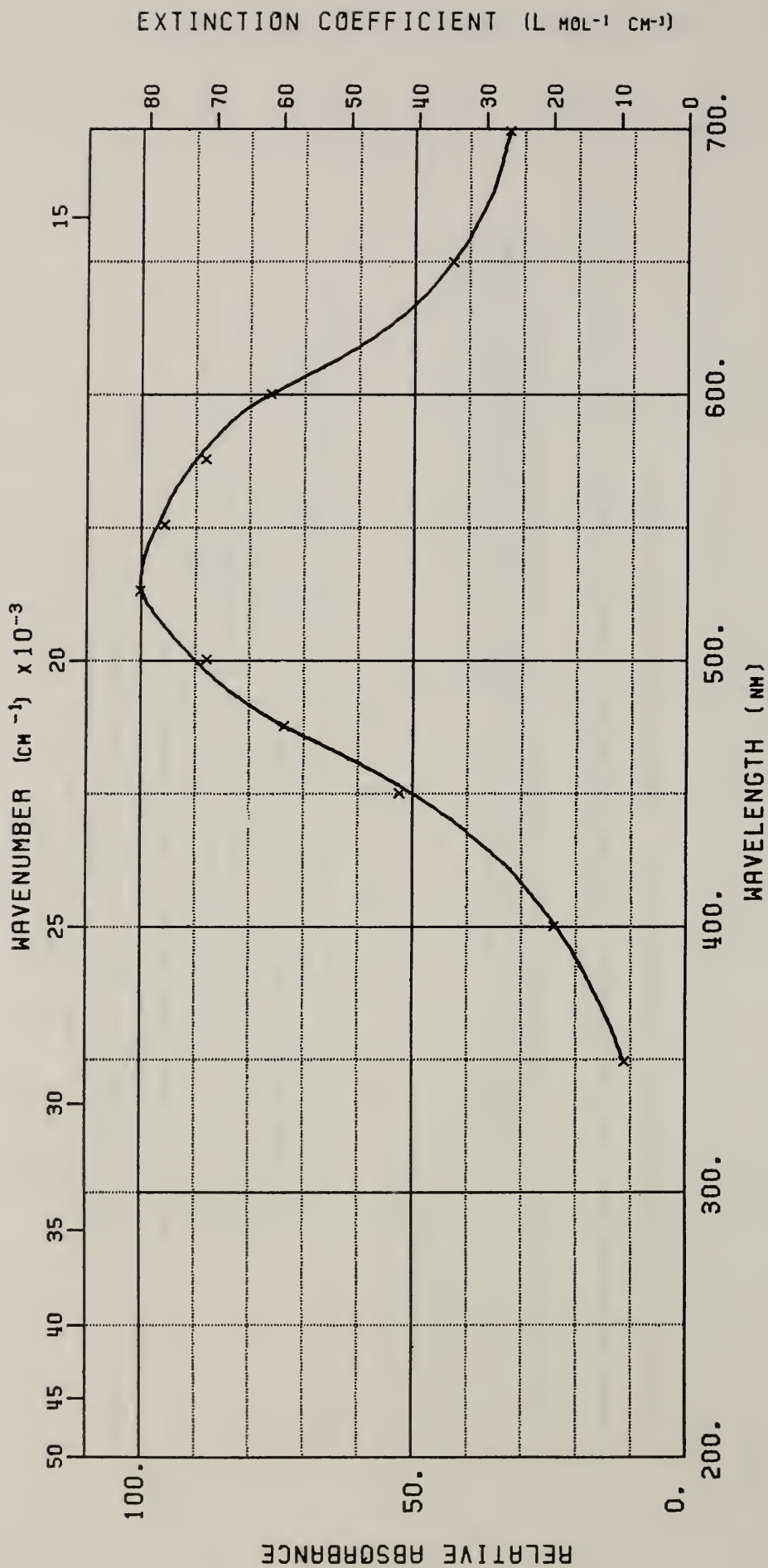
[4] Dosimeter consisted of air-saturated  $K_4Fe(CN)_6$  solution, taking  $\epsilon_{420}(Fe(CN)_6^{3-}) = 1000 L mol^{-1} cm^{-1}$  and  $G(Fe(CN)_6^{3-}) = 2.7$ .

[5] Experimental points were within 5% of smoothed curve.

[6] Spectrum was complicated by absorption by  $IO_3$  and  $IO$



NH<sub>2</sub>



Transient [1]: NH<sub>2</sub>, amino radical,  $\lambda(\text{max}) = 530 \text{ nm}$ ,  $\epsilon_{530} = 81 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2]

System: aqueous solution of ammonia, N<sub>2</sub>O saturated

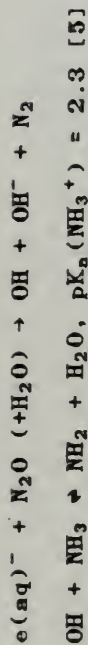
NH<sub>2</sub>

Reference: P.B. Pagsberg, RISO-256, Jan. 1972. p. 209-21 [Report, AEK-Riso, Roskilde, Denmark]

Transient generation: pulse radiolysis; dose rates during the pulse were 1-10 krad/ $\mu$ s;  
pulse length 0.4-2  $\mu$ s; dosimetry-ferrocyanide [3]

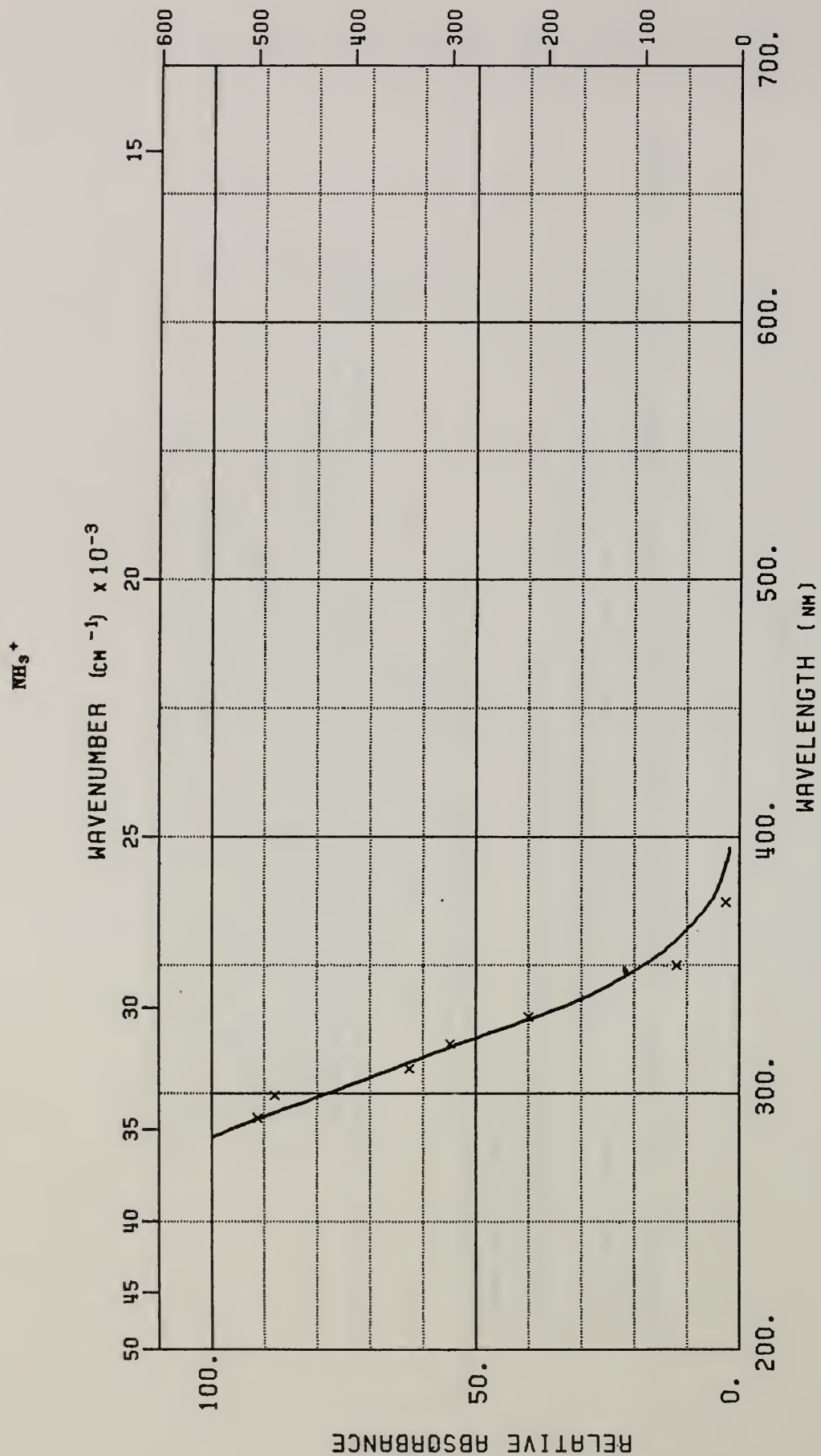
Spectral acquisition: optical path length of 8 cm [4]

Transient formation:



- Footnotes: [1] There was another band, that is not displayed, with a maximum at 215 nm. No extinction coefficient was given for this band, but it was assigned to the charge-transfer complexes (NH<sub>2</sub>, H<sub>2</sub>O) and (NH<sub>2</sub>, NH<sub>3</sub>).
- [2] Based on the solution to the rate equation for the above formation equations, assuming a constant production of OH during the pulse.
- [3] Dosimeter consisted of aqueous solution of 10<sup>-3</sup> mol L<sup>-1</sup> K<sub>4</sub>Fe(CN)<sub>6</sub>, 2.5 x 10<sup>-2</sup> mol L<sup>-1</sup> N<sub>2</sub>O, and about 10<sup>-4</sup> mol L<sup>-1</sup> O<sub>2</sub>. G(Fe(CN)<sub>6</sub><sup>3-</sup>) assumed to be equal to G(e(aq)<sup>-</sup>) + G(OH) and  $\epsilon_{420}(\text{ferricyanide}) = 1000 \text{ L mol}^{-1} \text{ cm}^{-1}$ .
- [4] Optical densities were of the order of 0.03. The signal to noise ratio was 100.
- [5] M.Z. Hoffman and K.R. Olson, J. Phys. Chem. 82(24): 2631-2 (1978).

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: NH<sub>3</sub><sup>+</sup>, protonated amino radical, ε<sub>290</sub> ≈ 500 L mol<sup>-1</sup> cm<sup>-1</sup> [1], 2k ≈ 7 × 10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of 2 × 10<sup>-5</sup> mol L<sup>-1</sup> Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, pH 1 [2], deaerated



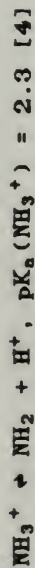


Reference: M.Z. Hoffman and K.R. Olson, *J. Phys. Chem.* **82**(24): 2631-2 (1978)

Transient generation: flash photolysis

Spectral acquisition: quartz-jacketed optical cell, path length 22 cm; time delay 50  $\mu\text{s}$  after pulse

Transient formation [3]:

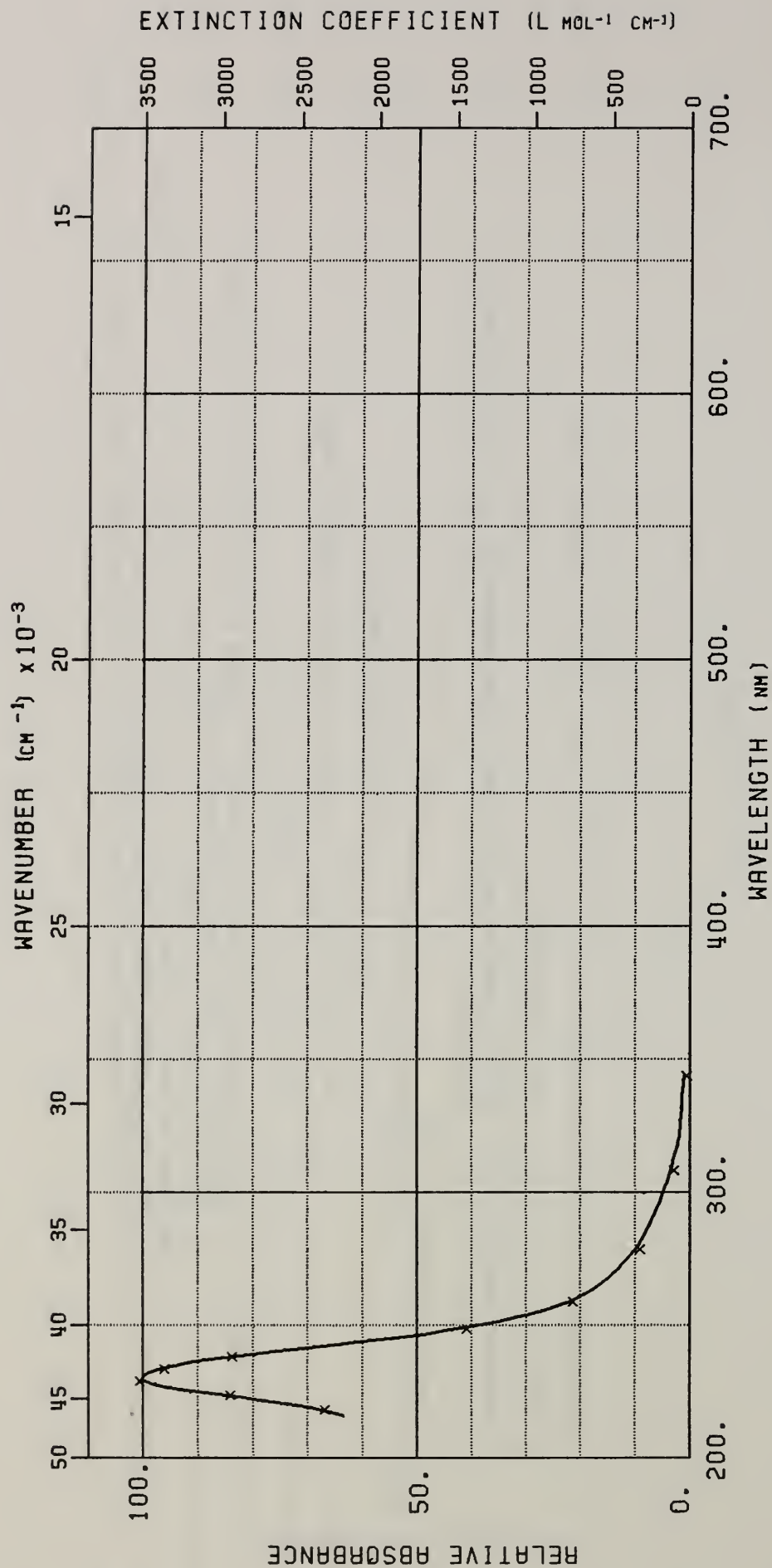


Footnotes: [1] Based on  $\approx 4 \times 10^{-6}$  mol  $\text{L}^{-1}$   $\text{Co(aq)}^{2+}$  formed as determined by the method of R.E. Kitson, *Anal. Chem.* **22**: 664-7 (1950)

[2] Acidity adjusted with  $\text{HClO}_4$ .

[3] Quantum yield at 254 nm = 0.16, M.F. Manfrin, G. Varani, L. Moggi, and V. Balzani, *Mol. Photochem.* **1**(4): 387-402 (1969).

[4] At pH 4, absorption spectrum could not be distinguished from scattered light.



Transient:  $N_2H_3$ , hydrazyl radical,  $\lambda_{(max)} = 230$  nm,  $\epsilon_{230} = 3500$  L mol<sup>-1</sup> cm<sup>-1</sup> [1],  
 $2k = 2.4 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of  $2 \times 10^{-2}$  mol L<sup>-1</sup>  $N_2H_4$ ,  $N_2O$  (1 atm), pH 9.2

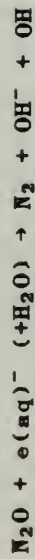
## N<sub>2</sub>H<sub>3</sub>

Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length  $\approx$  30 ns; dose  $\approx$  8 krad per pulse; dosimetry KSCN

Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of  $\approx$  20-25; time delay  $\approx$  0.1  $\mu$ s after pulse

Transient formation:

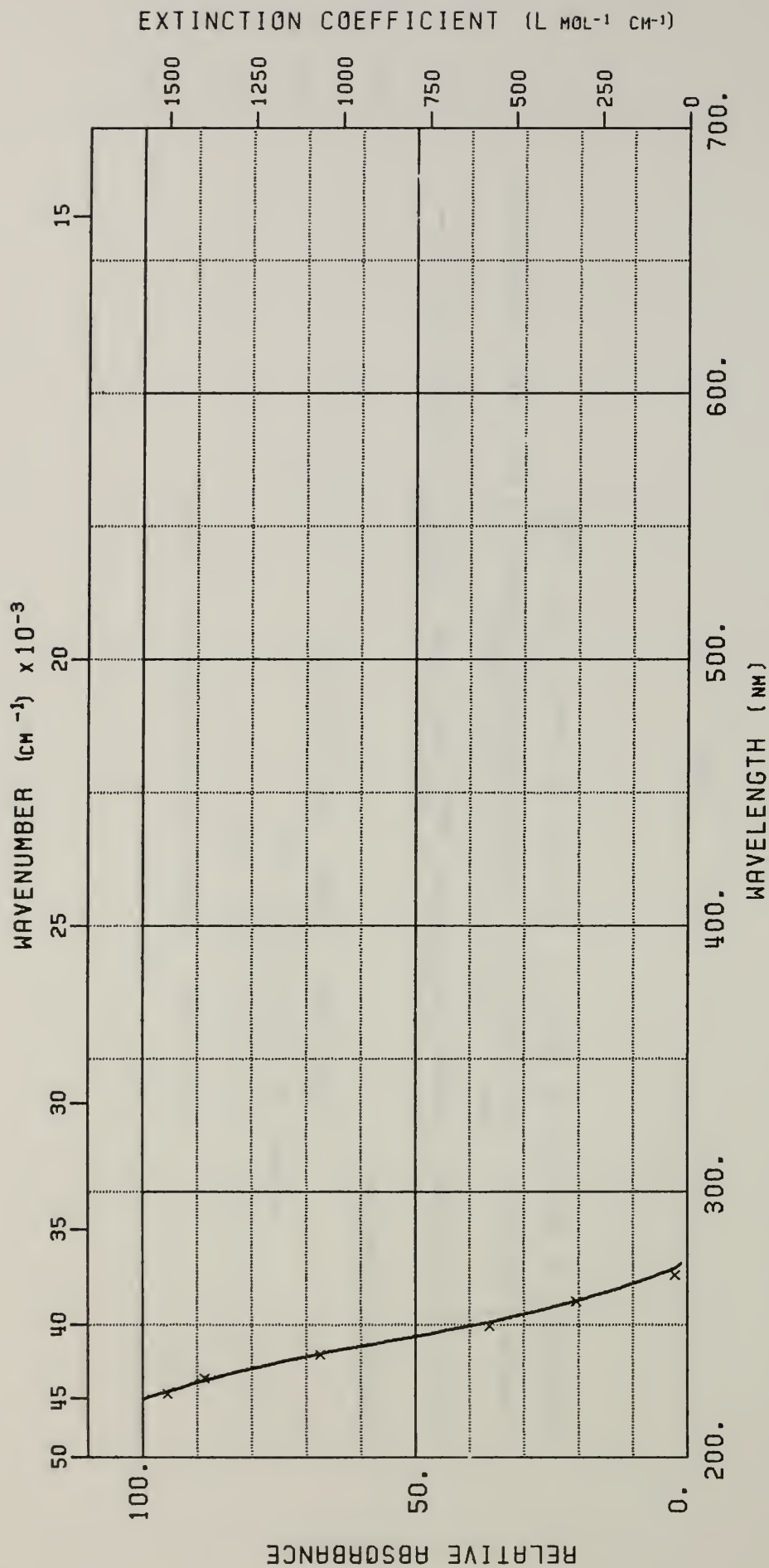


either  $\text{OH} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$

or  $\text{OH} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_4^+ + \text{OH}^-$



Footnote: [1] Using  $G(e(\text{aq})^-) = G(\text{OH}) = 2.8$ .



Transient:  $\text{N}_2\text{H}_4^+$ ,  $\epsilon_{225} = 1500 \text{ L mol}^{-1} \text{cm}^{-1}$  [1],  $2k = 6.0 \times 10^8 \text{ L mol}^{-1} \text{s}^{-1}$

System: aqueous solution of  $2 \times 10^{-2} \text{ mol L}^{-1} \text{N}_2\text{H}_4$ ,  $\text{N}_2\text{O}$  (1 atm), pH 3.7



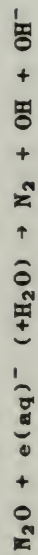


Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length  $\approx 30$  ns; dose  $\approx 8$  krad per pulse; dosimetry KSCN

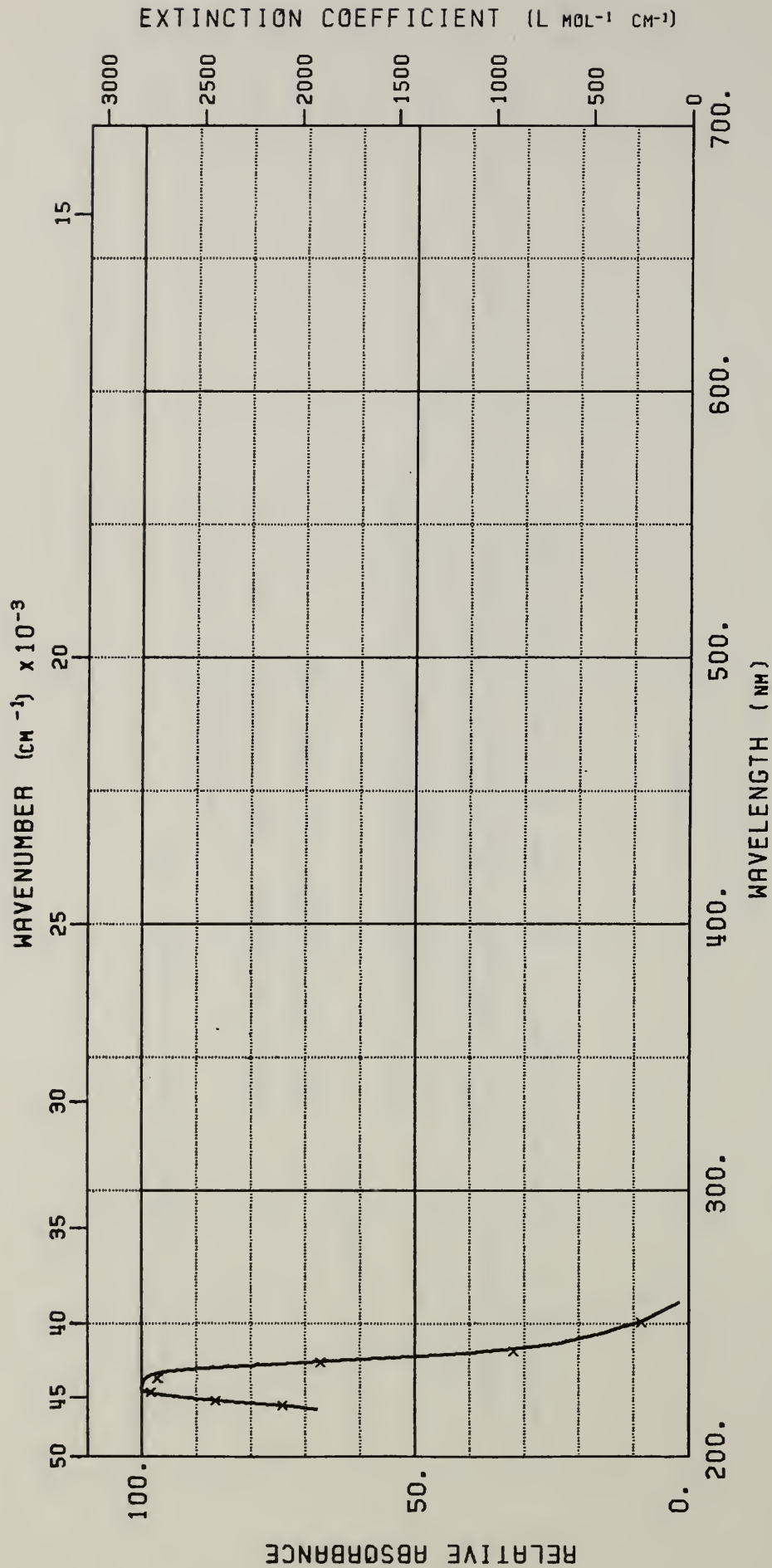
Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of  $\approx 20$ -25; time delay  $\approx 0.1$   $\mu$ s after pulse

Transient formation:



Footnote: [1] Using  $\text{C}(e(\text{aq})^-) = \text{C}(\text{OH}) = 2.8$ .

$N_3H_3$



Transient:  $N_3H_3$ ,  $\lambda(\text{max}) = 225 \text{ nm}$ ,  $\epsilon_{225} = 2800 \text{ L mol}^{-1} \text{ cm}^{-1}$

System: aqueous solution of  $2 \times 10^{-2} \text{ mol L}^{-1} N_2H_4$ ,  $N_2O$  (1 atm), pH 9.2

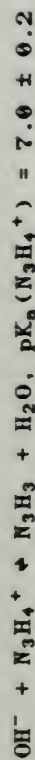
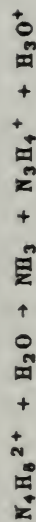
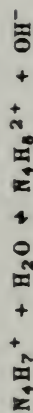
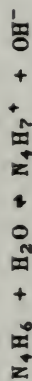
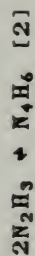
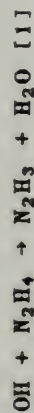
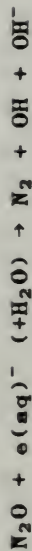
### $N_3H_3$

Reference: E. Hayon and M. Simic, J. Am. Chem. Soc. 94(1): 42-7 (1972)

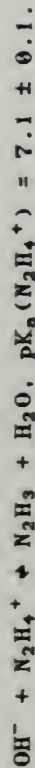
Transient generation: pulse radiolysis, Febetron 705; pulse energy 2.3 MeV; pulse length  $\approx 30$  ns; dose  $\approx 8$  krad per pulse; dosimetry KSCN

Spectral acquisition: double monochromator; 450 W xenon lamp, pulsed to increase output by a factor of  $\approx 20$ -25; time delay 10 ms after pulse

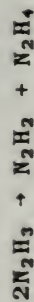
Transient formation:



Footnotes: [1] Alternative formation of  $N_2H_3$  radical is



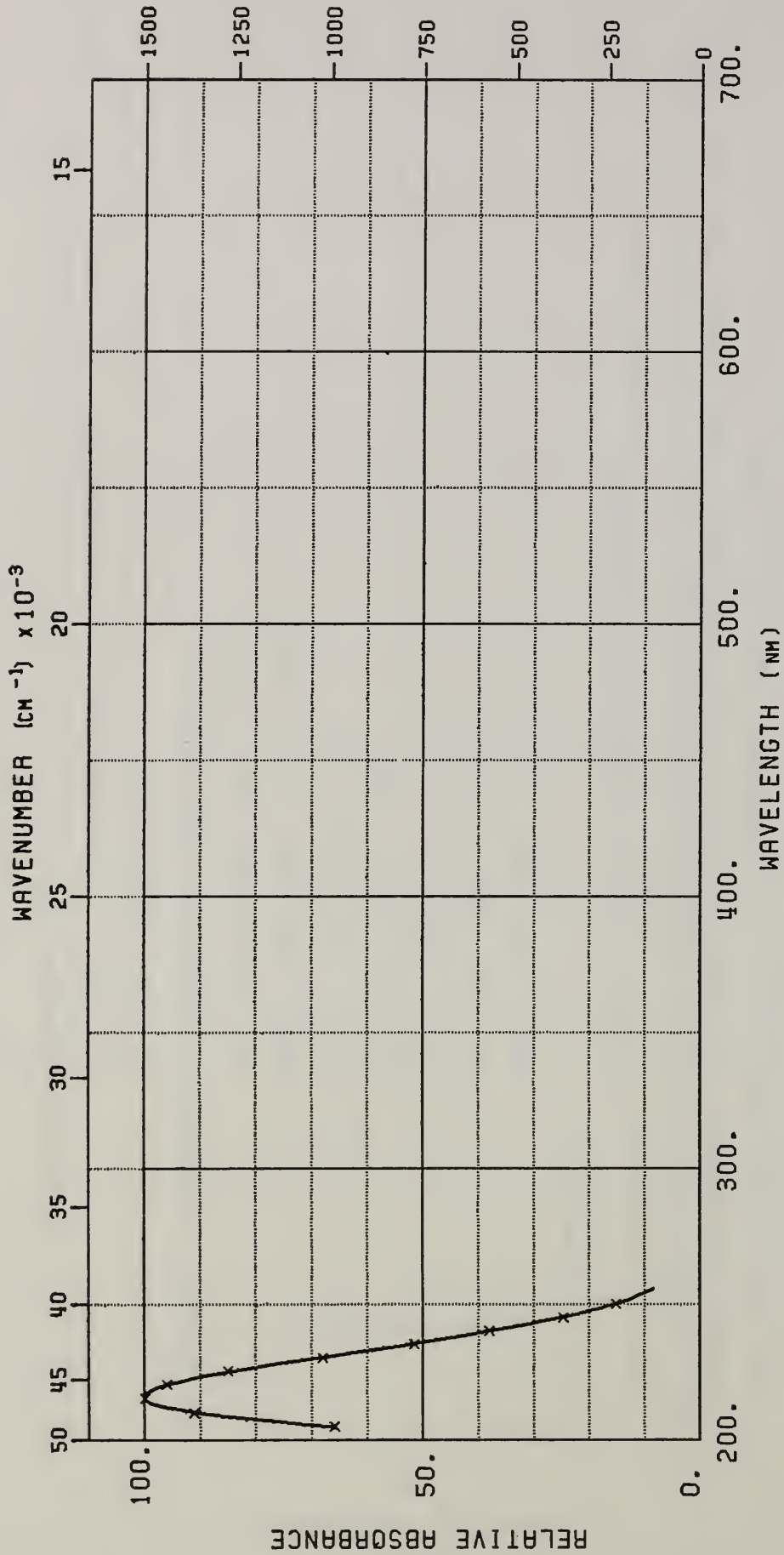
[2] Disproportionation



was ruled out because  $N_2H_2$  should give an equivalent amount of  $N_2$  and  $H_2$ , and this was not observed.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

NHOH or H<sub>2</sub>NO



Transient [1]: NHOH[2] or H<sub>2</sub>NO[3], λ(max) = 216 nm, ε<sub>216</sub> ≈ 1500 L mol<sup>-1</sup> cm<sup>-1</sup> [4,5]

System: aqueous solution of 10<sup>-3</sup> mol L<sup>-1</sup> hydroxylamine, 2 × 10<sup>-2</sup> mol L<sup>-1</sup> N<sub>2</sub>O, pH 7.6 or 5.4 [6]



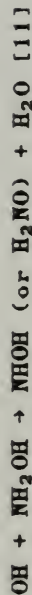
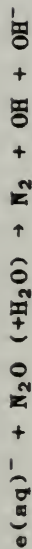
NHOH or H<sub>2</sub>NO

Reference: D. Behar, D. Shapira, and A. Treinin, J. Phys. Chem. 76(2): 180-6 (1972)

Transient generation: pulse radiolysis, using linear accelerator; pulse energy 5 MeV; dosimetry modified Frioke [8]

Spectral acquisition: 60 W deuterium monitoring lamp; "solar blind" R166 PMT [9]

Transient formation [10]:



Footnotes: [1] Due to conflicts between information given in footnotes 2 and 3, the assignment of the spectrum is currently in doubt. P. Neta, private communication, 1978.

[2] Simic and Hayon [7] assigned the spectrum to NHOH and not to H<sub>2</sub>NO because (a) the similarity of the spectra of the intermediates formed in the reaction of OH with NH<sub>2</sub>OH and NH<sub>2</sub>OCH<sub>3</sub> and (b) the large difference in the solid-base properties of these two radicals from NH<sub>2</sub>OH and NH<sub>2</sub>OCH<sub>3</sub>. Simic and Hayon used (a) and (b) to suggest that the radicals from NH<sub>2</sub>OH and NH<sub>2</sub>OCH<sub>3</sub> are NHOH and NHOCH<sub>3</sub>, respectively.

[3] From esr data O.P. Chawla and R.W. Fessenden, J. Phys. Chem. 79(24): 2693-700 (1975) assigned the radical, observed from the reaction of NH<sub>2</sub>OH with SO<sub>4</sub><sup>-</sup>, as H<sub>2</sub>NO.

[4] Measurement at 230 nm gave ε<sub>230</sub> = (1020 ± 30) L mol<sup>-1</sup> cm<sup>-1</sup> at pH 5.5.

[5] Another value was reported in the literature, ε<sub>217</sub> = 2500 L mol<sup>-1</sup> cm<sup>-1</sup> [7].

[6] Each data point is the average of six measurements, three measurements at each pH. The scatter of these points was ±5%.

[7] M. Simic and E. Hayon, J. Am. Chem. Soc. 93: 5982-6 (1971).

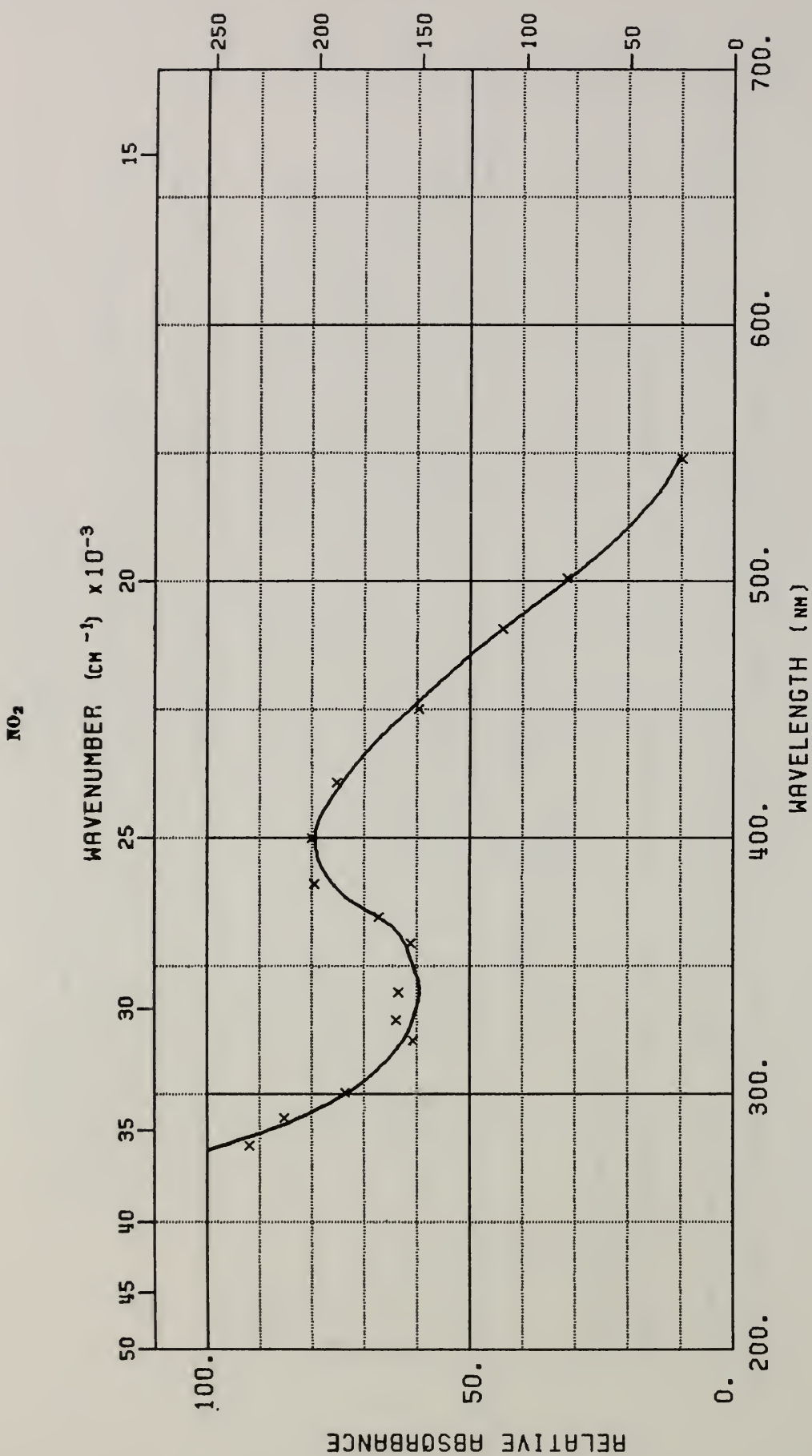
[8] M.S. Matheson and L.M. Dorfman, Pulse Radiolysis, MIT Press, Cambridge, 1969.

[9] Corrections were made for stray light.

[10] Written for pH 7.6.

[11] pK<sub>a</sub>(NH<sub>3</sub>OH<sup>+</sup>) = 6.0 ± 0.1 and pK<sub>a</sub>(NH<sub>2</sub>OH<sup>+</sup>) = 4.2 ± 0.1.

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: NO<sub>2</sub>, λ(max) = 400 nm, ε<sub>400</sub> = 201 L mol<sup>-1</sup> cm<sup>-1</sup>, 2k = (9.0 ± 2.0) × 10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of NO<sub>2</sub><sup>-</sup>, saturated with N<sub>2</sub>O

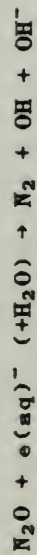
## NO<sub>2</sub>

Reference: M. Grsetzel, A. Henglein, J. Lillie, and G. Beck, Ber. Bunsenges. Physik. Chem. 73(7): 646-53 (1969)

Transient generation: pulse radiolysis [1] using Van de Graaff generator; energy 1.6 MeV

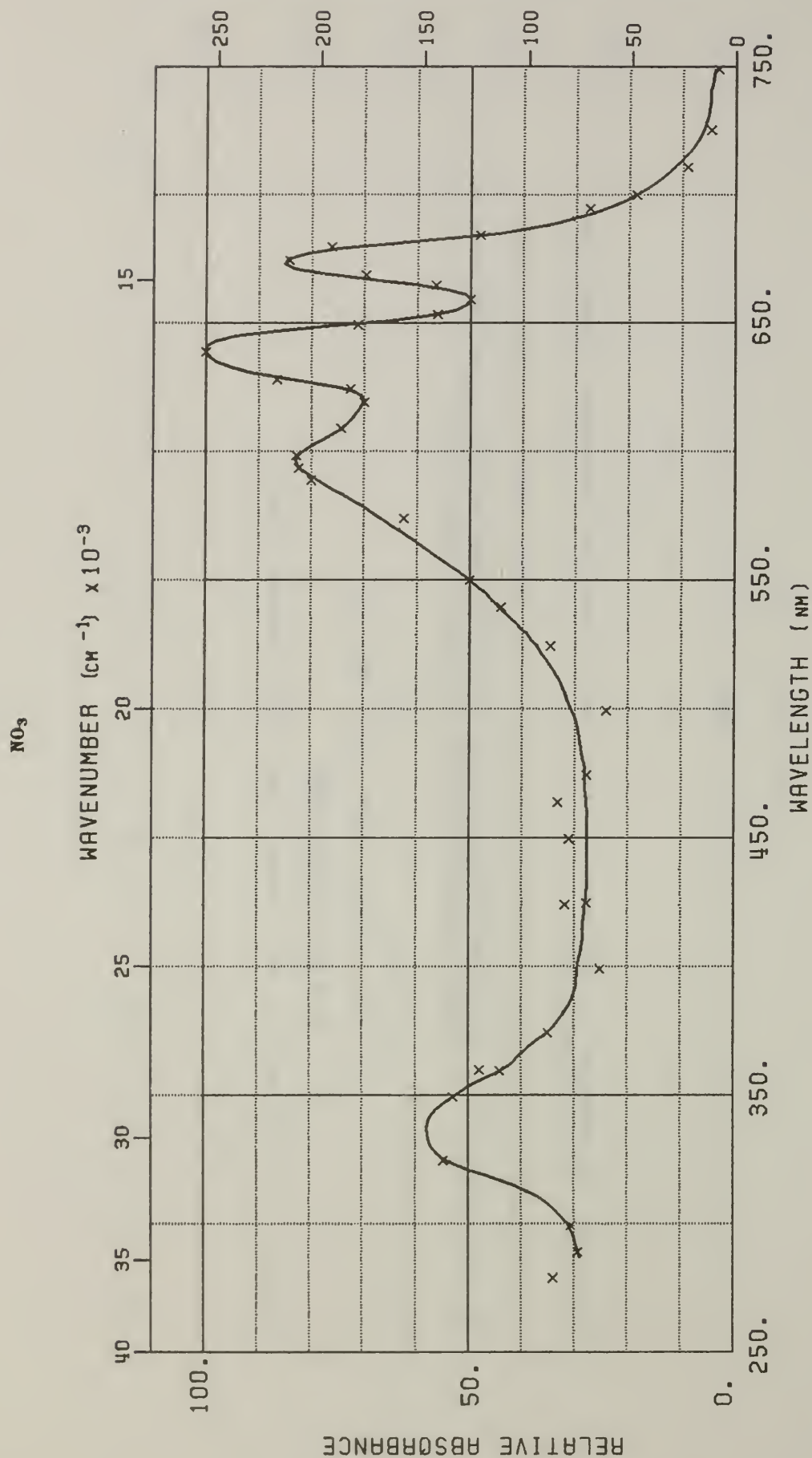
Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

Transient formation:



Footnote: [1] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1]: NO<sub>3</sub>, λ(max) = 595, 640, 675 nm, ε<sub>635</sub> = (250 ± 90) L mol<sup>-1</sup> cm<sup>-1</sup> [2]

System: aqueous solution of 0.1 mol L<sup>-1</sup> K<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, pH 0.65 [3]



## NO<sub>3</sub>

Reference: L. Degliotti and E. Hayon, *J. Phys. Chem.* 71: 3802-8 (1967)

Transient generation [4]: flash photolysis; oxygen flash lamp with total energy 1800 J per flash; total flash duration 70  $\mu$ s, duration at "1/e time" 5  $\mu$ s

Spectral acquisition [4]: Bausch & Lomb 250 nm grating monochromator; Oeram 450 W xenon monitoring lamp, attention given to minimize exposure of the solution to this lamp; EMI 9552 B PMT; Tektronix 535A oscilloscope, traces recorded on film; time delay 200  $\mu$ s after start of flash

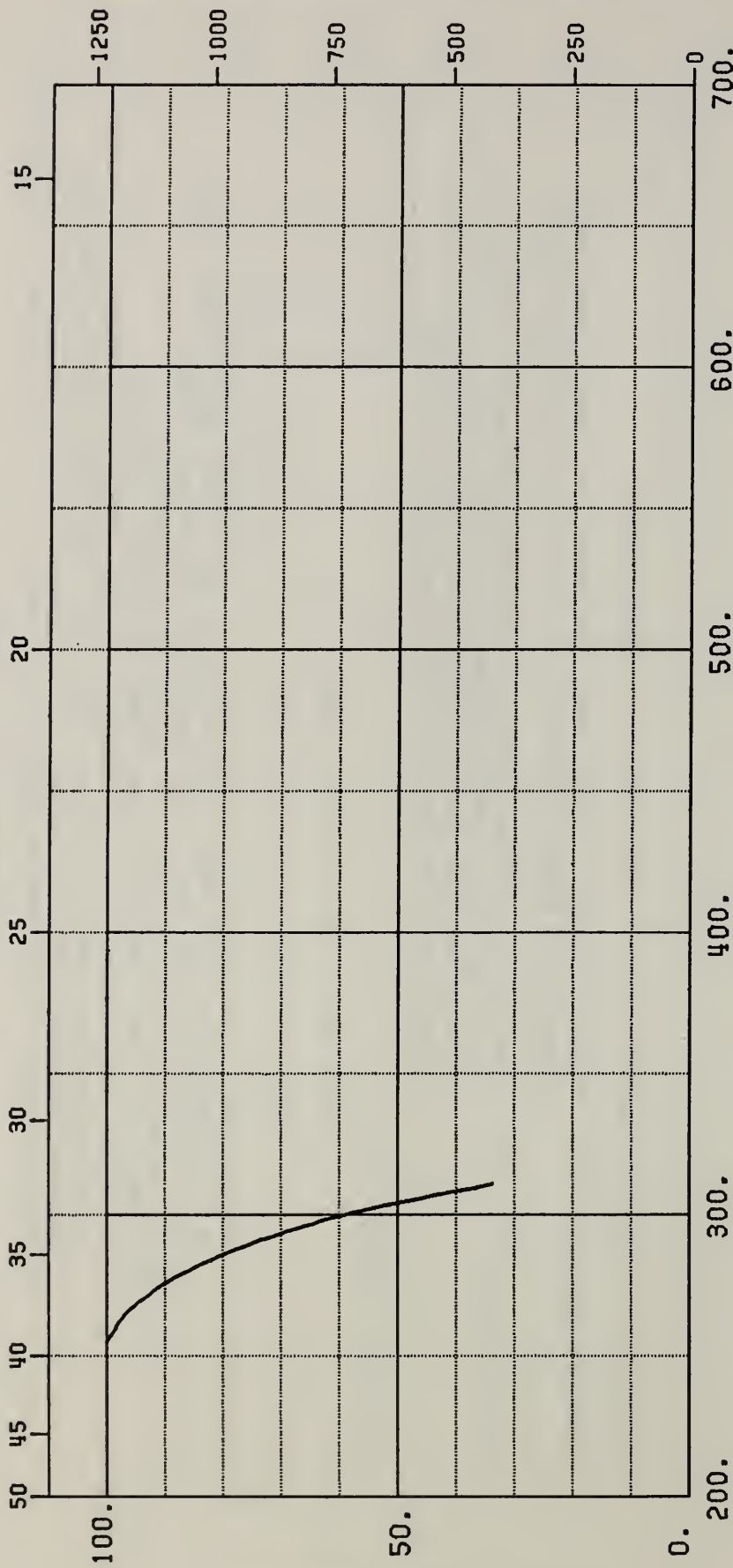
Transient formation [5,6]:



- Footnotes: [1] Band at 340 nm was tentatively suggested to be due to N<sub>2</sub>O<sub>4</sub>, not NO<sub>3</sub>. R.K. Broszkiewicz, *Bull. Acad. Pol. Sci., Ser. Chim.* 24(3): 221-9 (1976).  
[2] R.W. Glass and T.W. Martin, *J. Am. Chem. Soc.* 92: 5084-93 (1970).  
[3] Due to hydrolysis of the salt. Solutions were unbuffered.  
[4] L. Degliotti and E. Hayon, *J. Phys. Chem.* 71: 2511-6 (1967).  
[5] Mechanism proposed by T.W. Martin and M.V. Stevens, The 12th Informal Conference on Photochemistry, June 28 - July 1, 1976, Natl. Bur. Stds., Gaithersburg, MD, Extended Abstracts, G2, p.1-5.  
[6] Other mechanisms for formation have been proposed, i.e. see reference in footnote [4].

NO<sup>-</sup>

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

Transient: NO<sup>-</sup>, λ(max) ≈ 260 nm, ε<sub>260</sub> ≈ 1200 L mol<sup>-1</sup> cm<sup>-1</sup> [1,2]

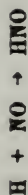
System: aqueous solution of ≈ 10<sup>-4</sup> mol L<sup>-1</sup> NO, pH 7.0 (buffered) [3]

Reference: W.A. Seddon, J.W. Fletcher, and F.C. Sopchyshyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1  $\mu$ s; dose per pulse  $\approx$  3 krad; dosimetry [4]

Spectral acquisition: monitoring lamp [5]; Bausch & Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time delay immediately after pulse

Transient formation [7]:

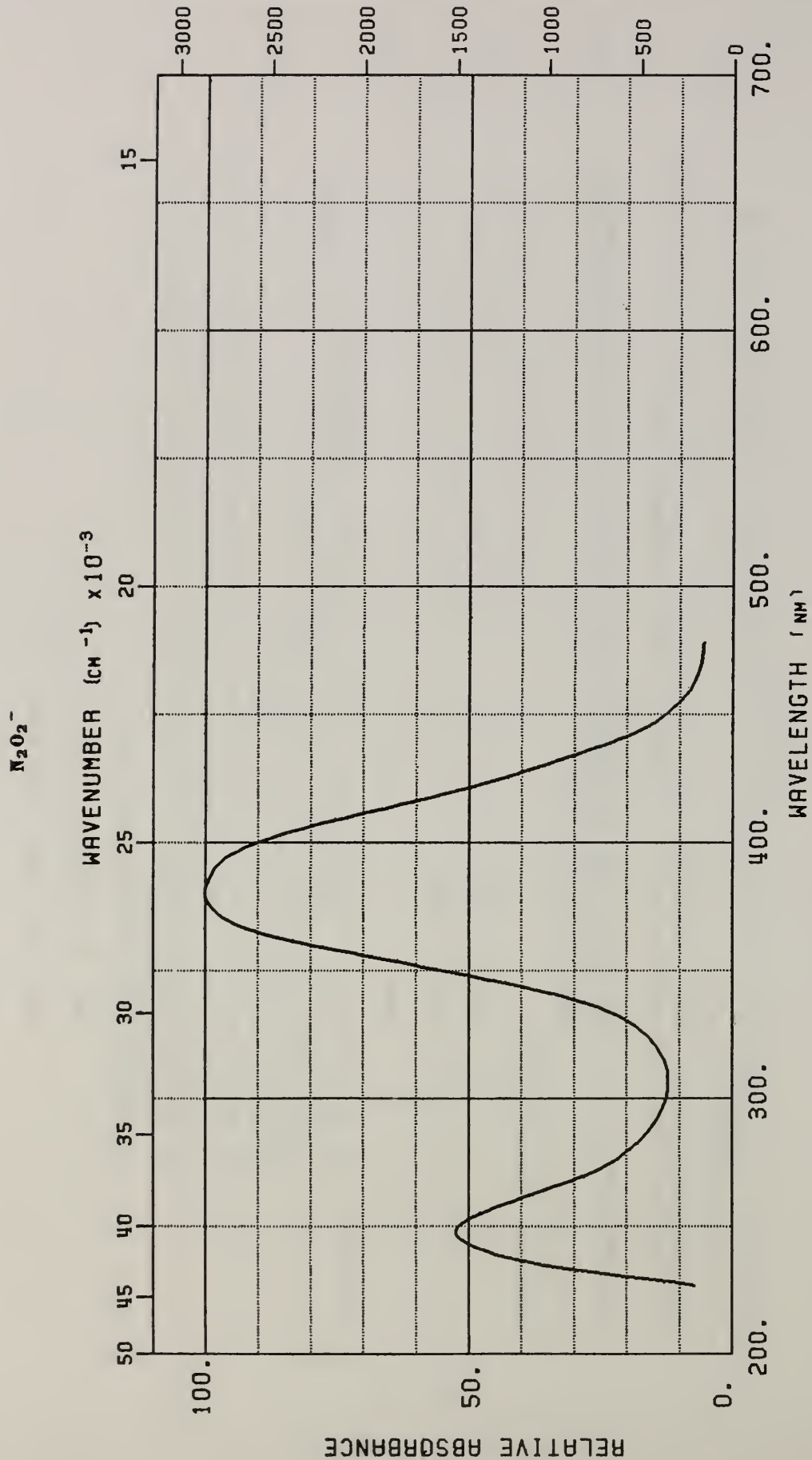


Footnotes:

- [1] Extinction coefficient based on  $C(NO^-) = C(e(aq)^-) + C(H) = 3.2$ .
- [2] Earlier value - 1400 L mol<sup>-1</sup> cm<sup>-1</sup>, M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1003-10 (1970).
- [3] Fresh solutions were used for each pulse.
- [4] Using aerated, 2 x 10<sup>-3</sup> mol L<sup>-1</sup> SCN<sup>-</sup> solutions and taking  $C_e = 2.10 \times 10^4$  for (SCN)<sub>2</sub><sup>-</sup> at 475 nm. Relative dose monitored by integrating current striking an Al block.
- [5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.
- [6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.
- [7] Hydroxyl radical reactions were



EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient: N<sub>2</sub>O<sub>2</sub><sup>-</sup>, λ(max) = 380 nm, ε<sub>380</sub> = (2850 ± 200) L mol<sup>-1</sup> cm<sup>-1</sup> [1,2]

System: aqueous solution of ~ 2 x 10<sup>-3</sup> mol L<sup>-1</sup> NO, pH 7.0 (buffered) [3]



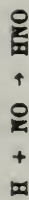
$$\text{N}_2\text{O}_2^-$$

Reference: W.A. Seddon, J.W. Fletcher, and F.C. Sopyshyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1  $\mu$ s; dose per pulse  $\approx$  3 krad; dosimetry [4]

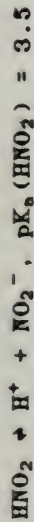
Spectral acquisition: monitoring lamp [5]; Bausch & Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time-delay-immediately after pulse

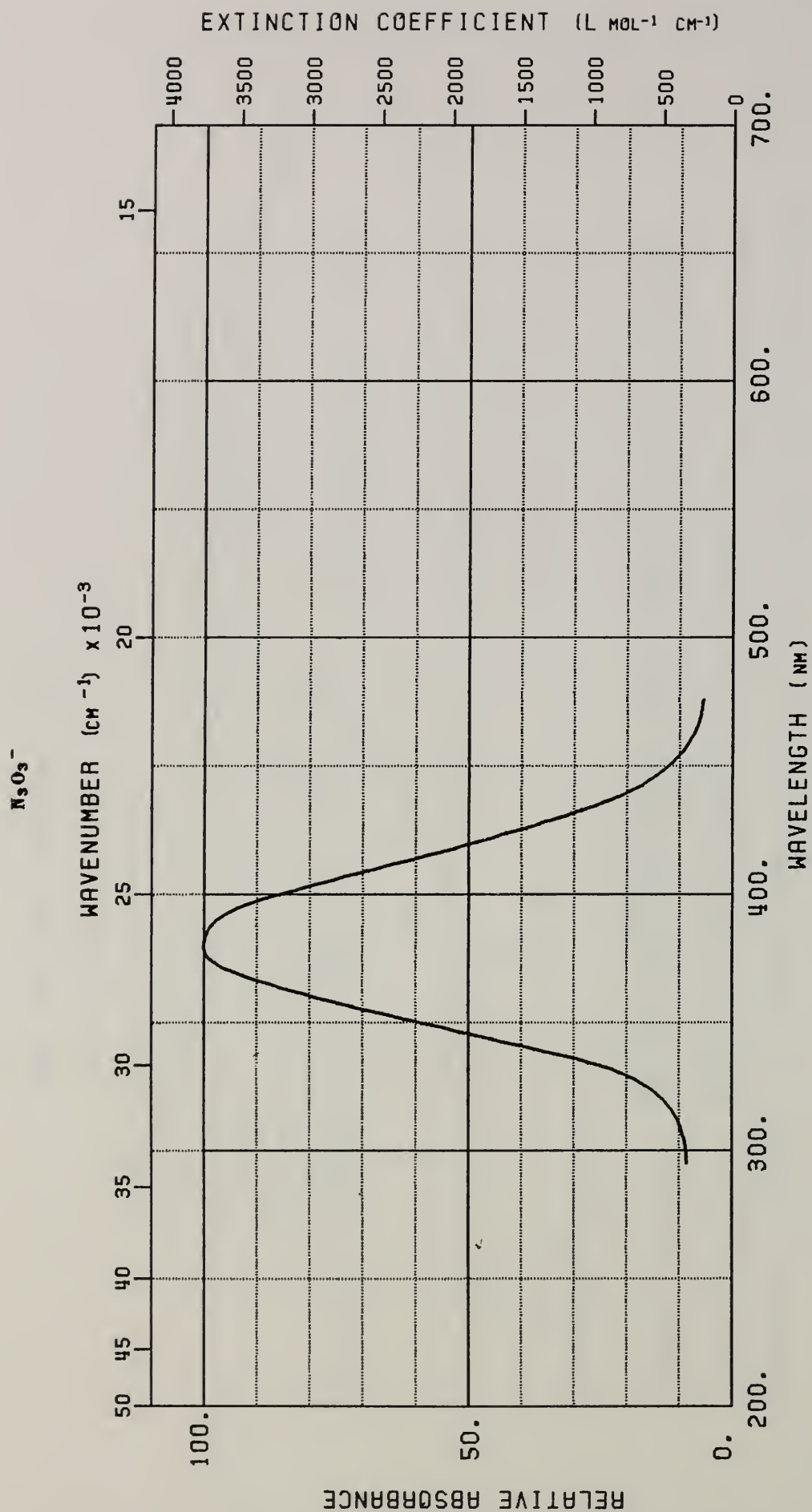
Transient formation [7]:



Footnotes:

- [1] Extinction coefficient based on  $\text{C}(\text{N}_2\text{O}_2^-) = \text{G}(e(\text{aq})^-) + \text{G}(\text{H}) = 3.2$ .
- [2] Earlier value -  $3300 \text{ L mol}^{-1} \text{ cm}^{-1}$ , M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1093-10 (1970).
- [3] Fresh solutions were used for each pulse.
- [4] Using aerated,  $2 \times 10^{-3} \text{ mol L}^{-1} \text{ SCN}^-$  solutions and taking  $\text{G}_e = 2.10 \times 10^4$  for  $(\text{SCN})_2^-$  at 475 nm. Relative dose monitored by integrating current striking on Al block.
- [5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, or a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.
- [6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.
- [7] Hydroxyl radical reactions were





Transient: N<sub>2</sub>O<sub>3</sub><sup>-</sup>, λ(max) = 380 nm, ε<sub>380</sub> = (3750 ± 300) L mol<sup>-1</sup> cm<sup>-1</sup> [1,2]

System: aqueous solution of ≈ 2 × 10<sup>-3</sup> mol L<sup>-1</sup> NO, pH 7.0 (buffered) [3]

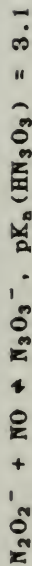
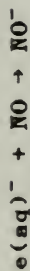
$\text{N}_3\text{O}_3^-$ 

Reference: W.A. Seddon, J.W. Fletcher, and F.C. Sopchysyn, Can. J. Chem. 51(7): 1123-30 (1973)

Transient generation: pulse radiolysis, using Van de Graaff generator; energy 2.25 MeV; pulse length 1  $\mu\text{s}$ ; dose per pulse  $\approx$  3 krad; dosimetry [4]

Spectral acquisition: monitoring lamp [5]; Bausch & Lomb f/3.5 high intensity monochromator; RCA 1P28 or HTV R166 PMT [6]; Tektronix 556 oscilloscope; time delay-extrapolated back to end of pulse

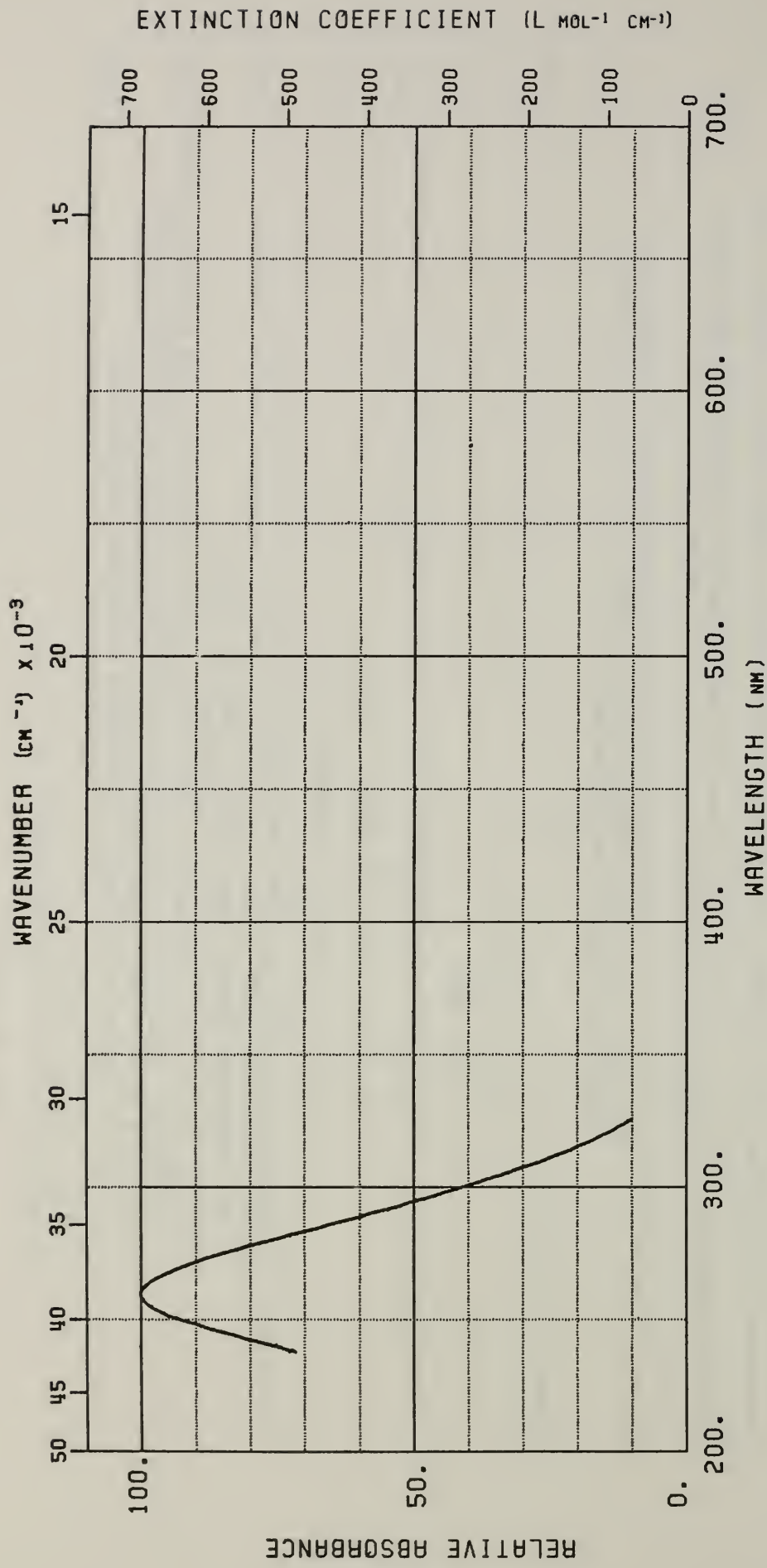
Transient formation [7]:



Footnotes:

- [1] Extinction coefficient based on  $\text{C}(\text{N}_3\text{O}_3^-) = \text{C}(e(\text{aq})^-) + \text{C}(\text{H}) = 3.2$ .
- [2] Earlier value - 4000 L mol<sup>-1</sup> cm<sup>-1</sup>, M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges Physik. Chem. 74(10): 1063-10 (1970).
- [3] Fresh solutions were used for each pulse.
- [4] Using aerated, 2 x 10<sup>-3</sup> mol L<sup>-1</sup> SCN<sup>-</sup> solutions and taking  $\text{C}_e = 2.10 \times 10^4$  for (SCN)<sub>2</sub><sup>-</sup> at 475 nm. Relative dose monitored by integrating current striking an Al block.
- [5] Either a Hanovia 300 W high pressure xenon lamp operated in DC or pulsed mode, or a GE 62 W quartz-iodine lamp, or a 30/50 W deuterium lamp was used.
- [6] For wavelengths shorter than 300 nm the R166 PMT was used with narrow band pass interference filters.
- [7] Hydroxyl radical reactions were





Transient:  $\text{NO}_2^{2-}$  [1],  $\lambda(\text{max}) = 260 \text{ nm}$ ,  $\epsilon_{260} = 680 \text{ L mol}^{-1} \text{ cm}^{-1}$

System: aqueous solution of  $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ NO}_2^-$  and  $0.25 \text{ mol L}^{-1}$  tert-butanol,  $\text{pH} = 9$ , Ar-saturated



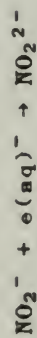
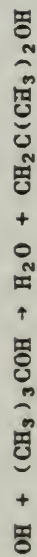
$\text{NO}_2^{2-}$

Reference: M. Graetzel, A. Henglein, J. Lillie, and G. Beck, Ber. Bunsenges. Physik. Chem. 73(7): 646-53 (1969)

Transient generation: pulse radiolysis [2] using Van de Graaff generator; energy 1.6 MeV

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display

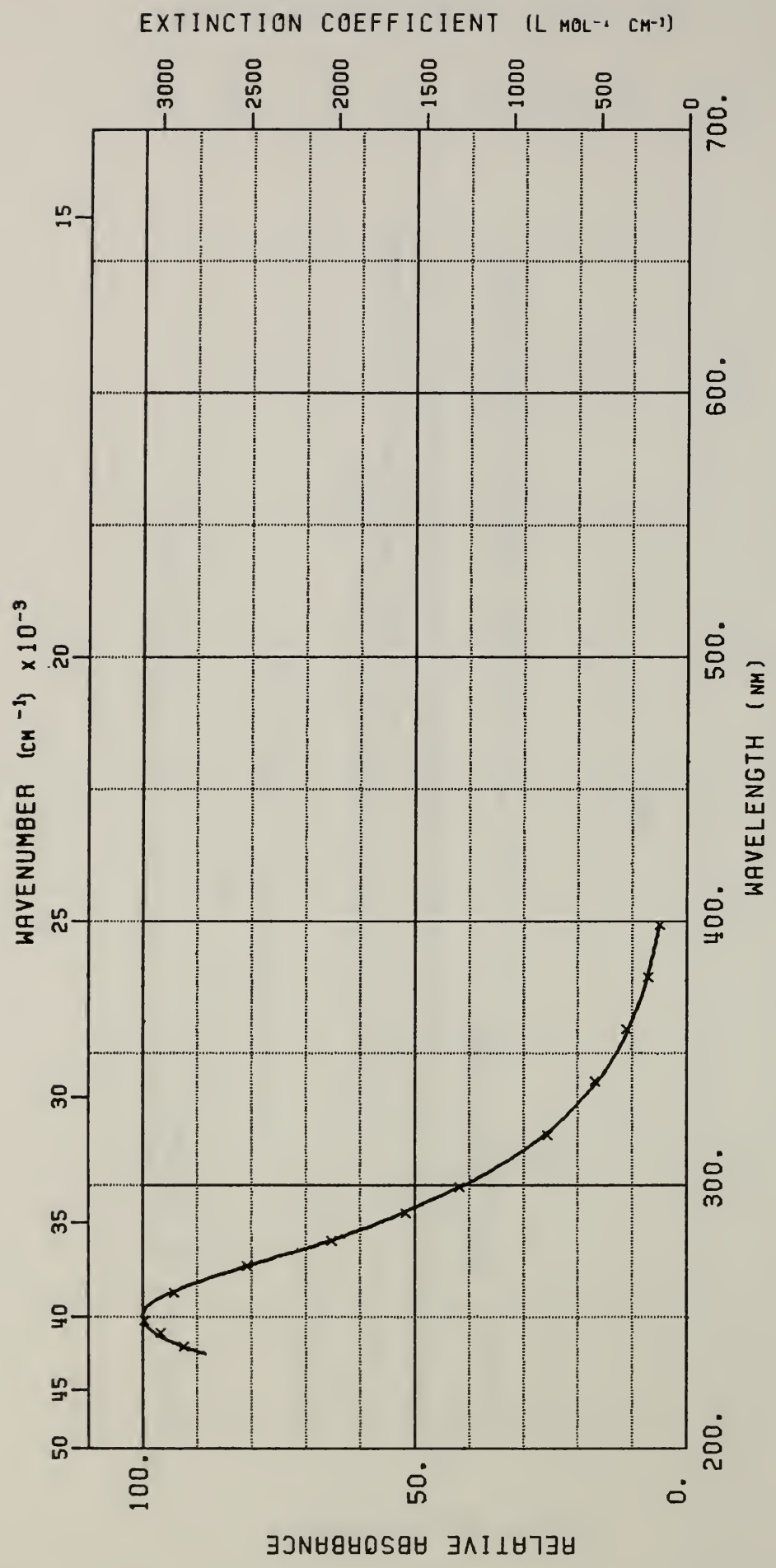
Transient formation:



Footnotes: [1]  $\text{p}K_a(\text{HNO}_2^-) = 7.7$ .

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

$\text{NO}_3^{2-}$



Transient:  $\text{NO}_3^{2-}$ ,  $\lambda(\text{max}) = 250 \text{ nm}$ ,  $\epsilon_{250} = 3100 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1]

System: aqueous solution of  $2 \times 10^{-4} \text{ mol L}^{-1} \text{ NO}_3^-$  and  $0.1 \text{ mol L}^{-1}$  tert-butanol, pH 9.5

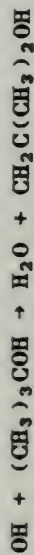
$\text{NO}_3^{2-}$

Reference: M. Graetzel, A. Henglein, and S. Taniguchi, Ber. Bunsenges. Physik. Chem. 74(3): 292-8 (1970)

Transient generation: pulse radiolysis [2], using Van de Graaff generator

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay, immediately after pulse

Transient formation:



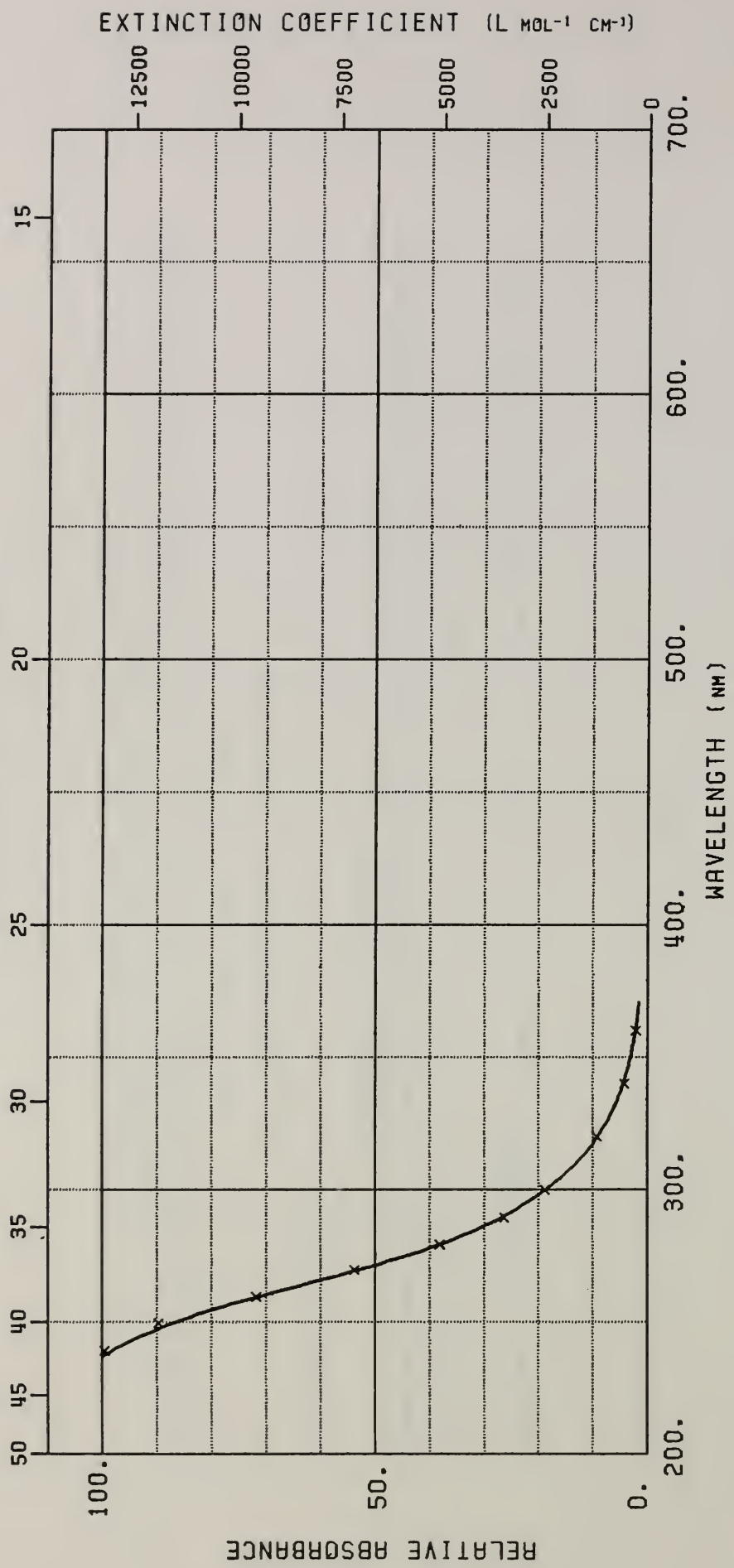
$$e(\text{aq})^- + \text{NO}_3^- \rightarrow \text{NO}_3^{2-}, \text{p}K_a(\text{HNO}_3^-) = 7.5$$

Footnotes: [1] Based on  $G(e(\text{aq})^-) \approx 2.7$ . Effect of H atom was neglected because rate constant for reaction of H with  $\text{NO}_3^-$  is small,  $k = 3.8 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  from G. Navon and C. Stein, J. Phys. Chem. 69: 1384-9 (1965).

[2] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

N2O3

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



EXTINCTION COEFFICIENT ( $\text{L MOL}^{-1} \text{ CM}^{-1}$ )

12500  
10000  
7500  
5000  
2500  
0

Transient: N2O3 [1,2]

System: aqueous solution of  $2.0 \times 10^{-5}$  to  $1.04 \times 10^{-4}$  mol  $\text{L}^{-1}$  NO,  $2 \times 10^{-4}$  to  $3 \times 10^{-4}$  mol  $\text{L}^{-1}$  NO2^-, and  $2.4 \times 10^{-2}$  mol  $\text{L}^{-1}$  N2O



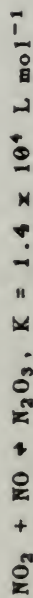
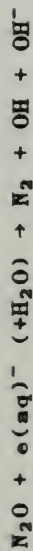
## $N_2O_3$

Reference: M. Graetzel, S. Taniguchi, and A. Henglein, Ber. Bunsenges. Physik. Chem. 74(5): 488-92 (1970)

Transient generation: pulse radiolysis [3], using Van de Graaff generator; energy 1.5 MeV; dose rate during the pulse was 700 rad per  $\mu s$

Spectral acquisition: Osram XB0 450 monitoring lamp; Zeiss M403 monochromator; EMI 9558 PMT; decay curves photographed from oscilloscope display; time delay 20  $\mu s$

Transient formation [4]:

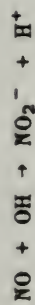


Footnotes: [1] Extinction coefficient was obtained by assuming that the yield of  $NO_2 + N_2O_3$  was equal to the initial yield of  $NO_2$ .

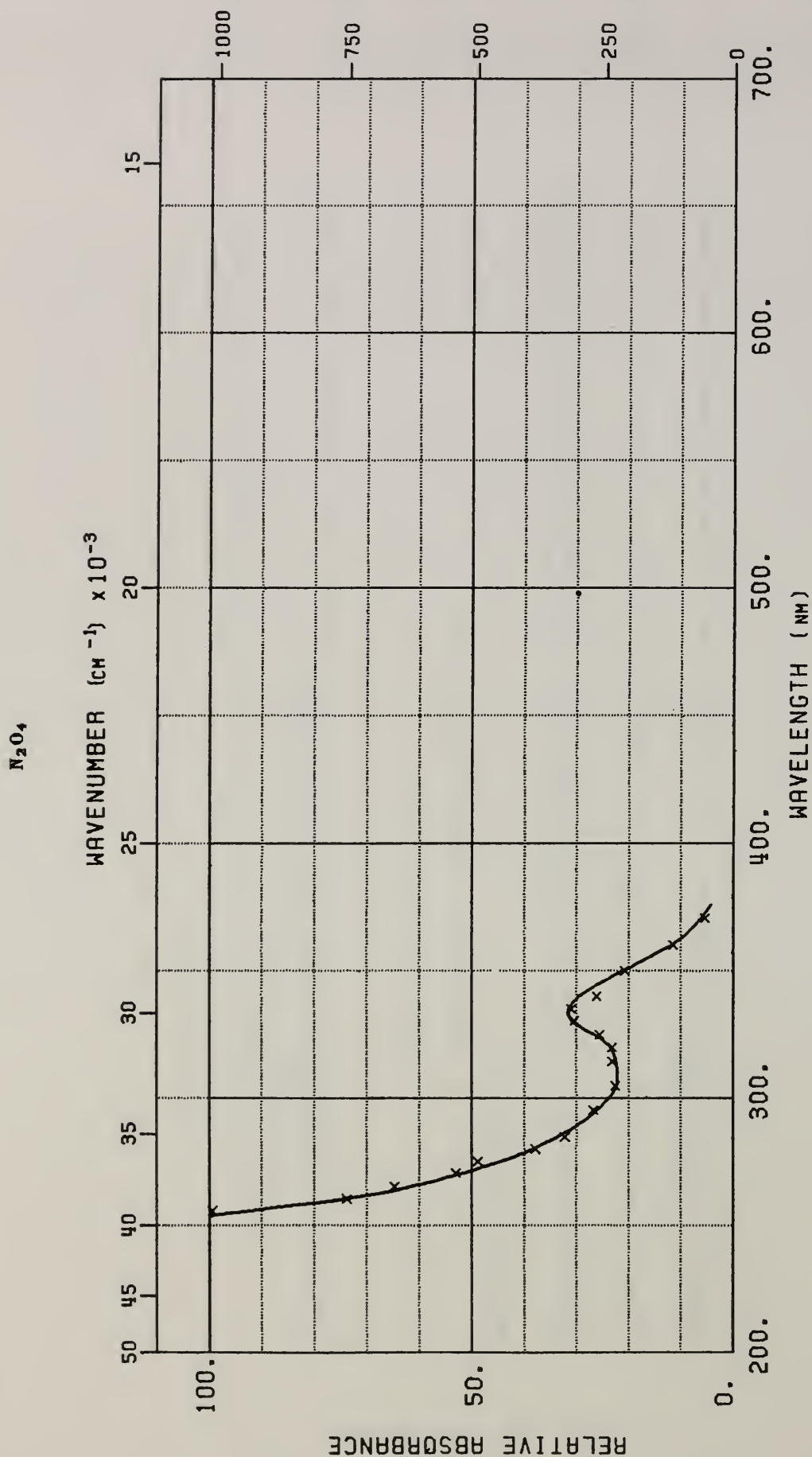
[2] Spectrum corrected for  $NO_2$  absorption.

[3] A. Henglein, Allg. Prakt. Chem. 17(5): 295-301 (1966).

[4] Reaction of OH with NO does not involve complications since little reacts under the experimental conditions. Any NO that does react with OH only reforms the initial reactants



EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



Transient [1]: N<sub>2</sub>O<sub>4</sub>, λ(max) ≈ 340 nm, ε<sub>335</sub> = (320 ± 60) L mol<sup>-1</sup> cm<sup>-1</sup> [2]

System: aqueous solution of 9.5 × 10<sup>-4</sup> mol L<sup>-1</sup> NO<sub>2</sub><sup>-</sup>, saturated with N<sub>2</sub>O (≈ 2.5 × 10<sup>-2</sup> mol L<sup>-1</sup>), pH 5.0

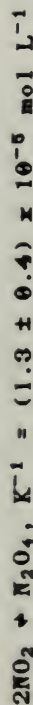
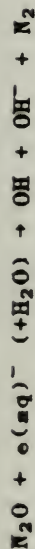
## N<sub>2</sub>O<sub>4</sub>

Reference: A. Treinin and E. Hayon, J. Am. Chem. Soc. 92(20): 5821-8 (1970)

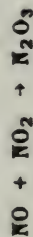
Transient generation [3]: pulse radiolysis, using Febetron 705 System (Field Emission Corp.); pulse energy 2.3 MeV; pulse length  $\approx$  30 ns; dosimetry using N<sub>2</sub>O-saturated aqueous solution of  $\theta$ .1 KSCN [4]

Spectral acquisition [3]: Osram XBO 450 W xenon lamp (pulsed); two high-intensity Bausch & Lomb monochromators, used in series to reduce scattered light [5]; two EMI 9558 QB PMT; dual beam Fairchild 777 oscilloscope; time delay 160  $\mu$ s after pulse

Transient formation:



Footnotes: [1] Absorption at wavelength shorter than 300 nm may be partially due to N<sub>2</sub>O<sub>3</sub> which can be formed by



where NO was produced by H atom reactions.

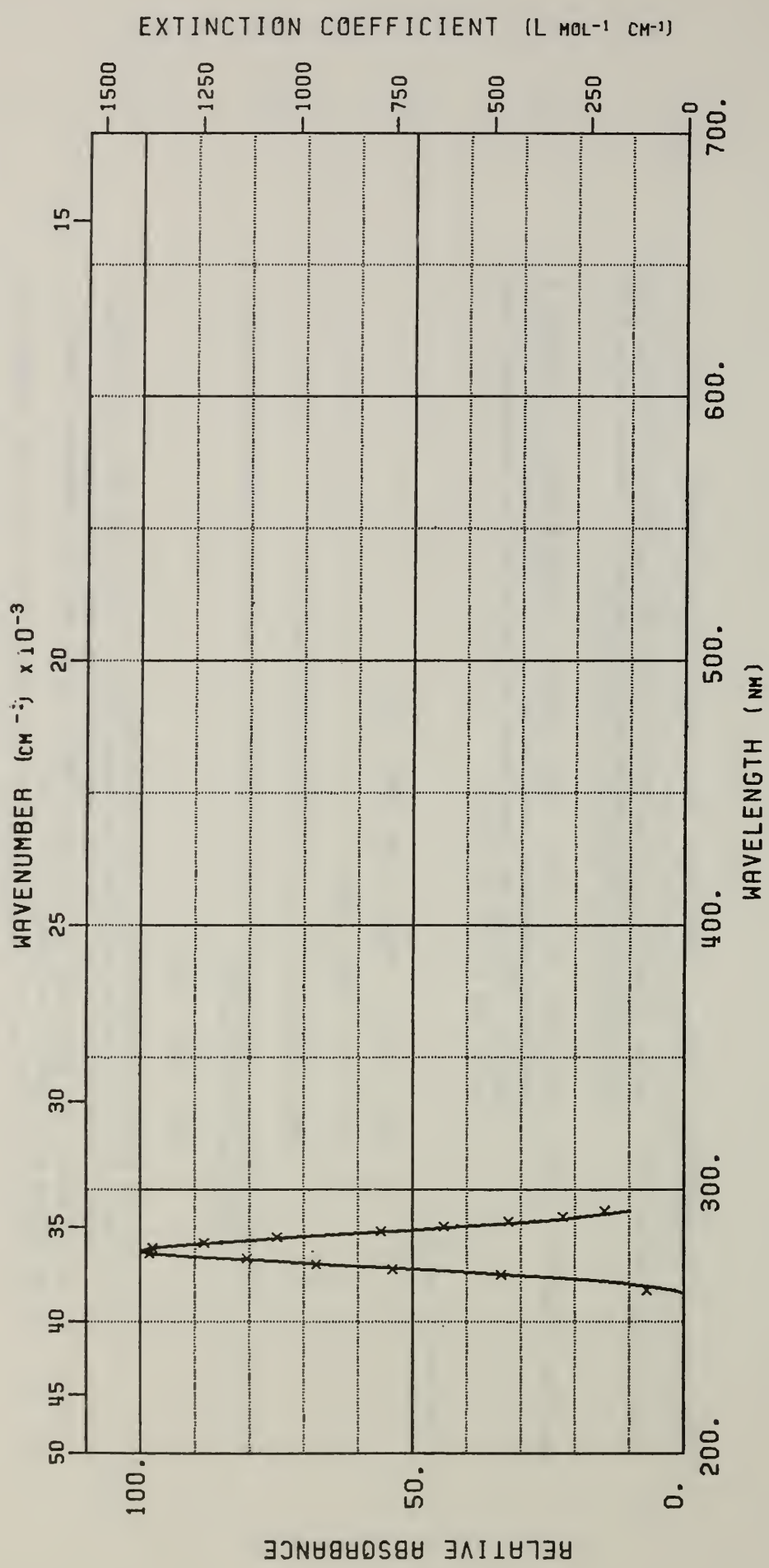
[2] Based on equilibrium equations for equilibrium of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> and taking  $c(\text{NO}_2) = 200 \text{ L mol}^{-1} \text{ cm}^{-1}$  at the maximum of the NO<sub>2</sub> spectrum.

[3] M. Simic, P. Neta, and E. Hayon, J. Phys. Chem. 73(11): 3794-800 (1969).

[4] Using  $\epsilon_{500}(\text{SCN})_2^- = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

[5] At 230 and 210 nm the amount of scattered light was 1% and 18%, respectively.

$N_3$



Transient [1]:  $N_3$ , azide radical,  $\lambda(\text{max}) = 277 \text{ nm}$ ,  $\epsilon_{275} = 1400 \text{ L mol}^{-1} \text{ cm}^{-1}$  [2,3],  
 $2k = (8.0 \pm 0.7) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  [2]

System: aqueous solution of  $10^{-4} \text{ mol L}^{-1} \text{ NaN}_3$ ,  $\text{pH} \approx 9.4$ ,  $N_2$ -saturated



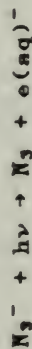
### $N_3$

Reference: A. Treinin and E. Hayon, J. Chem. Phys. 50: 538-9 (1969)

Transient generation [4]: flash photolysis with four oxygen flash lamps; total flash energy 1800 J; duration at "1/e" time 5  $\mu$ s, total flash duration 70  $\mu$ s

Spectral acquisition [4]: xenon Osram XBO 450 W monitoring lamp; Bausch & Lomb grating monochromator; PMT; Tektronix 535A oscilloscope; spectrum was obtained by a point-by-point method; time delay 120  $\mu$ s after start of flash

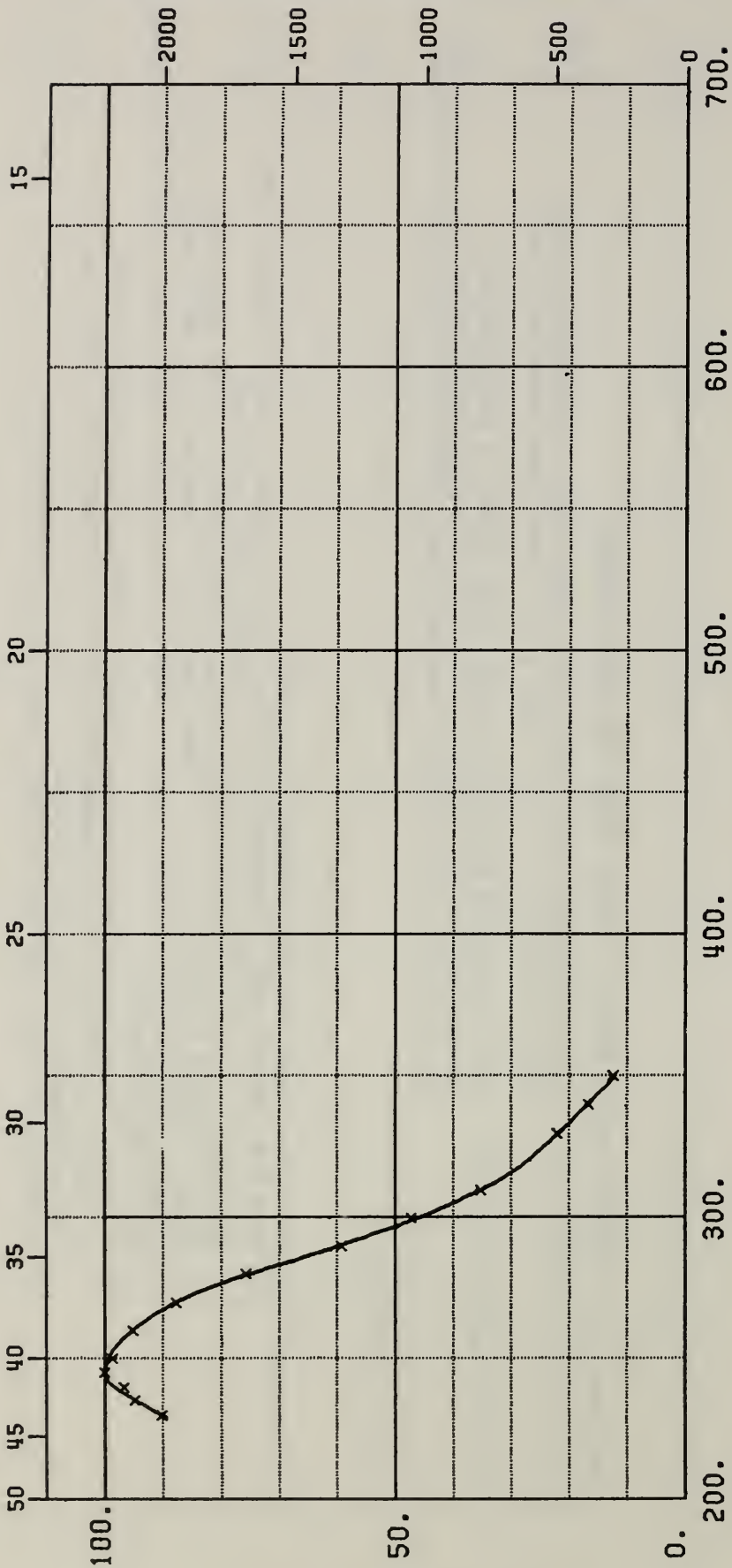
Transient formation:



- Footnotes: [1] Each data point was the average of six runs.  
[2] From C.V. Buxton and I. Janovsky, J. Chem. Soc., Faraday 1 72(8): 1884-6 (1976).  
Other sets of  $\epsilon$  and  $2k$  for  $N_3$  are  $\epsilon_{278} = 2300 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $2k = (9 \pm 1) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  from E. Hayon and M. Simic, J. Am. Chem. Soc. 92(25): 7486-7 (1970); and  $\epsilon_{278} = 1300 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $2k = 6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  from E.J. Land and W.A. Prutz, Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med. 36(1): 75-83 (1979).  
[3] Although the displayed spectrum has  $\lambda(\text{max}) = 277 \text{ nm}$ , the  $\epsilon(\text{max})$  is shown as  $1400 \text{ L mol}^{-1} \text{ cm}^{-1}$  on the assumption that all the authors in this case were making measurements at the maximum.  
[4] L. Dogliotti and E. Hayon, J. Phys. Chem. 71(8): 2511-6 (1967).

$\cdot\text{CONH}^-$

WAVENUMBER ( $\text{cm}^{-1}$ )  $\times 10^{-3}$



RELATIVE ABSORBANCE

WAVELENGTH (NM)

Transient:  $\cdot\text{CONH}^-$ ,  $\lambda(\text{max}) = 245 \text{ nm}$ ,  $\epsilon_{245} = 2200 \text{ L mol}^{-1} \text{ cm}^{-1}$  [1],  $2k = 2.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$

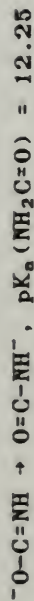
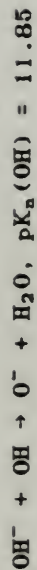
System: aqueous solution of  $10^{-3} \text{ mol L}^{-1} \text{ CN}^-$  in  $1 \text{ mol L}^{-1} \text{ KOH}$ , saturated with  $\text{N}_2\text{O}$

Reference: D. Behar, J. Phys. Chem. 78(26): 2660-3 (1974)

Transient generation: pulse radiolysis, using electrons from Van de Graaff generator; energy 2.8 MeV; pulse length 0.5-2  $\mu$ s; dose 1-5 krad [2]

Spectral acquisition [3]: single-pass cell, pulsed Osram 450 W XBO xenon monitoring lamp; Bausch & Lomb monochromator, focal length 500 cm, bandwidth 2 nm; EMI 9558 QC PMT; corrected for stray light below 240 nm

Transient formation [4]:



Footnotes: [1] Extinction coefficient determined by comparing absorption to  $(\text{SCN})_2^-$  with  $\epsilon(\text{max}) = 7600 \text{ L mol}^{-1} \text{ cm}^{-1}$  and by assuming  $\text{C}(\text{radicals}) = \text{C}(\text{e}(\text{aq})^-) + \text{C}(\text{OH})$ .

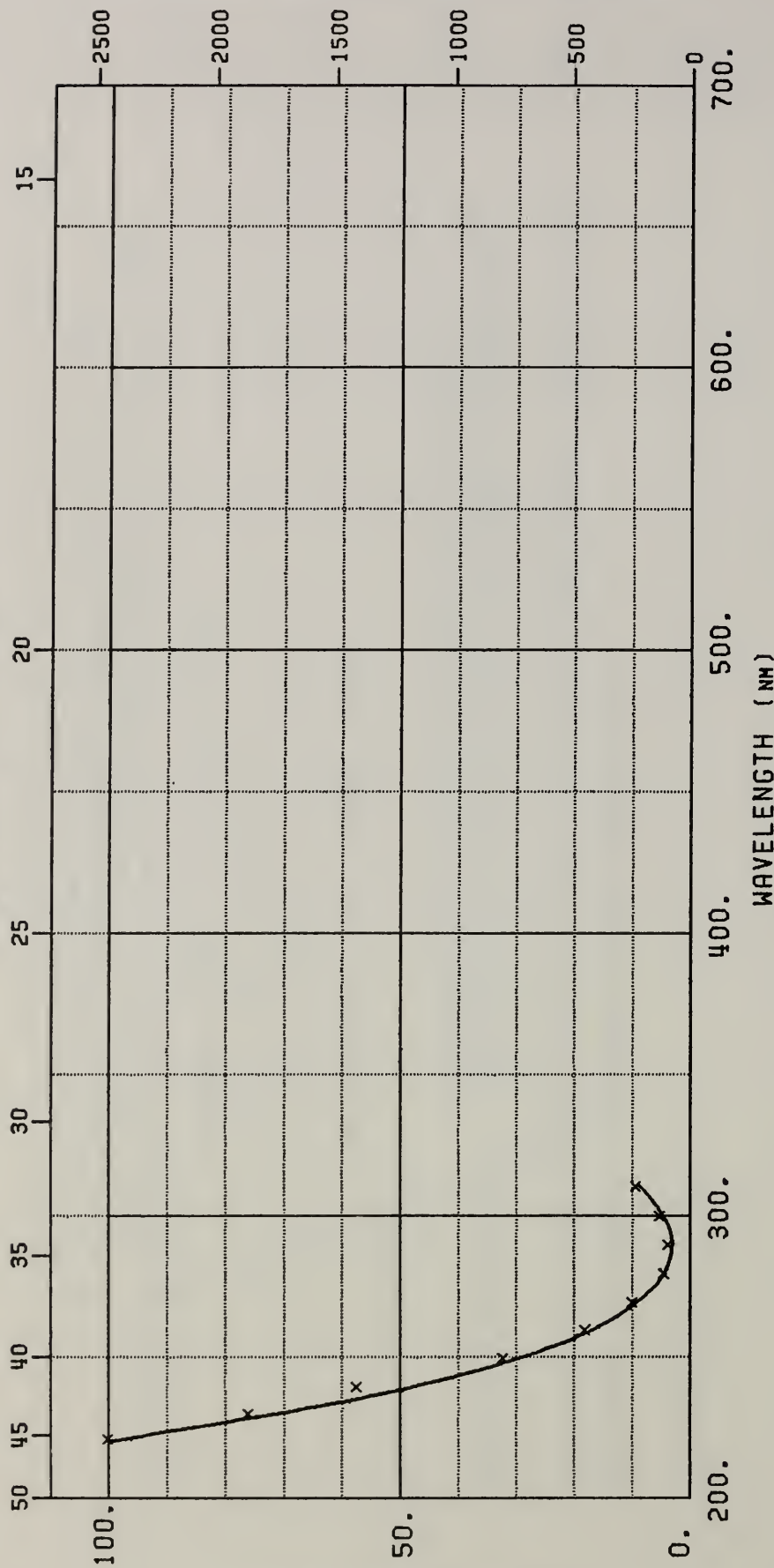
[2] Electron beam monitored by a secondary emission monitor.

[3] L.K. Patterson and K.M. Bansal, J. Phys. Chem. 76(17): 2392-9 (1972).

[4] H. Buechler, R.E. Buechler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976).

O=CNH<sub>2</sub>

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

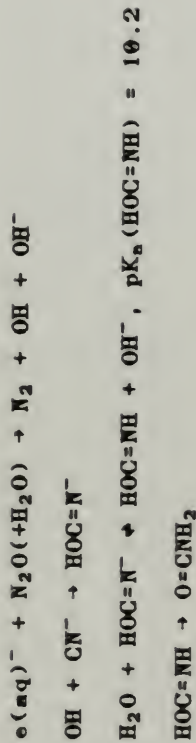
Transient: O=CNH<sub>2</sub> [1,2], 2k = 6.2 x 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>  
System: variety of aqueous solutions of either 10<sup>-1</sup> mol L<sup>-1</sup> CN<sup>-</sup> or 10<sup>-2</sup> mol L<sup>-1</sup> CN<sup>-</sup>, pH 9.85 to 11.5; all solutions saturated with N<sub>2</sub>O



O=CNH<sub>2</sub>

- Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)
- Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose 25.8 to 31.2 krad
- Spectral acquisition [3]: xenon XB0 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Phillips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

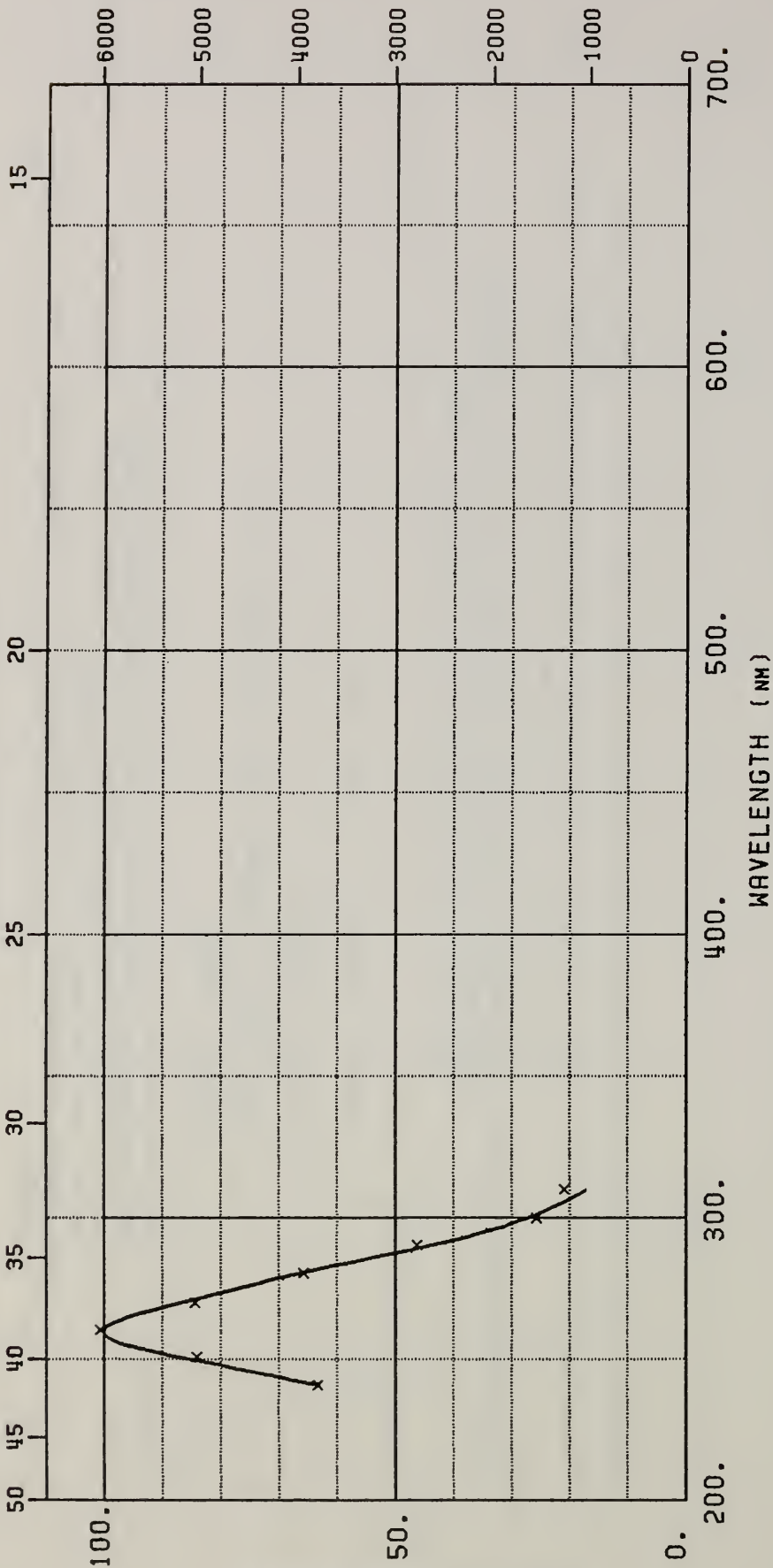
Transient formation:



- Footnotes: [1] Spectrum corrected for spectra of the precursors HOC=NH and HOC=N<sup>-</sup>. This was done by computer simulation of the kinetic scheme.
- [2] Earlier spectrum by D. Behar, J. Phys. Chem. 78(26): 2660-3 (1974), shows a weak maximum in the region of 320 nm.
- [3] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

HOC=NH

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

Transient: HOC=NH [1]

System [2]: aqueous solution of 10<sup>-2</sup> mol L<sup>-1</sup> CN<sup>-</sup>, pH 9.85, saturated with N<sub>2</sub>O

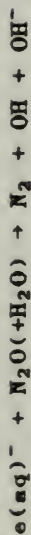
HOC=NH

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53. (1976)

Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 25.8 krad

Spectral acquisition [3]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556); time delay variable [4]

Transient formation:



Footnotes: [1] Spectrum was obtained from a computer simulation using the above equations in addition to known rate constants and

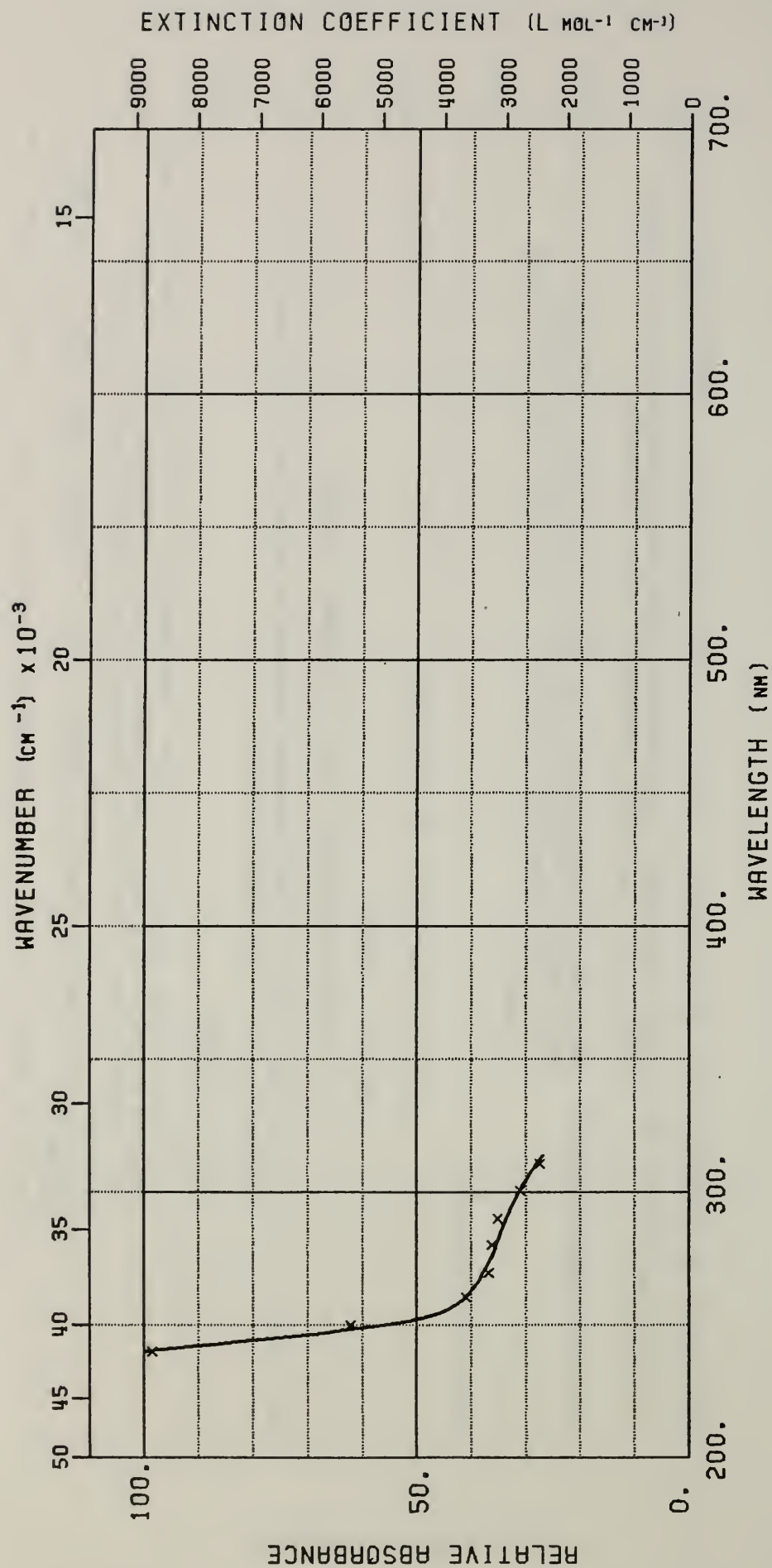


[2] Two other chemical systems were used. One had  $[CN^-] = 10^{-2} \text{ mol L}^{-1}$ , pH 10.7, and received a dose = 25.8 krad. The other had  $[CN^-] = 10^{-1} \text{ mol L}^{-1}$ , pH = 11.4, and received a dose = 28.1 krad. Both of these solutions were saturated with  $N_2O$ .

[3] B. Hurni, U. Bruehlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

[4] Transient makes contribution to experimental spectrum only for time less than 1  $\mu s$ .

HOC=N<sup>-</sup>



Transient: HOC=N<sup>-</sup> [1]

System [2]: aqueous solution of 10<sup>-2</sup> mol L<sup>-1</sup> CN<sup>-</sup>, pH 10.7, saturated with N<sub>2</sub>O



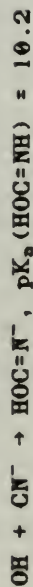
HOC=N<sup>-</sup>

Reference: H. Buechler, R.E. Buehler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [3]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 25.8 krad

Spectral acquisition [3]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556); time delay variable [4]

Transient formation:



Footnotes: [1] Spectrum was obtained from a computer simulation of the



system, using known rate constants.

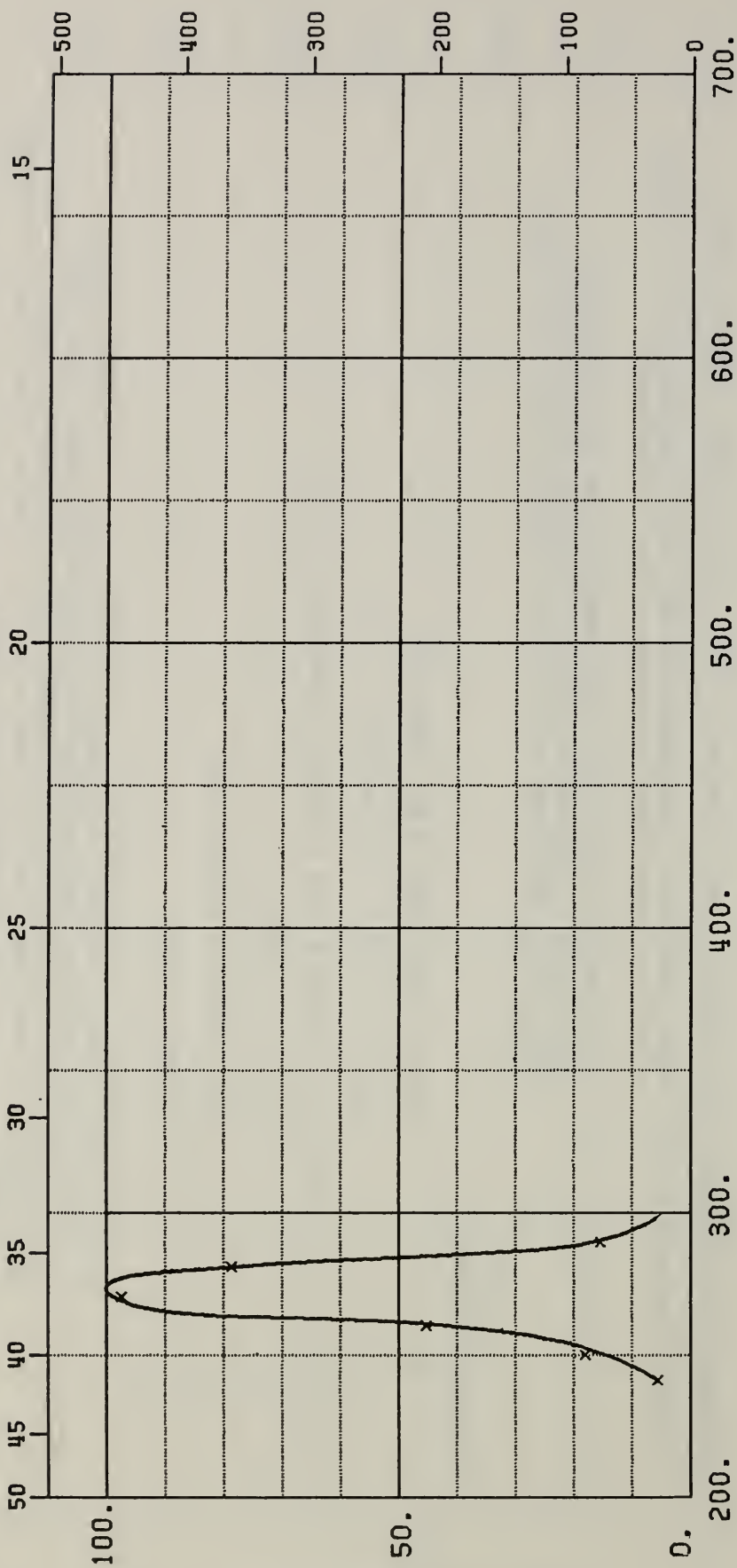
[2] Two other chemical systems were used at pH 9.85 and 11.4. [CN<sup>-</sup>], [N<sub>2</sub>O], and the dose were the same in the pH 9.85 system; but [CN<sup>-</sup>] = 10<sup>-1</sup> in the pH 11.4 system, and the dose was 28.1 krad in the pH 11.4 system.

[3] B. Hurnl, U. Bruchlman, and R.E. Buehler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

[4] Transient makes contribution to experimental spectrum only for time less than 1 μs.

H<sub>2</sub>CN

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



RELATIVE ABSORBANCE

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)

Transient: H<sub>2</sub>CN [1], 2k = (2.6 ± 0.8) × 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of 10<sup>-1</sup> mol L<sup>-1</sup> HCN, pH 1.9

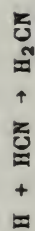
## H<sub>2</sub>CN

Reference: H. Buechler, R.E. Buehler, and R. Cooper, *J. Phys. Chem.* 80(14): 1549-53 (1976)

Transient generation [2]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 34.8 krad

Spectral acquisition [2]: xenon XBO 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Phillips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

Transient formation:

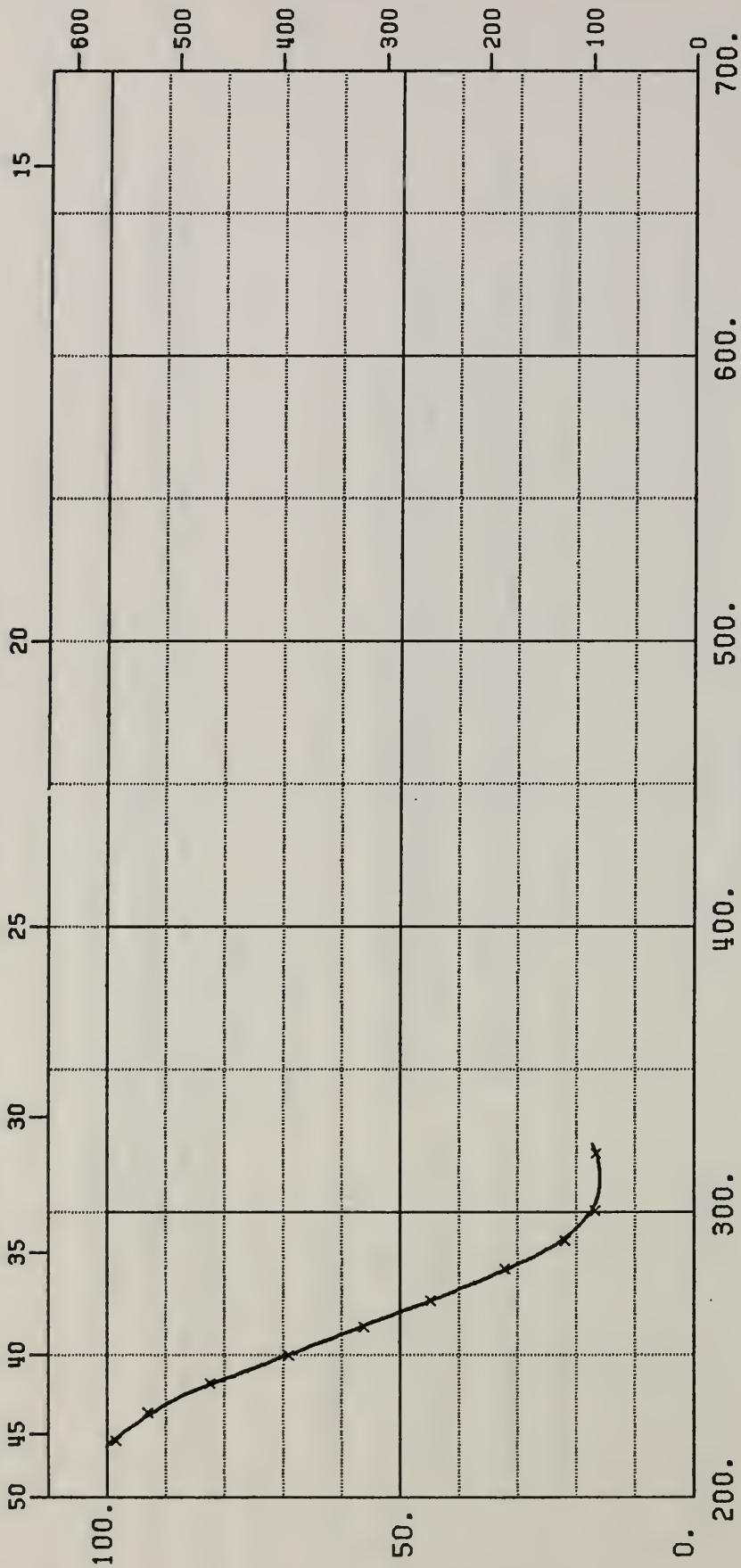


Footnotes: [1] Spectrum determined using computer optimization of some of the rate constants plus computer analysis of spectra from the pH 1.9 HCN system and other acidic HCN solutions which were saturated with N<sub>2</sub>O.

[2] B. Hurni, U. Bruehlman, and R.E. Buehler, *Int. J. Radiat. Phys. Chem.* 7: 499-506 (1975).

HOCH=N.

WAVENUMBER (CM<sup>-1</sup>) x 10<sup>-3</sup>



RELATIVE ABSORBANCE

WAVELENGTH (NM)

Transient: HOCH=N. [1], 2k = (2.8 ± 0.5) x 10<sup>9</sup> L mol<sup>-1</sup> s<sup>-1</sup>

System: aqueous solution of 10<sup>-1</sup> mol L<sup>-1</sup> HCN, pH 2.85, saturated with N<sub>2</sub>O

EXTINCTION COEFFICIENT (L MOL<sup>-1</sup> CM<sup>-1</sup>)



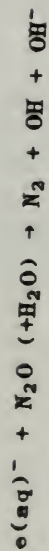
HOCH=N.

Reference: H. Buechler, R.E. Buechler, and R. Cooper, J. Phys. Chem. 80(14): 1549-53 (1976)

Transient generation [2]: pulse radiolysis, using Febetron 705 (Field Emission Corp.); energy 2 MeV; dosimetry using calorimetry; dose = 34.8 krad

Spectral acquisition [2]: xenon XB0 450 monitoring lamp; Bausch & Lomb High Intensity monochromator; Philips XP 1003 PMT; Keithley pulse amplifier (Model 105); dual-beam oscilloscope (Tektronix 556)

Transient formation:



Footnotes:

- [1] Spectrum corrected for OH absorption and the H atom reaction product, H<sub>2</sub>CN. This was done using computer simulation.
- [2] B. Hurni, U. Bruehlman, and R.E. Buechler, Int. J. Radiat. Phys. Chem. 7: 499-506 (1975).

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