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SPECTROCHEMISTRY AND SPECTRUM RESOLUTION OF SOME IODINE SPECIES IN ACIDIC, NEUTRAL, AND BASIC SOLUTIONS

W. Davis, Jr.
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W. Davis, Jr., and A. H. Kibbey

JANUARY 1972

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CONTENTS

	Page
Abstract	1
1. Introduction	1
2. Experimental	3
2.1 Solutions	4
3. Results	5
3.1 Resolution into Overlapping Gaussian Bands	5
3.2 Standard Spectra for Linear Resolution and Chemical Analysis	8
3.3 A Practical Example	9
4. Discussion	10
5. Summary and Conclusions	15
6. Tables and Figures	16
7. References	49

SPECTROCHEMISTRY AND SPECTRUM RESOLUTION OF SOME IODINE SPECIES IN ACIDIC, NEUTRAL, AND BASIC SOLUTIONS

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ABSTRACT

Spectra of various species of iodine in acidic, neutral, and basic solutions (from 3 *M* HNO_3 to 1 *M* NaOH) were recorded over the wavelength region 190 to 700 nm. We were able to fit these spectra to the model of a series of overlapping bands of Gaussian shape within the stated limit of accuracy of the Cary 14R spectrophotometer. Regardless of whether the bands are of this, or a more complicated, shape, the model allows us to relate a portion of the measured absorption to a specific ionic or molecular component, such as I^-, I_3^-, and $I_2 \cdot aq$, in a more quantitative manner than has been done previously. The model has been used to provide tabular values of molar absorptivities and to initiate the formation of a "library" of standard spectra. This library should find application in the determination of the ionic and molecular structures of various iodine (and other) species in solution just as the standard gamma-ray spectra have been useful for determining, by spectrum resolution, how much of each of many gamma-ray emitting nuclides is present in a solution. In addition to providing some standard spectra, the present study has cast doubt on the accuracy of a textbook method for preparing hypoiodous acid (HOI). Also presented are results of the conversion of I^- to I_2 in nitric acid solution, of I_2 to I^- in basic solution, and of other species, probably including hypoiodite ion (IO^-), to additional, unidentified components.

1. INTRODUCTION

The purpose of this report is to present some new variations on the use of optical absorption spectrometry for identifying iodine species in aqueous solutions such as those that will be encountered in processing Liquid Metal Cooled Fast Breeder Reactor (LMFBR) fuels.

"The retention or control of iodine is one of the major problems to be solved in the development of short-decay processing capability for LMFBR fuels. Overall

plant retention factors approaching 10^8 will be required for ^{131}I when 30-day-decay fuel is processed. In order to achieve an iodine retention of this order, new and highly reliable systems for removing iodine from plant effluent streams must be developed."[1] This quotation illustrates the importance of the iodine-control problem in the future LMFBR fuel processing economy. To achieve the goal of plant retention by factors approaching 10^8, we will require additional knowledge of the chemistry of iodine in acidic and basic solutions. Our lack of knowledge concerning the aqueous-phase chemistry of iodine, its liquid-vapor equilibrium, and the existence of short-lived species has been amply documented in the Proceedings of the Panel on "The Control of Iodine and Other Constituents of Airborne Radioactive Wastes"[2] and the Proceedings of the Eleventh AEC Air Cleaning Conference.[3] In addition, there are many individual articles, such as those of Eggleton,[4] Parsly,[5] Yuill et al.,[6] and Nishizawa et al.[7] on vaporization of iodine from solution, and of Grossweiner and Matheson[8] and of Arotsky et al.[9] on short-lived iodine species. Yarbro[3] of Oak Ridge National Laboratory has recently summarized his observations concerning "strange forms of iodine."

This report summarizes results obtained by use of optical absorption in the visible and UV regions, down to a wavelength of 190 nm. Previous workers have used this technique, but over narrower wavelength regions, to study iodine in strongly acid solutions,[9] in nearly neutral solutions,[10,11] and in alkaline solutions.[12] In general, interpretations of data were based on the assumptions of formation of various species, such as I^-, I_3^-, $I_2 \cdot aq$, HOI, IO^-, IO_3^-, etc., the existence of which was not demonstrated by alternative methods.

Since these earlier studies, several technological advances have made optical spectroscopy in the visible and UV regions considerably more useful in identifying chemical species in solution. First, extension of the spectra to about 190 nm, from earlier low values of 220 to 240 nm, has provided a considerable increase in the amount of useful information, as previously noted;[13] second, the increase in speed and memory size of digital computers has greatly extended the type of numerical analysis of data that can be performed. At least two types of numerical analysis of

an optical spectrum of a solution can provide useful information. First, a linear resolution can be used to calculate the quantities of each of several species if the spectra of the separate species are known and if it has been established that these spectra add together to form a composite spectrum. This concept has had great success in gamma-ray spectroscopy.[14] In particular, it is now standard practice[15-17] to determine the spectrum of a sample that may contain up to 20 gamma-ray emitters and to calculate the amount of each such nuclide in the sample at a cost of $50 to $75 per sample[18] for a few samples when no complications are encountered. Linear resolution has also been demonstrated[13] to be of potential use in determining the quantities of each of several urinary constituents from visible-UV spectra.

The second type of spectrum resolution is nonlinear; that is, the spectrum is represented by a series of overlapping (Gaussian or non-Gaussian) bands[19-21] whose parameters may be interpreted in terms of chemical species. The scope of the present report includes analyses of the spectra of some iodine-containing solutions according to the nonlinear technique to obtain band parameters that may have application to species identification and that will be useful in constructing composite spectra from partial spectra obtained with different absorption-cell lengths and different solute concentrations. Finally, we indicate how the smoothed spectra can become a part of a library of standards for use in estimating concentrations of at least some of the iodine species by linear resolution.

2. EXPERIMENTAL

Absorption spectra were obtained by use of a Cary 14R spectrophotometer interfaced[22] with a digital voltmeter and an IBM-026 keypunch, which produced cards listing the absorptivity at 0.5- or 1-nm intervals. All spectra of the present study were taken over the range 190 to 700 nm. "Pyrocell" (Pyrocell Manufacturing Co.) cylindrical absorption cells were of grade S18-260; lengths were 0.01 to 10 cm. Recorded spectra were usually of the differential type. For example, the spectrum of a test solution of 10^{-3} *M* I_2 in 0.1 *M* HNO_3 was obtained with 0.1 *M* HNO_3

in the reference cell. Thus, in this case, the resulting differential spectrum was nearly devoid of any contribution due to absorption by nitric acid.

2.1 Solutions

Solutions were prepared from high-purity chemicals and distilled-deionized water; in some cases, nitrogen-sparged water was used to eliminate oxygen. Some of the preparations were stored in 500-ml red, Kimble "Ray-Sorb" glass Erlenmeyer flasks with standard-taper stoppers (Kimax No. 26610) to minimize photochemical decomposition by laboratory lights; the others were stored in a refrigerator. Generally, the solutions were not subsequently analyzed since they were made up, by weight, in volumes sufficiently large to make composition errors negligible. Two exceptions were the solutions related to the preparation of hypoiodous acid (HOI) and the solubility of iodoform (CHI_3).

Hypoiodous acid was "made" according to textbook directions (see refs. 23 and 24), that is, by adding an excess of equimolar portions of HgO and I_2 to distilled-deionized water. The reaction is stated to be:

$$2\ HgO + 2\ I_2 + H_2O \rightarrow 2\ HOI + HgO \cdot HgI_2\ . \qquad (1)$$

The solution-precipitate from this preparation was filtered before use. Such a solution was analyzed for both mercury and iodine by neutron activation techniques. Separate solutions, with and without nitrogen sparging, were subsequently prepared, stored in an ice bath or refrigerator, and similarly filtered immediately before polarographic analysis for the oxidation states of all iodine species present. Reference solutions of HgI_2 and HgO in water were analyzed, respectively, for mercury and iodine and for mercury; a solution of iodoform, CHI_3, in water was prepared and analyzed for iodine.

3. RESULTS

Spectral data on iodine-containing and related solutions are summarized in two ways in this section and in the section on Tables and Figures. First, we present a few examples of spectra that have been resolved into overlapping Gaussian bands and tables of the parameters of these bands for which the assignment of species seems to be reasonably certain. Second, we summarize spectra of a number of solution systems in terms of molar absorptivities, both in graphical and tabular form. It seems likely that an extension of this second method of summary could lead to the development of a library of reference spectra similar to that used in gamma-ray spectrum resolution.[15] Such a library would prove advantageous for determining the nature of iodine species in solutions, acidic or alkaline, that have been proposed for use in removing iodine at various points during the processing of LMFBR fuels.

3.1 Resolution into Overlapping Gaussian Bands

Spectral resolution into overlapping Gaussian bands was performed by use of the Marquardt[25,26] nonlinear least-squares algorithm, in double-precision arithmetic, for which we wrote our own subroutines. Examples of some of the results of this resolution are shown in Fig. 1 for KI in water, in Fig. 2 for I_2 in water, in Fig. 3 for I_2 and KI in water, in Fig. 4 for I_2 in 0.025 M HNO_3, in Fig. 5 for I_2 in 3 M HNO_3 (the I_2 and some nitrogen oxides having been produced by oxidation of I^-). Values of the parameters that describe the bands of these figures are presented in Tables 1-5.

The number of Gaussian bands used to resolve a spectrum was adjudged from the error analysis. For example, the representation of the absorption spectrum of 10^{-5} M I_2 in 10^{-2} M KI solution by five bands leads to the error analysis of Fig. 6. Clearly the fluctuation of the difference between observed and calculated absorbances is not random. However, if we resolve this spectrum into six bands as in Fig. 7, the difference is much more nearly randomly distributed. Each spectrum described in this report was resolved into a number of bands that produced an error analysis that at least appeared to be randomly distributed.

The spectrum of KI in water (Fig. 1) shows two very sharp peaks, not previously measured, that are nearly certainly due to the I^- ion. Spectral resolution shows that the two obvious peaks are most accurately resolved into three overlapping Gaussian bands, one of which is only 5 to 7% as intense as the other two. The parameters of these three bands are presented in Table 1.

The spectra of iodine in water (Fig. 2) and the triiodide ion in water (Fig. 3) show some features that have been described previously,[10,11] as well as some that have not been reported. In particular, the band at about 453 nm (22,071 cm^{-1}) has been assigned to $I_2 \cdot aq$ and the two bands at 348 nm (28,708 cm^{-1}) and 288 nm (34,684 cm^{-1}) have been assigned to the triiodide ion, I_3^-. However, the peaks at 196.2 nm (50,968 cm^{-1}) and 208.6 nm (47,928 cm^{-1}) of I_2 in water have not previously been described.

The presence of absorption due to iodine species in nitric acid solutions is shown in Figs. 4 (0.025 M HNO_3) and 5 (3 M HNO_3). In both of these figures, the absorption maximum at about 450 nm is very pronounced. In 0.025 M HNO_3 (Fig. 4), we also see the maxima ascribed to I_3^- at 348 and 288 nm. However, in the 3 M HNO_3 solution (Fig. 5) obtained by adding KI to a nitric acid solution, there is, quite apparently, absorption due to nitrogen oxides. Further, the high absorption by 3 M HNO_3 in the reference cell has prevented measurement of photon absorption at wavelengths below about 320 nm. We cannot, at present, assign the four narrow bands of Fig. 5 (also Table 5) to any particular nitrogen oxide or nitrogen-oxygen anion, but they are the result of NO_3^- reduction. This pair of elements can produce exceedingly complex — yet resolvable — spectra. The spectrum of nitric acid, presented for comparison in Fig. 8, was obtained by "joining"* a number of spectra of solutions that were 0.001 to 1 M in HNO_3. Gaussian-band parameters for this spectrum are presented in Table 6.

*The "joining" process performed on the computer, as it would be with a desk calculator, is based on Eq. (8) or (9) or Sect. 6. Thus, in the wavelength region 190 to 225.5 nm, we used 0.000814 M HNO_3 in a cell 0.05 cm long; in the region 226 to 233.5 nm, we used 0.00959 M HNO_3 in a 0.05-cm cell, etc. By this technique we obtained sections of spectra, all having optical densities (OD) a reasonable fraction of the 0-1 OD scale of the Cary spectrophotometer. The "joining" simply means that the values C_i and ℓ of Eqs. (8) and (9) are different for each of the segments.

A detailed example of the oxidation of I^- to I_2, the formation of the I_3^- ion during this process, and the final oxidation of all I_3^- to I_2 is shown in Fig. 9. The time scale in this case at 25°C in 3 *M* HNO_3 is on the order of a few hours. Conversion of 5×10^{-3} *M* I^- to 2.5×10^{-3} *M* I_2 produces a solution that is supersaturated with respect to iodine (whose solubility[27] in 3 *M* HNO_3 is about 1.8×10^{-3} *M*). The decrease in absorption at about 460 nm corresponds to the precipitation of I_2. This can be readily seen to occur in a flask over a time interval of 15 min to several hours.

According to many textbooks, for example, those listed in refs. 23 and 24, hypoiodous acid can be made by contacting equimolar quantities of HgO and I_2 with water. The chemical reaction is given by Eq. (1) (see Sect. 2.1). The spectrum of the solution prepared in this manner is shown in Fig. 10, while the band parameters are summarized in Table 7. Several solutions of HgO + I_2, HgI_2, and HgO in nitrogen-sparged and unsparged water were prepared as summarized in Table 8. Spectra of these solutions were measured after various aging periods up to one week. The main features of their spectra (Fig. 11) are the two bands at about 211 nm (47,400 cm^{-1}) and 267 nm (37,400 cm^{-1}), which are present in fresh and aged HgO-I_2 solutions and in aged HgI_2 solutions. Beyond the superficial similarity of the curves of Fig. 11, there is other information shown by them. First, the absorption by HgO-I_2 solutions [HOI (?)] decreases about 25% in one week (runs 168, 171, and 173 of Fig. 11); second, some of the Gaussian-band parameters of the HgO-I_2 solutions (Table 7) are slightly different from the parameters of HgI_2 solutions (Table 9).

In alkaline solution, hypoiodous acid is reported[12] to attain equilibrium with hypoiodite ion according to the reaction

$$HOI + OH^- \rightleftharpoons OI^- + H_2O \quad . \qquad (2)$$

Many equilibria including those yielding I_2O^{2-}, I_2OH^-, and I_3^- have been postulated for these alkaline solutions. We recorded the spectra of several solutions, including 10^{-3} *M* I_2 in 0.01 *M* NaOH, 5×10^{-4} *M* I_2 in 0.1 *M* NaOH (recorded at varying times up to 24 hr), and 1.8×10^{-3} *M* I_2--3.6×10^{-3} *M* NaI in 1 *M* NaOH solution. The spectrum of the last solution was included in order to test for agreement with,

and extend the results of, Chia.[12] All of these data are summarized as line spectra in Fig. 12; other associated data are given in Tables 10 and 11 and in Figs. 12-13. Four of the bands of spectrum 6 are represented by dashed lines because the intensities of these bands decreased with, roughly, a 16-hr half-life. The height of each line corresponds to the logarithm of molar absorptivity at zero time, based on the assumption that all of the iodine existed as IO^-. Two of these transient bands also appear in the spectrum of 1.8×10^{-3} *M* I_2--3.6×10^{-3} *M* NaI in 1 *M* NaOH (spectrum 7). Parameters of this latter spectrum are given in Table 11; the composite spectrum obtained by matching partial spectra obtained with cells 0.01, 0.50, and 5.0 cm long is shown in Fig. 13.

3.2 Standard Spectra for Linear Resolution and Chemical Analysis

Resolution of an absorption spectrum into a series of overlapping Gaussian bands can provide considerable information concerning the species in solution if, in fact, the bands due to vibrational levels within the electronic transitions have a Gaussian shape. When we assume the band shape to be Gaussian, we can obtain parameters that fit the data within the accuracy of the instrument. We emphasize that there are two envelope curves plotted in Figs. 1-5, 8, 10, and 13; one is of experimental data, one is of (smoothed) calculated values. In very few sections of spectra can fluctuations of experimental data about the calculated curve be seen, except in cases when a spectrophotometer slide-wire with a full range of 0 to 0.1 OD is used. Therefore, the nonlinear spectral resolution provides a means for obtaining smoothed spectra for subsequent use in calculating solution composition by linear least-squares resolution, as in the case of analysis of a solution of radioactive elements by resolution of a gamma-ray spectrum. Figures 14 and 15 show typical smoothed spectra, some of which may be used for analytical purposes (e.g., those of nitric acid, potassium iodide, and sodium hydroxide). Other reference spectra can be obtained from data presented earlier in this report. For example, the spectrum of KI_3 may tentatively be assumed to be described entirely by bands 4 and 5 of Table 3 (or Fig. 3); the spectrum of molecular iodine in water may then be obtained by subtracting these two bands from

the composite iodine spectrum of Fig. 2 or Table 2. A preliminary library of some of the species is presented at 5-nm intervals in Tables 12 and 13. Reducing the interval size to, for example, 1 nm for chemical analysis would be a very simple matter.

3.3 A Practical Example

J. M. Schmitt, of the Chemical Technology Division at ORNL, has been studying the "chemistry of uncommon volatile iodine species." We quote him from page 1 of ref. 1 as follows: "As described previously,[28] reaction of I_2 with caustic solutions produces an unstable active iodine species (presumably hypoiodite) that is readily extractable (or reacts) with organic solvents. Relatively large amounts (10 to 40%) of the iodine have been volatilized from these solutions, and it appeared from earlier tests that the active iodine species (HOI has been postulated[29] as a volatile iodine species) itself was being volatilized.

"Recent results do not confirm this. It now appears that the highly reactive iodine species rapidly iodinates any organic impurities in the solution or in the sparging air stream and that the iodine volatilized in our tests probably has been, for the most part, in the form of alkyl iodides."

Schmitt sparged some caustic-nitrate solutions and passed the exit gases into a trap cooled with dry ice (-80°C); he then added water to the trap in the hope of dissolving at least a part of the volatile iodine-containing compound(s). We subsequently recorded the visible-UV spectra of some of these solutions, as shown in Fig. 16; also in this figure we have plotted the spectrum of a saturated aqueous solution of what is believed to be relatively pure iodoform (CHI_3). There are a number of interesting aspects, of considerable practical importance, of these spectra as follows. First, the spectrum of CHI_3 contains a large contribution due to $I_2 \cdot aq$, which appears as the broad band with a peak absorption at 21,300 cm^{-1} (470 nm) and which should be compared with band 9 (22,071 cm^{-1} or 453 nm) of Table 2. Neglecting this peak as well as the peak at the lowest wavelength (195 to 200 nm), which could be due to I^-, I_2, or other species, there are three obvious peaks (at

about 230, 295, and 347 nm) in the CHI_3 spectrum. Some of these same peaks appear in the spectra of the water extracts of gaseous species obtained by Schmitt from dry-ice cold traps. It is apparent, however, that the "mixtures" of band intensities of CHI_3 and Schmitt's samples are different. The differences and similarities imply (and spectrum resolution confirms) that Schmitt's distillates contain some CHI_3 along with other materials. The fact that a band centered at 265 to 270 nm (37,000 to 38,000 cm^{-1}), corresponding fairly closely to the well-defined band 4 of the "HOI" spectrum of Table 9, is present in all of Schmitt's samples does not become apparent except after spectrum resolution. Thus, for comparison with Schmitt's comments[1] (above), we have noted the presence of "alkyl iodides," namely CHI_3, in caustic iodine-containing solution; we have also noted the presence of a species that is usually, and without certain knowledge, referred to as HOI. We have not tested for the presence of other obvious alkyl iodides such as CH_3I and CH_2I_2.

4. DISCUSSION

From the brief survey just presented, we may draw some rather definite conclusions from the resolution of the visible and UV spectra of iodine species in acidic and alkaline solutions such as may be encountered during LMFBR fuel processing; we also need to question some interpretations, in the literature, that are based on other types of experiments. On the positive side, the spectrum of I^- is well defined (Table 1 and Fig. 1). From this basis, we can accurately define the spectrum of I_3^- (Table 3 and Fig. 3) and then the components of the iodine spectrum (Table 2 and Fig. 2) that are not due to I_3^-. These features may be seen in the line spectra 1-3 of Fig. 12. In these three spectra the parameters of the highest-frequency bands have small or very small uncertainties, a situation that frequently does not apply to bands located at either the high- or the low-frequency end of the measured spectra. Often the parameters of these extremum bands have relatively large uncertainties. At present, we can attribute most of the absorption by iodine-in-water to two strong bands at 50,968 and 47,928 cm^{-1} (Table 2), to the I_3^- bands at 34,684 and 28,708 cm^{-1}, and to $I_2 \cdot aq$ at 22,071 cm^{-1}. The species (if any), impurities, artifacts, or

numerical requirements responsible for the remaining six bands (bands 3, 5, 7, 8, 10, and 11 of Table 2) of Fig. 2 or of spectrum 2 in Fig. 12 are not known; however, this lack of knowledge need not prevent us from defining an I_3^--free iodine spectrum for analytical purposes. In Fig. 14 we present the apparent I_3^- spectrum separate from the other bands due to iodine-in-water. This spectrum is simply the sum of bands 4 and 5 of Table 3. The residual spectrum of iodine-in-water, labeled I_3^--free iodine, was obtained by subtracting 0.0123 times the I_3^- spectrum from the gross iodine spectrum. Here, 0.0123 is the fraction of iodine existing as I_3^-, as stated in Table 2.

Allen and Keefer,[11] Eggleton,[4] and others have expressed equilibria in iodine-containing solutions at values of pH down to 1 (approximately 10^{-1} *M* acid) in terms of the four reactions

$$I_2(aq) + H_2O \rightleftarrows H_2OI^+ + I^- \qquad K_1 \qquad (3)$$

$$I_2(aq) + H_2O \rightleftarrows HOI + H^+ + I^- \qquad K_2 \qquad (4)$$

$$3I_2(aq) + 3H_2O \rightleftarrows IO_3^- + 5I^- + 6H^+ \qquad K_3 \qquad (5)$$

$$I_2(aq) + I^- \rightleftarrows I_3^- \qquad K_4 \qquad (6)$$

Since equilibria (3), (4), and (6) are established in freshly prepared iodine solutions and equilibrium (5) may be neglected, we can derive the following equation to relate the acid, iodine, and triiodide concentrations:

$$K_1 + \frac{K_2}{(H^+)} = \frac{(I_3^-)^2 y_\pm^2}{K_4 (I_2)^2} \left[1 + \frac{1}{K_4 (I)_2} \right] , \qquad (7)$$

where $y_\pm$ is the mean ionic molar activity coefficient. Eggleton[4] presents the following values of equilibrium constants for 25°C: $K_1 = 1.2 \times 10^{-11}$; $K_2 = 5.4 \times 10^{-13}$; $K_4 = 768$. Concentrations are in units of moles liter^{-1}. Using these constants in Eq. (7) we calculated the product $(I_3^-)y_\pm$ for a few conditions under which we recorded

spectra of iodine-containing solutions. For example, the product equals 1.06×10^{-7} and 7.62×10^{-8} for 10^{-3} M I_2 in 0.025 and 0.1 M HNO_3, respectively. If we use the nitric acid activity coefficients of Davis and deBruin,[30] the products $(I_3^-)y_\pm$ are changed by only small amounts to 1.11×10^{-7} and 7.92×10^{-8}, respectively. The activity-coefficient corrections are small since $y_\pm$ has values[30] of 0.869 and 0.796 corresponding to 0.025 and 0.1 M HNO_3. Thus, the expected concentrations of I_3^- are 1.1×10^{-7} and $(7.6\text{–}7.9) \times 10^{-8}$ M, respectively; these correspond to 0.011% iodine as I_3^- in 0.025 M HNO_3 and 0.0076 to 0.0079% iodine as I_3^- in 0.1 M HNO_3. By contrast, the observed intensities of the I_3^- bands of 10^{-3} M I_2 in 0.025 M HNO_3 (Table 4) correspond to 1.65% of the iodine existing as I_3^-. Similarly, 10^{-3} M I_2 in 0.1 M HNO_3 also contains approximately 2% I_3^- instead of a calculated value less than 0.008% I_3^-. These discrepancies show that Eq. (7) is seriously in error for dilute nitric acid solutions and can be expected to be even more erroneous for the more concentrated solutions that will be encountered in processing LMFBR fuels.

In addition to presenting some of the data needed to define "library spectra" of iodine species in Table 12, we list data from two spectra each of KI in water and 0.001 M I_2 in 0.025 M HNO_3 to indicate the reproducibility of the results. It is apparent that the reproducibility is generally in the range 1 to 3%. Spectra of duplicate solutions of I_3^- in water were also used to check the reproducibility of parameters and numbers of bands needed for resolution. In these tests, with six bands, good agreement was obtained. However, this was the most complicated case in which such duplication was performed.

An example of the utility of visible-UV spectroscopy in elucidating the structure of some iodine species in nitric acid solution is shown in Fig. 9. Initially the solution was of the composition 10^{-2} M KI in 3 M HNO_3; the reference cell contained 3 M HNO_3. At the shortest aging time, 6 min, the spectrum is much like that of KI in water, although some absorption at about 350 nm is evident. This absorption is nearly certainly due to the longer wavelength band of I_3^-, which, according to Table 3 or Fig. 12, is located at 352 nm. This, of course, means that I^- is being oxidized to I_2, which rapidly combines with more I^- to form the I_3^- ion. In this particular

experiment, the oxidation of I^- proceeded until all of the I^- had been converted to I_3^- (i.e., ~ 180 min); then a very rapid (within 5 min) oxidation of all I_3^- to $I_2 \cdot aq$ occurred. This hydrated iodine species is evident as the strong band centered at about 470 nm (see curves 16-20 of Fig. 9). The decrease in intensity of this band is caused by precipitation of iodine, whose solubility is only (1.7-1.8) x 10^{-3} M in 3 M HNO_3.[27] Oxidation of 10^{-2} M I^- produced an initially supersaturated solution, conceivably 5 x 10^{-3} M in I_2. This oxidation was accompanied by the formation of nitrogen oxides or nitrous acid, as shown by the three peaks (at 350 to 400 nm) of curves 16-20 in Fig. 9. These five curves should be compared with the curve of Fig. 5, which also represents the oxidation of KI in nitric acid solution. Parameters of the four narrow bands of Fig. 5 are listed as bands 3-6 in Table 5. At present we cannot assign these bands to any particular nitrogen oxide; in addition, the listed molar absorptivities of these bands are only relative, although the band center and the half-width are accurately calculable.

Hypoiodous acid is an iodine-containing species that is well characterized and readily prepared, according to well-known textbooks.[23,24] However, the results of our studies with spectroscopic, polarographic,[31] and neutron activation techniques suggest that the procedures given in the textbooks may be somewhat inaccurate. Figure 11 contains the spectra of filtrates from the "preparation" of HOI according to textbook procedures after various periods of aging; it also contains, for reference, spectra obtained by the extensive contact of HgI_2 or HgO with water. The similarity of the spectra of the filtrates from HgI_2-H_2O and HgO-I_2-H_2O is quite evident. Comparison of Tables 7 (for HgO-I_2-H_2O filtrate) and Table 9 (for HgI_2-H_2O filtrate) shows that bands 2 and 4 (which are dominant features) are nearly certainly the same in each case, corresponding to the sharp band at 210 nm (Figs. 10 and 11, plus spectrum 6 of Fig. 12) and the broad band centered at about 267 nm. The highest-frequency band at about 193 nm could be due to I_2 or I^-. Comparison of spectra 6 and 2 in Fig. 12 suggests that the band at 210 nm may be due to I_2. However, the residual absorption by HOI (HgO-I_2-H_2O) or HgI_2 in water is not like any of the others shown in Fig. 12. Thus, if an equimolar mixture of HgO and I_2 in

water produces HOI, then HgI_2 may also produce it; or, as a second possibility, $HgO + I_2$ in water may produce HgI_2.

We attempted to learn more about the dissolved species in aqueous solution in contact with HgI_2 or $HgO + I_2$ by neutron activation and polarographic analyses. The former showed that the I/Hg atom ratio in solution is about 3/1 in the case of HgI_2 and that this ratio exceeds 5/1 in the case of $HgO + I_2$. This means that iodine-containing species other than HgI_2 were present in solution. The polarographic analyses[29] of freshly prepared solutions of HgI_2 and $HgO-I_2$, with or without nitrogen sparging to remove dissolved oxygen, indicated the presence of IO_3^- and the absence of I^- and IO^- in all cases. Thus, we must conclude that the textbook procedures for preparing HOI may be in error and that the spectra of Figs. 10 and 11, as well as spectrum 5 of Fig. 12, may not represent HOI.

Our brief studies of caustic solutions of iodine have served mainly to emphasize some of the changes in chemical species that occur slowly or rapidly. Thus, the molar absorptivities of the first four bands of Table 10 indicate that the original 10^{-3} *M* I_2 of this 0.01 *M* NaOH solution was 85.5% converted to I^- during the 5 days between the preparation of the solution and the recording of the spectrum. We do not know whether this was the equilibrium species distribution. The second four bands of Table 10, for initially 5×10^{-4} *M* I_2 in 0.1 *M* NaOH, are all transitory and correspond roughly to a first-order kinetic change with a half-life of about 16 hr. We (arbitrarily) assigned these four bands to IO^- since they decay at the same rate as IO^- bands and since the band at 28,728 cm^{-1} (348 nm) is probably the origin of the absorption at 360 nm used by Chia[12] in her study of +1 iodine in alkaline solution. Except for the parallel decay rates, we have no basis for species assignment.

Only 85.5% of the iodine was reduced to iodide in the solution initially of the composition 10^{-3} *M* I_2 in 0.01 *M* NaOH (Table 10); however, the reduction of 1.8×10^{-3} *M* I_2 in 1 *M* NaOH--3.6×10^{-3} *M* NaI was complete within the resolution of the equipment we used. The oxidation-reduction reaction of Eq. (5) corresponds to 83.3% reduction and 16.7% oxidation of I^-. Our value of 85.5% for 10^{-3} *M* I_2 in 0.01 *M* NaOH is, therefore, in close accord with this reaction, although we did not

establish that equilibrium had been achieved. This single oxidation-reduction Eq. (5) does not appear to represent the complete reduction of I^- in the 1 *M* NaOH--3.6×10^{-3} *M* NaI solution. Since caustic solutions in the range of 1 *M* NaOH are being evaluated as a means for scrubbing iodine from air streams, a more careful search for I_2 in such solutions is warranted.

5. SUMMARY AND CONCLUSIONS

Optical spectra, in the wavelength region 190 to 700 nm, of acidic (3 *M* HNO_3), nearly neutral, and alkaline (1 *M* NaOH) solutions containing various iodine species have been recorded and resolved into series of overlapping, Gaussian-shaped bands. Although it is not certain that the bands have a Gaussian shape, this assumption makes it possible for us to describe the data with an accuracy equal to the stated accuracy of the Cary 14R spectrophotometer and to present reference spectra for several species such as I^-, I_3^-, and probably I_2. These reference spectra will be useful for quantitative analyses and, as a library, would represent a convenient technique for accurately determining how iodine is combined in solution and the fate of the species present in the solutions to be encountered during LMFBR fuel processing.

Changes in the chemical nature of iodine species were observed in both acidic and alkaline solutions. In acidic solution, I^- was observed to oxidize essentially completely to I_2, with the subsequent formation of nitrous acid or dissolved nitrogen oxides; in alkaline solution, I_2 was observed to be reduced to I^- to the extent of 85.5% in 5 days (or less). This degree of reduction in basic solution corresponds very closely to Eq. (5), which involves reduction of 83.3% of the iodine to I^- and oxidation of 16.7% of the iodine to IO_3^-. Intensities of several bands, including one probably due to IO^- ion, were observed to decrease with a first-order half-life of about 16 hr.

Attempts to interpret spectra of a solution that should, according to textbook procedures for contacting HgO + I_2 with water, contain hypoiodous acid were seriously compromised by similar spectra from HgI_2 in water.

We conclude that visible-UV spectroscopy in the region 190 to 700 nm, combined with spectrum resolution into overlapping Gaussian (or other) shaped bands, can provide valuable information concerning the nature of iodine in acidic, neutral, or caustic solutions. This knowledge should provide considerable aid in our efforts to ensure that iodine will be properly contained during the processing of LMFBR fuels.

6. TABLES AND FIGURES

In this section we present tables of Gaussian-band parameters of some of the solutions for which spectra were taken. Punched-card spectral data were obtained in terms of photon wavelength, λ (in nanometers), and optical density, OD. Spectral resolution was based on minimizing the uncertainty in the area under the plot of OD vs photon frequency ($\nu = 10^7/\lambda$, cm^{-1}). Here the calculated absorbance, $\hat{a}_i$, due to species i is related to the photon frequency and band parameters by the equation

$$\hat{a}_i = \frac{C_i \ell}{\sqrt{2\pi}} \frac{\kappa_i}{\sigma_i} \exp\{[-(\nu - \nu_i)/\sigma_i]^2/2\} , \qquad (8)$$

where

ℓ = cell length, cm,

C_i = concentration of the species to which band i is assigned, moles $liter^{-1}$,

κ_i = the area under band i, liter $mole^{-1}$ cm^{-2},

σ_i = half-width of band i at 0.36788 (1./e) times the absorbance of band i at its band center, cm^{-1},

ν = frequency of photon, cm^{-1},

ν_i = band center, cm^{-1}.

The minimization process is performed by summing Eq. 8 over all bands that can contribute to absorption at frequency ν and then summing over all frequencies corresponding to all wavelengths at which OD was punched. In our program, this

absorption by a band was extended to frequencies from $\nu_i - 8.3\,\sigma_i$ to $\nu_i + 8.3\,\sigma_i$. The difference between observed and predicted optical densities at each frequency ν is the residual (RES) to be minimized by the nonlinear least-squares analysis.

$$\mathrm{RES} = (\mathrm{OD}) - \frac{\ell}{\sqrt{2\pi}} \sum_i \frac{C_i \kappa_i}{\sigma_i} \exp\{-[(\nu - \nu_i)/\sigma_i]^2/2\} \,. \qquad (9)$$

Tables 1-7 and 9-11 summarize values of ν_i, of half-width at half-maximum absorption ($=\sigma_i\sqrt{2.\ln 2.}$), and of molar absorptivity. Standard deviations of all these quantities were calculated by the program, but, for brevity, we have summarized these on a letter scale as follows:

vs for uncertainties less than 0.1 times the value;

s for uncertainties in the range 0.1 to 0.25 times the value;

m for uncertainties in the range 0.25 to 1.0 times the value;

ℓ for uncertainties in the range 1 to 3 times the value;

vℓ for uncertainties greater than 3 times the value.

When two letter combinations are used, the first refers to the uncertainty of the half band width and the second to the uncertainty of the maximum molar absorptivity. No such specification is needed for the band center since the uncertainty of its location was significantly less than 0.1 ν_i for nearly all bands.

It is necessary that we define two aspects of the species assignment of the tables of this section: (1) the assignment used in the computer program for calculating the molar absorptivity; and (2) the use of a (?) if there is no good basis for assigning a band to a molecular species. The absorptivity requires the assignment of a concentration. Thus, for example, the first three bands of Table 3 (I_2-KI in water) were assigned to the I^- ion because of the location of the band centers (see Table 1), and the I^- concentration was set at $1.0 \times 10^{-2}\,M$ (not corrected for the $1.0 \times 10^{-5}\,M\,I^-$ that would be combined as I_3^-). Similarly, to make the molar absorptivities of bands 4 and 6 of I_3^- from Table 2 (Fig. 2) agree reasonably closely with bands 4 and 5 of I_3^- from Table 3 (in which the I_3^- concentration is assumed to be 1.0×10^{-5} as a

result of all I_2 complexing with I^-), we assumed that the I_3^- concentration in the I_2-H_2O solution (Table 2) was 1.23% of the stoichiometric I_2 concentration in the range 10^{-4} to 10^{-3} M I_2. In effect, this is simply a quantitative analysis for I_3^- in I_2 (Table 2) using I_2 in KI (Table 3) as a standard.

The resolution into overlapping Gaussian bands was performed to provide a standard deviation of fit as good as, or better than, the specified precision of the Cary 14R spectrophotometer,[32] which is 0.002 OD unit on the 0-1 or 1-2 OD scales. It is not the purpose of this report to establish the validity of the Gaussian contour; instead, we have tried to provide the basis for a library of iodine-species spectra for use in solution analysis.

Table 1. Gaussian Parameters[a] of the Three Bands of KI in Water[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (s)	51,634	2456	1.56×10^4	I^-
2 (s)	44,233	2119	1.31×10^4	I^-
3 (sm)	43,518	1118	7.03×10^2	I^-

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]The solution was 10^{-4} M KI and was measured over the wavelength range 190 to 245.5 nm. The reference cell contained water.

Table 2. Gaussian Parameters[a] of the Eleven Bands of I_2 in Water[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity[c] (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (vs)	50,968	3988	1.41×10^4	I_2 (?)
2 (vs)	47,928	2528	1.07×10^4	I_2 (?)
3 (ml)	35,907	3658	1.90×10^2	I^- (?)
4 (sl)	34,684	1923	3.18×10^4	I_3^-
5 (lvl)	31,872	947	8.95×10^0	I_2 (?)
6 (vl)	28,708	2010	2.29×10^4	I_3^-
7 (vl)	27,598	1407	3.23×10^1	I_2 (?)
8 (vl)	25,899	1885	7.91×10^1	I_2 (?)
9 (lvl)	22,071	2134	6.20×10^2	$I_2 \cdot aq$
10 (lvl)	20,294	1658	1.54×10^2	I_2 (?)
11 (mvl)	17,127	2308	3.06×10^1	I_2 (?)

[a]See text of this section for explanation of the parenthetical letters in column 1.

[b]The solutions were 10^{-4} *M* I_2 in the wavelength range 191 to 224 nm, 5×10^{-4} *M* I_2 in the range 225 to 231 nm, 1×10^{-3} *M* I_2 in the range 232 to 686 nm.

[c]Molar absorptivities of bands 4 and 6 are based on the assumption that the concentration of I_3^- is 1.23% of the stoichiometric I_2 concentration. This assumption (corresponding to an analysis for I_3^-) makes these absorptivities essentially equal to those of bands 4 and 5 of Table 3. Correspondingly, the I_2 concentration was assumed to be equal to 98.16% of the stoichiometric value, i.e., 100 − 1.5 (1.23). The reference cells contained water.

Table 3. Gaussian Parameters[a] of the Six Bands of I_3^- in KI-Water[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity[c] (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (vs)	51,609[d]	2368	1.64×10^4	I^-
2 (vs)	44,295[d]	2039	1.39×10^4	I^-
3 (vsm)	43,310[d]	1554	1.71×10^3	I^-
4 (vs)	34,730	2080	3.34×10^4	I_3^-
5 (vs)	28,413	2196	2.19×10^4	I_3^-
6 (vs)	23,667	1701	1.39×10^3	$I_2 \cdot aq$ (?)

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]The solutions were 10^{-5} *M* I_2 and 10^{-2} *M* KI in the wavelength region 190 to 259 nm, and 5×10^{-5} *M* I_2 and 5×10^{-2} *M* KI in the wavelength region 260 to 553 nm. The reference cell contained water.

[c]The molar absorptivities of bands 4 and 5 are based on the assumption that all the I_2 was complexed as I_3^-.

[d]Compare the parameters of bands 1-3 with those in Table 1.

Table 4. Gaussian Parameters[a] of the Ten Bands of 10^{-3} *M* I_2 in 0.025 *M* HNO_3

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})	Species Assignment
1[b]	50,968[b]	3988[b]	5.57×10^4	I_2
2 (l)	44,897	1728	2.07×10^4	I_2
3 (lvl)	38,598	1292	1.11×10^0	HNO_3 (?)
4 (mvl)	34,811	1740	8.61×10^3	I_3^- (?)
5 (sm)	34,405[c]	2739	3.64×10^4	I_3^-
6 (sm)	29,078	1004	2.91×10^1	I_2 or nitrogen oxide (?)
7 (vss)	28,103[c]	1970	1.92×10^4	I_3^-
8 (mvl)	22,553	2343	3.43×10^2	$I_2 \cdot aq$
9 (mvl)	21,090	2057	3.35×10^2	I_2 (?)
10 (m)	16,435	1110	1.21×10^1	I_2 (?)

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]Band center and half-width were held constant at these values in accordance with the first band of Table 2 because data did not extend to wavelengths that were sufficiently low to permit these values to be fixed independently. The wavelength range was 246 to 600 nm.

[c]These are almost certainly the I_3^- bands. To make the molar absorptivities agree with those of Table 3, we assumed the I_3^- concentration to be 1.65% of the stoichiometric I_2 concentration. The reference cell contained water.

Table 5. Gaussian Parameters[a] of the Nine Bands of 1.8×10^{-3} *M* I_2 (Produced[b] by Oxidation of I^-) in 3 *M* HNO_3

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (lvl)	55,247	23776	7.57×10^{-2}	HNO_3
2 (vsm)	33,989	1684	1.93×10^{1}	HNO_3 [I_3^- (?)]
3 (s)	28,942	269	1.91×10^{1}	NO_2^- (?)[c]
4 (vss)	27,918	256	3.70×10^{1}	NO_2^- (?)[c]
5 (vss)	26,917	295	5.68×10^{1}	NO_2^- (?)[c]
6 (vss)	25,889	302	4.57×10^{1}	NO_2^- (?)[c]
7 (sm)	23,964	1295	3.89×10^{1}	I_2
8 (vs)	21,522	2055	7.01×10^{2}	I_2
9 (sm)	19,893	1202	4.44×10^{1}	I_2

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]Initial KI concentration was 5×10^{-3} *M*. The solubility of I_2 in 3 *M* HNO_3 is given in ref. 27. The spectrum was measured from 330 to 575.5 nm. The reference cell contained water.

[c]The concentration of the nitrite - or nitrogen oxide - was assumed to be 1×10^{-3} *M*. This estimate may be reasonable or grossly in error.

Table 6. Gaussian Parameters[a] of the Eleven Bands of 0.001 to 1 *M* HNO_3 in Water[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})
1 (s)	51,394	3563	9.54×10^3
2 (m)	48,414	2261	4.54×10^3
3 (l)	46,411	1813	2.19×10^3
4 (m)	43,641	332	6.43×10^1
5 (m)	43,024	255	1.88×10^1
6 (l)	42,858	640	3.94×10^1
7 (l)	42,120	1011	1.98×10^1
8 (vl)	36,196	1796	2.23×10^0
9 (vl)	34,159	1479	4.48×10^0
10 (vl)	32,670	1227	4.74×10^0
11 (vl)	31,490	1014	1.45×10^0

[a]See text of this section for explanation of the parenthetical letters of column 1. The reference cells contained water.

[b]All bands were assigned to nitric acid; however, some, for example 4, 5, and 6, may be due to nitrogen oxides or nitrite ion.

Table 7. Gaussian Parameters[a] of the Five Bands of Hypoiodous Acid[b] (?) in Water[c]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})
1 (vs)	52,271	2698	1.41×10^4
2 (s)	47,436	2123	7.73×10^3
3 (s)	45,787	2980	3.14×10^3
4 (vs)	37,408	3251	1.75×10^3
5 (vs)	30,900	1381	4.70×10^1

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]Prepared according to procedure described in refs. 23 and 24 (run 168).

[c]All species were assigned to the supposed HOI at the measured concentration of 9.85×10^{-4} M I (sample 16-3, Table 8). The spectrum was measured from 197 to 370 nm. The reference cell contained water.

Table 8. Analyses of Some Solutions Associated with Hypoiodous Acid and Iodoform

Sample (A-6188-)	Salts	Conditions	Concentrations (M) I	Concentrations (M) Hg	I/Hg Atom Ratio	Description of Method
71-1	$HgO + I_2$	No N_2 sparge	2.3×10^{-4} (ref. a)	-	-	Samples mixed at room temperature for 1/2 hr; stored immediately at 0°C. Phases were separated just prior to polarographic analysis.[b]
71-2	$HgO + I_2$	Sparged with N_2	4.3×10^{-4} (ref. a)	-	-	
72-1	HgI_2	No N_2 sparge	$<5 \times 10^{-6}$ (ref. a)	-	-	
72-2	HgI_2	Sparged with N_2	$<5 \times 10^{-6}$ (ref. a)	-	-	
16-1	HgO	No N_2 sparge	-	2.09×10^{-4} (ref. c)	-	Salts mixed with water for 6 days at room temperature; no attempt to keep cold prior to neutron activation analysis. Phases were separated before being sent for analysis.
16-2	HgI_2	No N_2 sparge	2.09×10^{-4} (ref. c,d)	7.13×10^{-5} (ref. c)	2.93	
16-3	$HgO + I_2$	No N_2 sparge	9.85×10^{-4} (ref. c)	1.86×10^{-4} (ref. c)	5.28	
53-1	CHI_3	No N_2 sparge	2.71×10^{-4}	-	-	Stirred for severol days with excess salt; decanted and supernatant analyzed by neutron activation.

[a] Polarographic method indicates IO_3^-; no IO^- or I^- was found.

[b] See ref. 29.

[c] Neutron activation gives only total iodine and total mercury.

[d] The solubility of HgI_2 in water at 25°C is 0.01 g/100 cc (which is equivalent to 2.2×10^{-4} M) according to Handbook of Chemistry and Physics, 47th ed., p. B-196, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966-67.

Table 9. Gaussian Parameters[a] of the Five Bands of HgI_2 in Water[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})
1 (s)	51,710	1556	6.98×10^3
2 (vs)	47,618	2287	1.54×10^4
3 (m)	43,042	2026	9.33×10^2
4 (s)	37,873	2534	2.77×10^3
5 (ml)	34,491	1887	5.87×10^2

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]All species were assigned to HgI_2 at the measured concentration of 2.09×10^{-4} M (sample 16-2, Table 8, run 167). The spectrum was measured from 197 to 370 nm. The reference cell contained water.

Table 10. Gaussian Parameters[a] of the Eight Bands of I_2 in Aqueous 0.01 *M* NaOH Solution[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity[c] (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (vs)	51,672	2141	2.46×10^4	I^-
2 (s)	47,540	1038	8.76×10^3	I_2 (?)
3 (vs)	44,276	2039	1.31×10^4	I^-
4 (m)	43,620	330	1.78×10^2	I^-
5 (sm)	38,775	3320	3.20×10^2	IO^- (?)
6 (m)	29,365	1444	2.56×10^0	IO^- (?)
7 (vs)	28,728	4799	4.85×10^1	IO^- (?)
8 (s)	26,414	1289	8.67×10^0	IO^- (?)

[a]See text of this section for explanation of the parenthetical letters in column 1.

[b]The first four bands were derived from a solution initially of the composition 1×10^{-3} *M* I_2 in 0.01 *M* NaOH; the wavelength region was 197 to 396 nm. From the well-defined band at 44,276 cm^{-1} of this solution, corresponding to the band at 44,233 cm^{-1} of Table 1, we calculated that 85.5% of the I_2 was reduced to I^-, thereby producing a concentration of 1.71×10^{-3} *M* I^- and 0.145×10^{-3} *M* I_2.

[c]Bands 5-8 were derived from a 4-min-old solution initially of the composition 5×10^{-4} *M* I_2 in 0.1 *M* NaOH; the wavelength region was 280 to 459 nm. Apparent molar absorptivities of all of these bands decreased essentially according to first-order kinetics with a half-life of about 16 hr. The band assignment is arbitrary except that the band at 28,728 cm^{-1} (348 nm) probably is the origin of the absorption at 360 nm used by Chia[12] in her studies.

Table 11. Gaussian Parameters[a] of the Six Bands of I_2 + NaI in Aqueous 1 *M* NaOH[b]

Band No.	Band Center (cm^{-1})	Half-Width at Half Maximum Absorption (cm^{-1})	Molar Absorptivity (liter $mole^{-1}$ cm^{-1})	Species Assignment
1 (m)	49,281	2887	3.30×10^4	I^- (I^- and I_2)
2 (vs)	44,130	1927	4.25×10^4	I^-
3 (vs)	38,669	3100	4.15×10^2	IO^-
4 (sm)	29,982	3583	7.46×10^4	IO^- (?)
5 (vsm)	26,390	1907	3.23×10^1	IO^-
6 (m)	23,049	1779	8.34×10^0	IO^- (?)

[a]See text of this section for explanation of the parenthetical letters of column 1.

[b]The solutions, in cells of three different lengths, were all 1.8×10^{-3} *M* I_2 + 3.6×10^{-3} *M* NaI in 1 *M* NaOH. The reference cell contained 1.0 *M* NaOH.

Table 12. Molar Absorptivities of Some Iodine Species in Neutral or Acidic Solution and of Nitric Acid

WAVE LENGTH (NM)	MOLAR ABSORPTIVITIES (LITER/MOLE/CM)							
	KI IN WATER		I2 IN WATER	0.001 M I2 IN 0.025 M HNO3		HNO3 IN WATER	HYPOTHETICAL SPECTRA	
	RUN 101	RUN 121		RUN 117	RUN 119		I2 FREE OF I3-	I3-
190.00	1.39E 04	1.40E 04				9.18E 03		
195.00	1.54E 04	1.52E 04	1.72E 04			1.10E 04	1.72E 04	
200.00	1.16E 04	1.13E 04	2.02E 04			1.19E 04	2.02E 04	
205.00	6.66E 03	6.46E 03	2.13E 04			1.17E 04	2.13E 04	
210.00	4.68E 03	4.49E 03	1.92E 04			1.02E 04	1.92E 04	
215.00	6.64E 03	6.55E 03	1.45E 04			7.56E 03	1.45E 04	
220.00	1.07E 04	1.08E 04	9.26E 03			4.58E 03	9.26E 03	
225.00	1.35E 04	1.37E 04	5.08E 03			2.19E 03	5.08E 03	
230.00	1.27E 04	1.28E 04	2.48E 03			9.18E 02	2.48E 03	
235.00	8.89E 03	8.88E 03	1.13E 03			3.25E 02	1.13E 03	
240.00	4.84E 03	4.76E 03	5.10E 02			1.04E 02	5.10E 02	3.41E 00
245.00	2.17E 03	2.07E 03	2.57E 02		1.04E 03	3.23E 01	2.56E 02	2.76E 01
250.00			1.68E 02	4.20E 02	4.15E 02	9.68E 00	1.66E 02	1.59E 02
255.00			1.53E 02	2.45E 02	2.49E 02	3.37E 00	1.45E 02	6.78E 02
260.00			1.79E 02	2.31E 02	2.38E 02	1.80E 00	1.52E 02	2.19E 03
265.00			2.36E 02	2.88E 02	2.99E 02	1.78E 00	1.67E 02	5.55E 03
270.00			3.22E 02	3.92E 02	4.05E 02	2.36E 00	1.81E 02	1.13E 04
275.00			4.25E 02	5.22E 02	5.37E 02	3.23E 00	1.89E 02	1.88E 04
280.00			5.17E 02	6.46E 02	6.65E 02	4.29E 00	1.90E 02	2.61E 04
285.00			5.71E 02	7.31E 02	7.51E 02	5.47E 00	1.84E 02	3.09E 04
290.00			5.68E 02	7.55E 02	7.73E 02	6.63E 00	1.71E 02	3.17E 04
295.00			5.13E 02	7.19E 02	7.32E 02	7.58E 00	1.55E 02	2.86E 04
300.00			4.27E 02	6.42E 02	6.49E 02	8.09E 00	1.37E 02	2.32E 04
305.00			3.39E 02	5.44E 02	5.49E 02	7.85E 00	1.20E 02	1.75E 04
310.00			2.69E 02	4.48E 02	4.51E 02	6.82E 00	1.03E 02	1.32E 04
315.00			2.24E 02	3.66E 02	3.69E 02	5.25E 00	8.66E 01	1.10E 04
320.00			2.07E 02	3.09E 02	3.13E 02	3.52E 00	6.91E 01	1.10E 04
325.00			2.14E 02	2.79E 02	2.88E 02	2.00E 00	5.37E 01	1.28E 04
330.00			2.39E 02	2.78E 02	2.92E 02		4.30E 01	1.56E 04
335.00			2.72E 02	2.98E 02	3.16E 02		3.81E 01	1.87E 04
340.00			3.04E 02	3.28E 02	3.47E 02		3.90E 01	2.12E 04
345.00			3.29E 02	3.53E 02	3.73E 02		4.51E 01	2.26E 04
350.00			3.41E 02	3.66E 02	3.87E 02		5.55E 01	2.28E 04
355.00			3.41E 02	3.64E 02	3.85E 02		6.85E 01	2.18E 04
360.00			3.29E 02	3.49E 02	3.69E 02		8.22E 01	1.97E 04
365.00			3.09E 02	3.25E 02	3.44E 02		9.56E 01	1.70E 04
370.00			2.85E 02	2.97E 02	3.14E 02		1.08E 02	1.41E 04
375.00			2.62E 02	2.70E 02	2.85E 02		1.22E 02	1.12E 04
380.00			2.44E 02	2.46E 02	2.60E 02		1.36E 02	8.57E 03
385.00			2.34E 02	2.30E 02	2.43E 02		1.54E 02	6.35E 03
390.00			2.34E 02	2.24E 02	2.35E 02		1.77E 02	4.56E 03
395.00			2.45E 02	2.30E 02	2.39E 02		2.05E 02	3.18E 03
400.00			2.67E 02	2.47E 02	2.53E 02		2.40E 02	2.16E 03
405.00			2.99E 02	2.73E 02	2.78E 02		2.81E 02	1.44E 03
410.00			3.39E 02	3.08E 02	3.10E 02		3.28E 02	9.35E 02
415.00			3.86E 02	3.49E 02	3.49E 02		3.79E 02	5.96E 02
420.00			4.37E 02	3.93E 02	3.91E 02		4.33E 02	3.74E 02

Table 12 (continued)

WAVE LENGTH (NM)	MOLAR ABSORPTIVITIES (LITER/MOLE/CM)							
	KI IN WATER		I2 IN WATER	0.001 M I2 IN 0.025 M HNO3		HNO3 IN WATER	HYPOTHETICAL SPECTRA	
	RUN 101	RUN 121		RUN 117	RUN 119		I2 FREE	I3- OF I3-
425.00			4.89E 02	4.38E 02	4.35E 02		4.87E 02	2.30E 02
430.00			5.40E 02	4.82E 02	4.78E 02		5.38E 02	1.40E 02
435.00			5.87E 02	5.23E 02	5.17E 02		5.86E 02	8.38E 01
440.00			6.28E 02	5.59E 02	5.52E 02		6.27E 02	4.96E 01
445.00			6.61E 02	5.89E 02	5.80E 02		6.61E 02	2.91E 01
450.00			6.85E 02	6.10E 02	6.00E 02		6.85E 02	1.69E 01
455.00			7.00E 02	6.24E 02	6.13E 02		7.00E 02	9.69E 00
460.00			7.06E 02	6.28E 02	6.17E 02		7.06E 02	5.53E 00
465.00			7.02E 02	6.24E 02	6.13E 02		7.02E 02	3.13E 00
470.00			6.89E 02	6.12E 02	6.01E 02		6.89E 02	1.76E 00
475.00			6.68E 02	5.93E 02	5.83E 02		6.68E 02	
480.00			6.40E 02	5.67E 02	5.58E 02		6.40E 02	
485.00			6.07E 02	5.37E 02	5.29E 02		6.07E 02	
490.00			5.68E 02	5.02E 02	4.96E 02		5.68E 02	
495.00			5.27E 02	4.65E 02	4.60E 02		5.27E 02	
500.00			4.84E 02	4.26E 02	4.22E 02		4.84E 02	
505.00			4.40E 02	3.87E 02	3.85E 02		4.40E 02	
510.00			3.97E 02	3.48E 02	3.47E 02		3.97E 02	
515.00			3.55E 02	3.11E 02	3.11E 02		3.55E 02	
520.00			3.15E 02	2.75E 02	2.77E 02		3.15E 02	
525.00			2.77E 02	2.42E 02	2.44E 02		2.77E 02	
530.00			2.43E 02	2.11E 02	2.15E 02		2.43E 02	
535.00			2.12E 02	1.83E 02	1.88E 02		2.12E 02	
540.00			1.84E 02	1.58E 02	1.63E 02		1.84E 02	
545.00			1.60E 02	1.36E 02	1.42E 02		1.60E 02	
550.00			1.39E 02	1.17E 02	1.23E 02		1.39E 02	
555.00			1.20E 02	9.99E 01	1.06E 02		1.20E 02	
560.00			1.05E 02	8.55E 01	9.25E 01		1.05E 02	
565.00			9.13E 01	7.33E 01	8.05E 01		9.13E 01	
570.00			8.02E 01	6.32E 01	7.05E 01		8.02E 01	
575.00			7.09E 01	5.47E 01	6.21E 01		7.09E 01	
580.00			6.31E 01	4.77E 01	5.51E 01		6.31E 01	
585.00			5.66E 01	4.19E 01	4.93E 01		5.66E 01	
590.00			5.11E 01	3.71E 01	4.46E 01		5.11E 01	
595.00			4.65E 01	3.31E 01	4.06E 01		4.65E 01	
600.00			4.26E 01	2.96E 01	3.73E 01		4.26E 01	

Table 13. Molar Absorptivities of Some Iodine Species in Neutral or Basic Solution and of Sodium Hydroxide

WAVE LENGTH (NM)	MOLAR ABSORPTIVITIES (LITER/MOLE/CM)				
	HGO + I2 IN WATER	HGO IN WATER	HGI2 IN WATER	NAOH IN WATER	0.0018 M I2 0.0036 M NAI 1 M NAOH
195.00				2.28E 03	
200.00	1.22E 04	4.49E 03	1.03E 04	1.11E 03	
205.00	1.18E 04	3.69E 03	1.35E 04	3.91E 02	
210.00	1.19E 04	2.96E 03	1.55E 04	1.05E 02	3.06E 04
215.00	1.04E 04	2.19E 03	1.32E 04	2.24E 01	3.22E 04
220.00	7.53E 03	1.50E 03	8.65E 03	3.93E 00	4.04E 04
225.00	4.79E 03	9.72E 02	4.76E 03		4.65E 04
230.00	2.93E 03	5.97E 02	2.59E 03		4.14E 04
235.00	1.89E 03	3.50E 02	1.67E 03		2.76E 04
240.00	1.41E 03	1.98E 02	1.41E 03		1.42E 04
245.00	1.28E 03	1.08E 02	1.53E 03		5.85E 03
250.00	1.36E 03	5.76E 01	1.90E 03		2.15E 03
255.00	1.52E 03	3.00E 01	2.37E 03		8.81E 02
260.00	1.67E 03	1.53E 01	2.72E 03		5.21E 02
265.00	1.76E 03	7.71E 00	2.85E 03		4.12E 02
270.00	1.74E 03	3.84E 00	2.74E 03		3.49E 02
275.00	1.63E 03	1.89E 00	2.46E 03		2.88E 02
280.00	1.45E 03		2.12E 03		2.28E 02
285.00	1.23E 03		1.75E 03		1.75E 02
290.00	9.98E 02		1.39E 03		1.31E 02
295.00	7.81E 02		1.05E 03		9.84E 01
300.00	5.94E 02		7.52E 02		7.58E 01
305.00	4.44E 02		5.04E 02		6.13E 01
310.00	3.31E 02		3.15E 02		5.28E 01
315.00	2.50E 02		1.84E 02		4.83E 01
320.00	1.90E 02		1.00E 02		4.62E 01
325.00	1.44E 02		5.15E 01		4.55E 01
330.00	1.05E 02		2.50E 01		4.56E 01
335.00	7.29E 01		1.15E 01		4.62E 01
340.00	4.75E 01		5.09E 00		4.73E 01
345.00	2.91E 01		2.16E 00		4.87E 01
350.00	1.70E 01				5.06E 01
355.00	9.62E 00				5.26E 01
360.00	5.36E 00				5.44E 01
365.00	2.99E 00				5.57E 01
370.00	1.69E 00				5.61E 01
375.00					5.53E 01
380.00					5.32E 01
385.00					5.00E 01
390.00					4.60E 01
395.00					4.15E 01
400.00					3.69E 01
405.00					3.24E 01
410.00					2.84E 01
415.00					2.48E 01
420.00					2.17E 01
425.00					1.91E 01
430.00					1.68E 01
435.00					1.49E 01
440.00					1.31E 01
445.00					1.15E 01
450.00					9.96E 00
455.00					8.58E 00
460.00					7.31E 00

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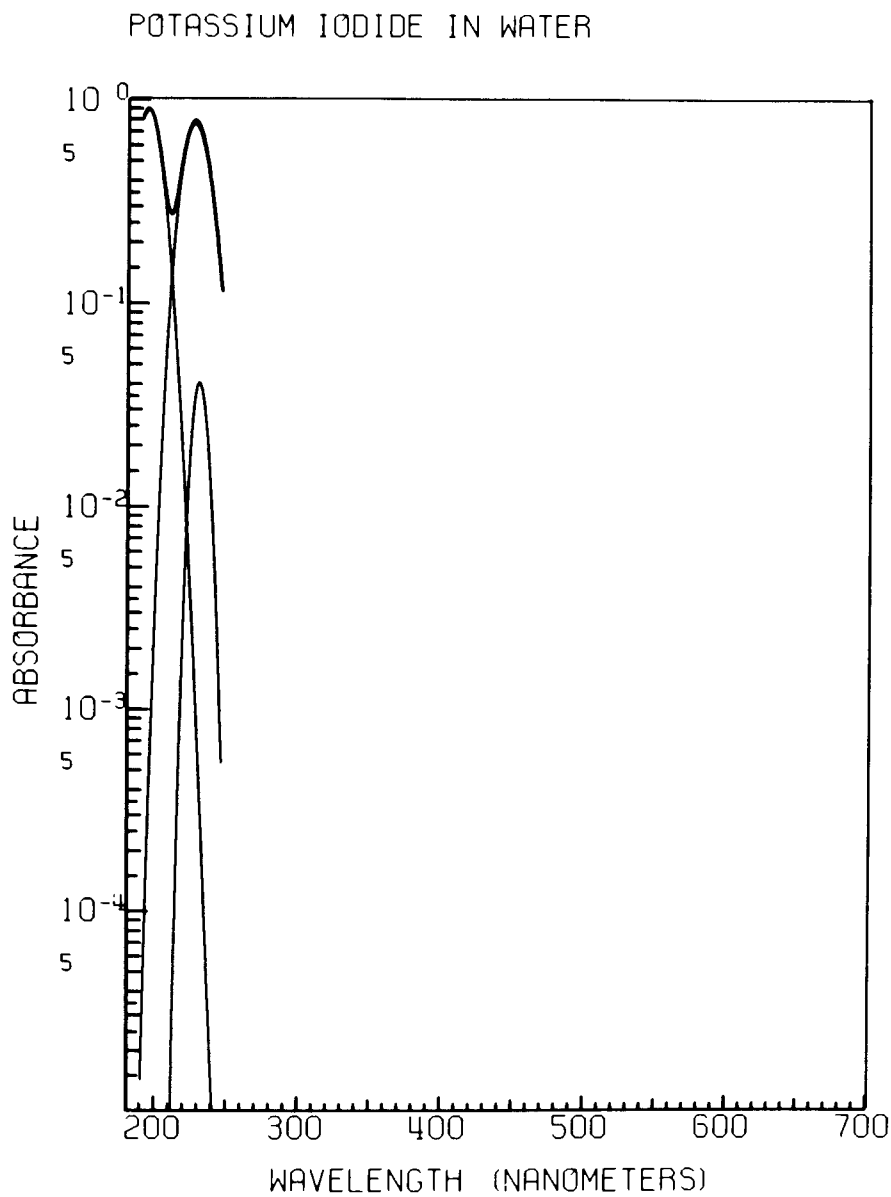


Fig. 1. Ultraviolet Spectrum of 10^{-4} M KI in Water Resolved into Three Gaussian Bands (See Table 1).

ORNL DWG 71-10843

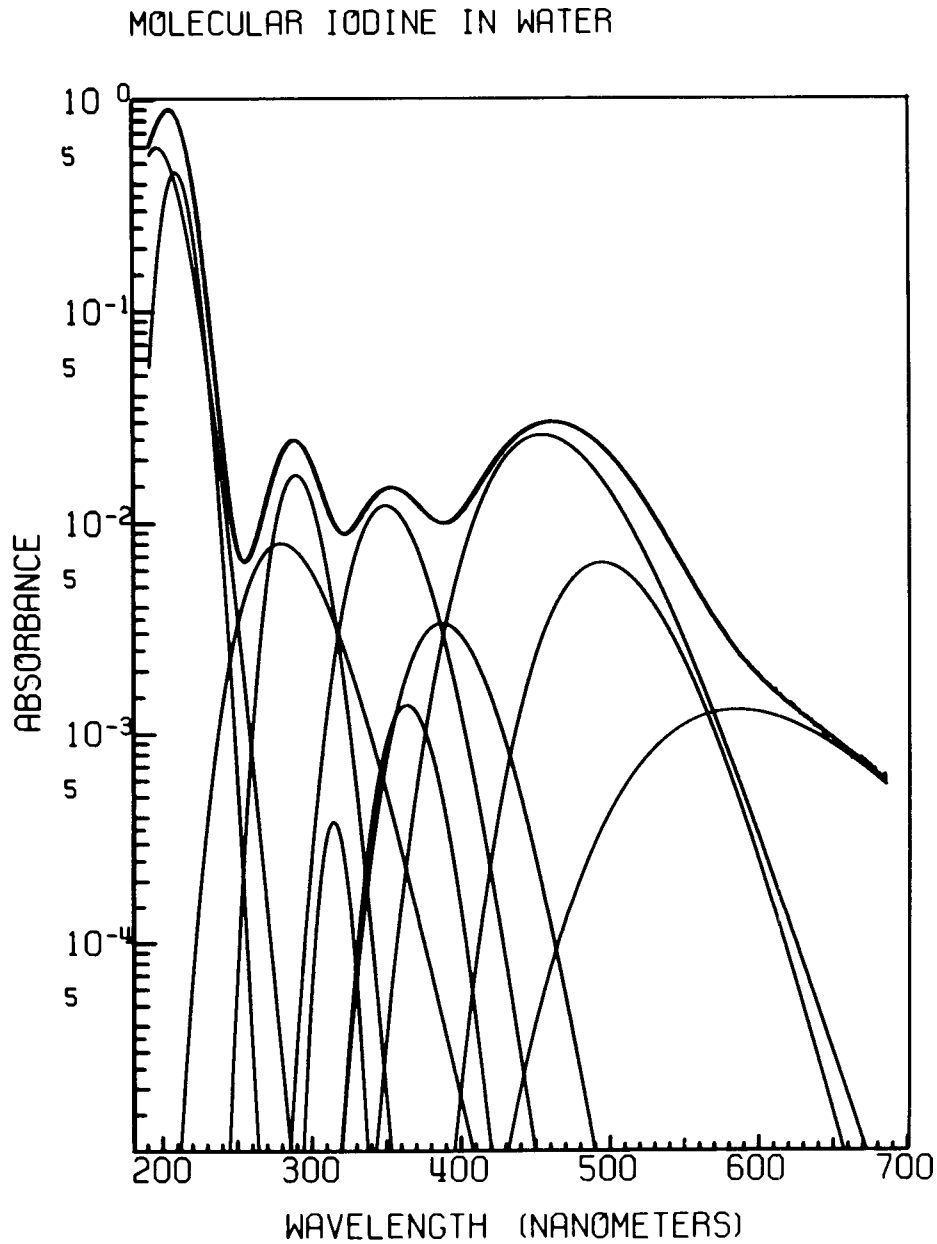


Fig. 2. Visible-UV Spectrum of 10^{-4} to 10^{-3} M I_2 in Water Resolved into Eleven Gaussian Bands (See Table 2).

ORNL DWG 71-10844

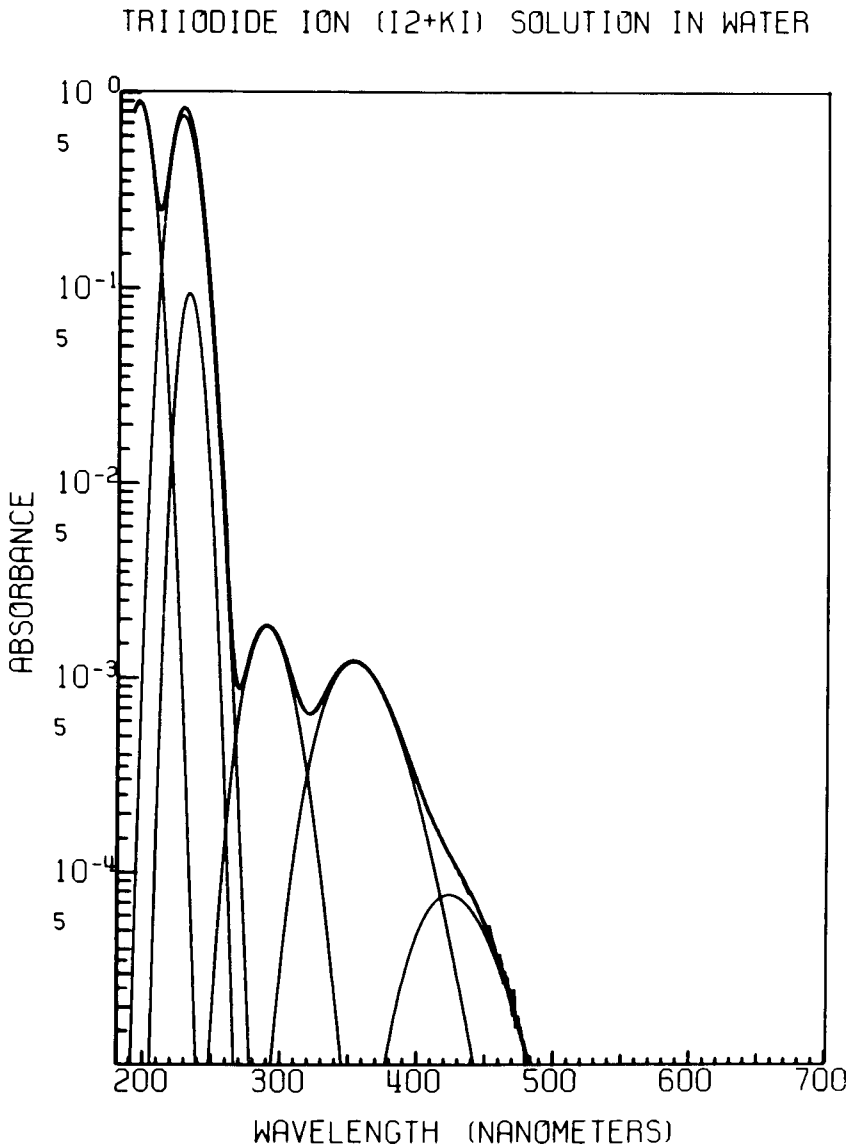


Fig. 3. Visible-UV Spectrum of 10^{-5} *M* I_2--10^{-2} *M* KI and 5×10^{-5} *M* I_2--5×10^{-2} *M* KI in Water Resolved into Six Gaussian Bands (See Table 3).

ORNL DWG 71-10845

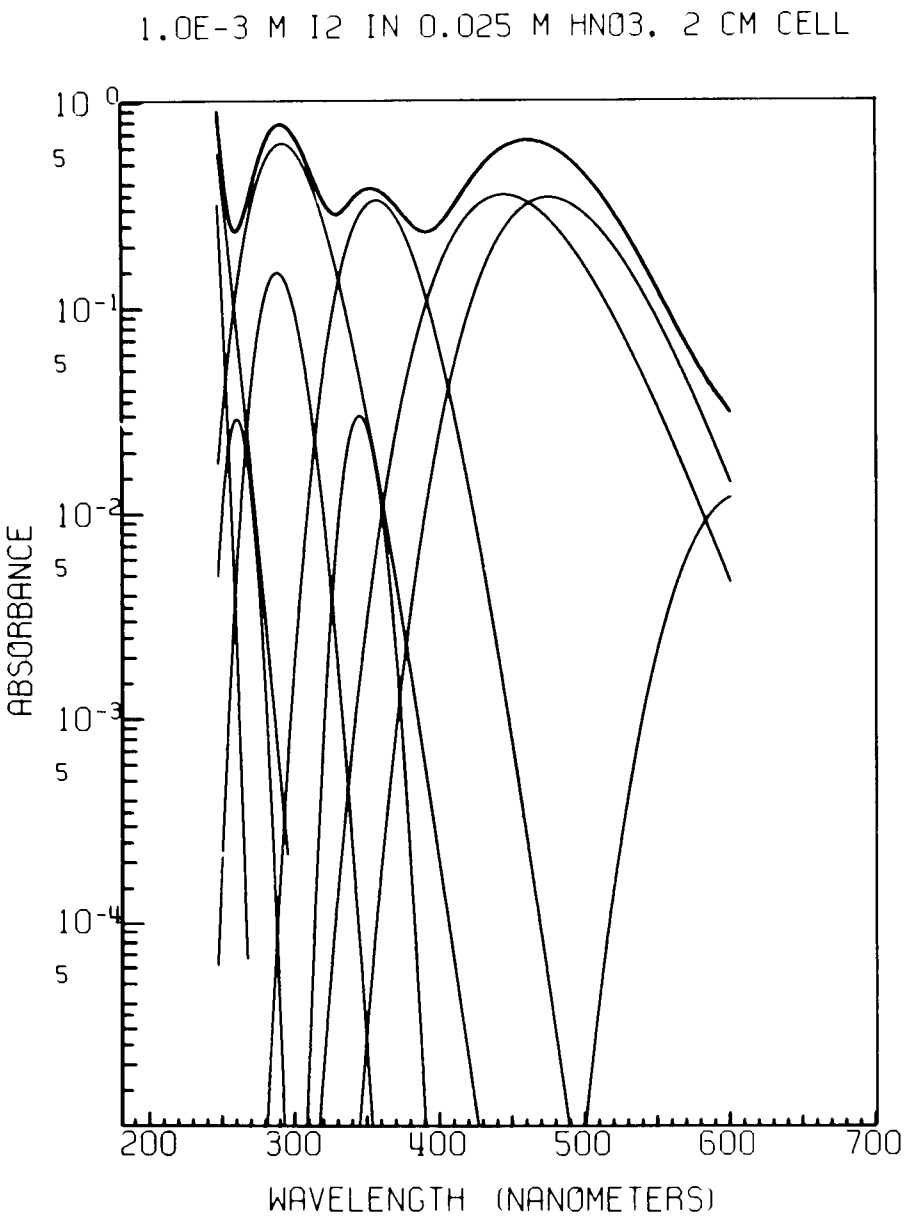


Fig. 4. Visible-UV Spectrum of 10^{-3} M I_2--0.025 M HNO_3 in Water Resolved into Ten Gaussian Bands (See Table 4).

ORNL DWG 71-10846

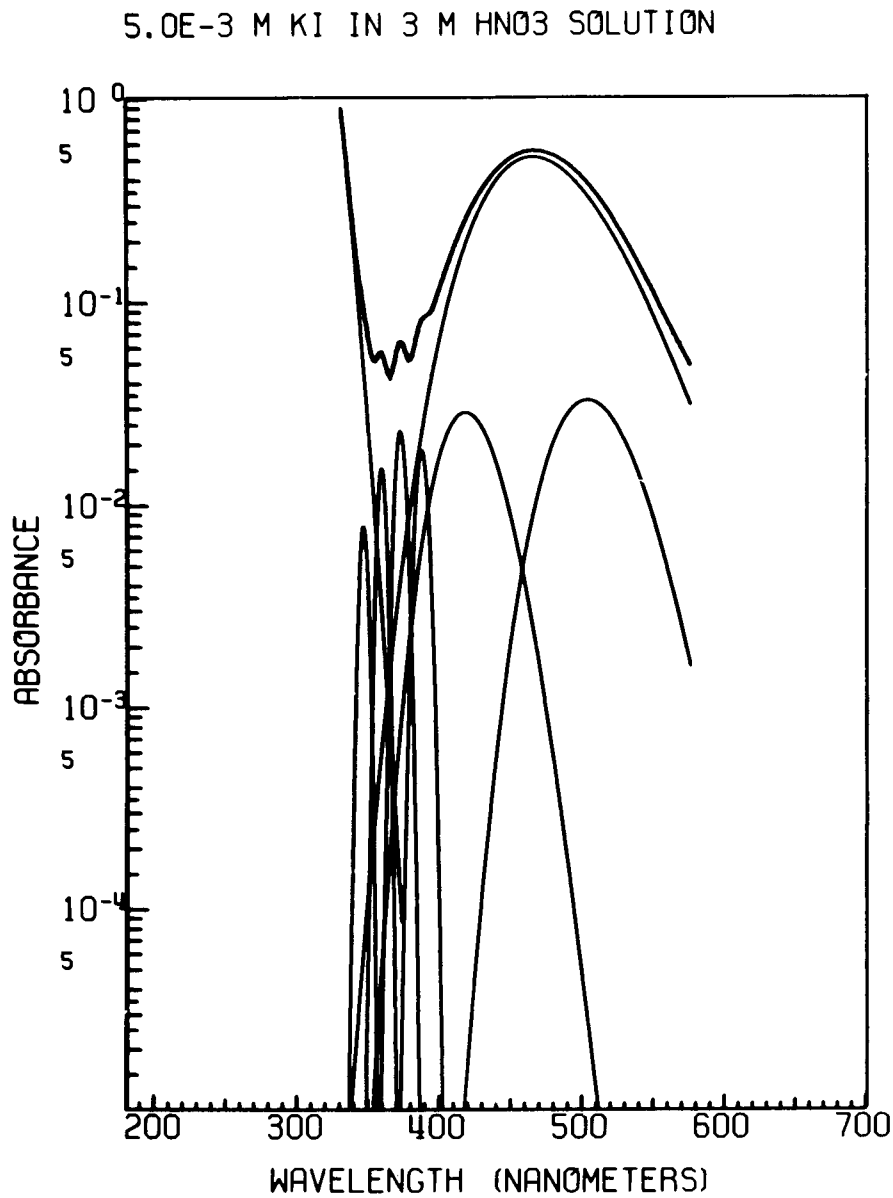


Fig. 5. Visible-UV Spectrum of a Solution Originally 5×10^{-3} *M* KI in Aqueous 3 *M* HNO_3. The I^- has been oxidized to I_2 (the broad band centered at 470 nm), some of which precipitated. The four narrow bands are probably due to NO_2^- or nitrogen oxides (see Table 5).

ORNL DWG 71-10847

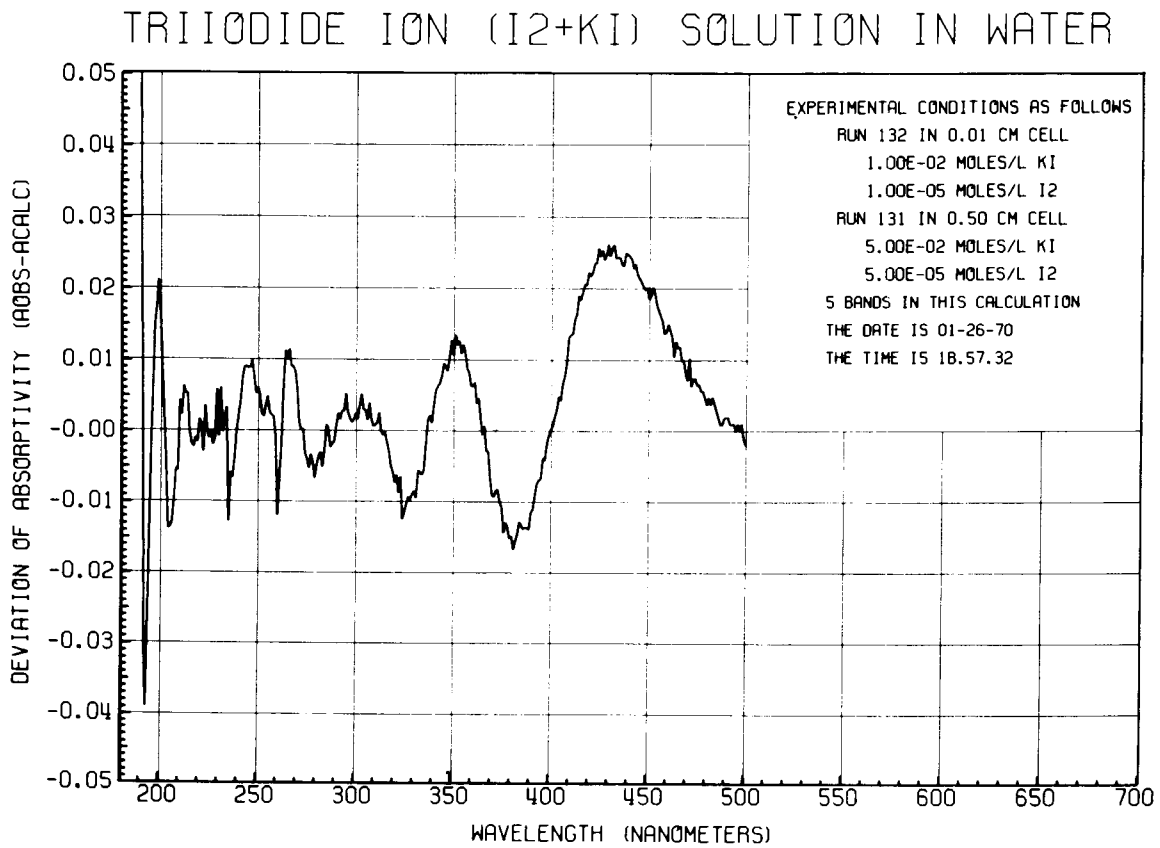


Fig. 6. Error Analysis of the I_2-KI Spectrum of Figure 3 When Only Five Bands Are Postulated. The error distribution is not random.

ORNL DWG 71-10848

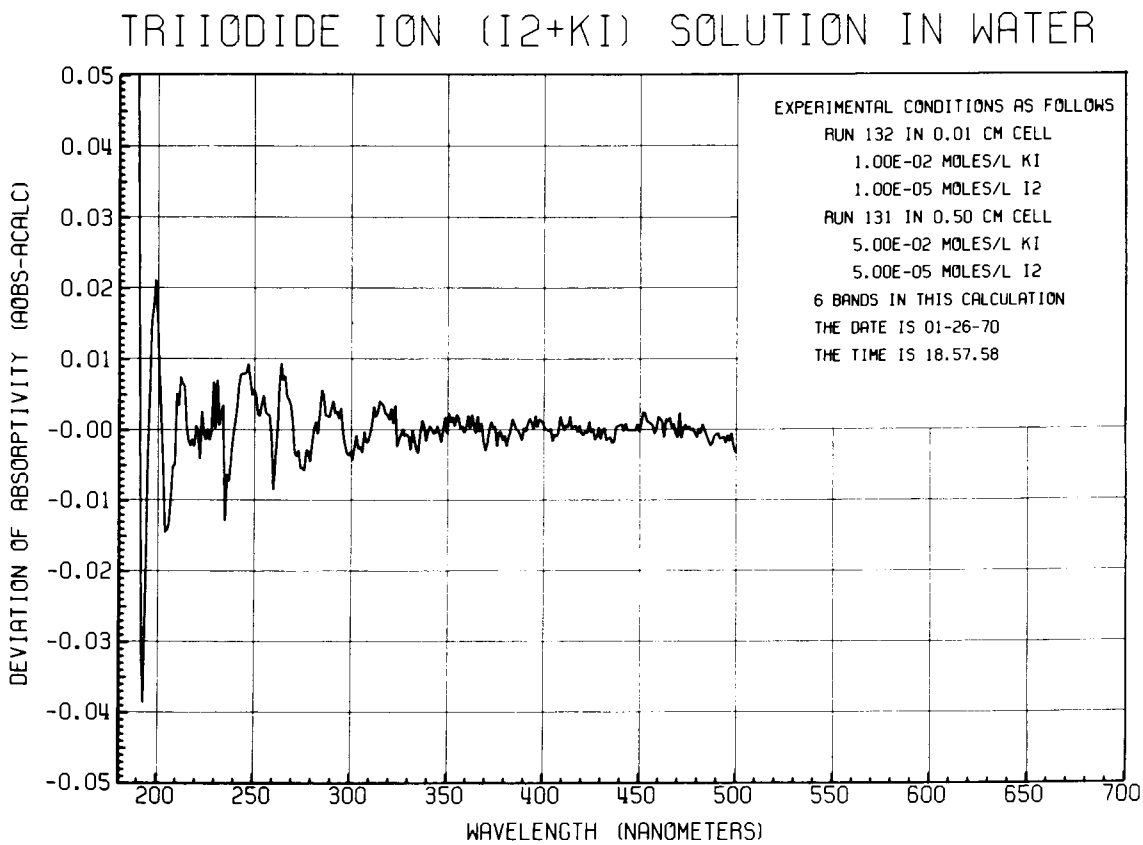


Fig. 7. Error Analysis of the I_2-KI Spectrum of Figure 3 When Six Bands Are Postulated. The error distribution is essentially random.

ORNL DWG 71-10849

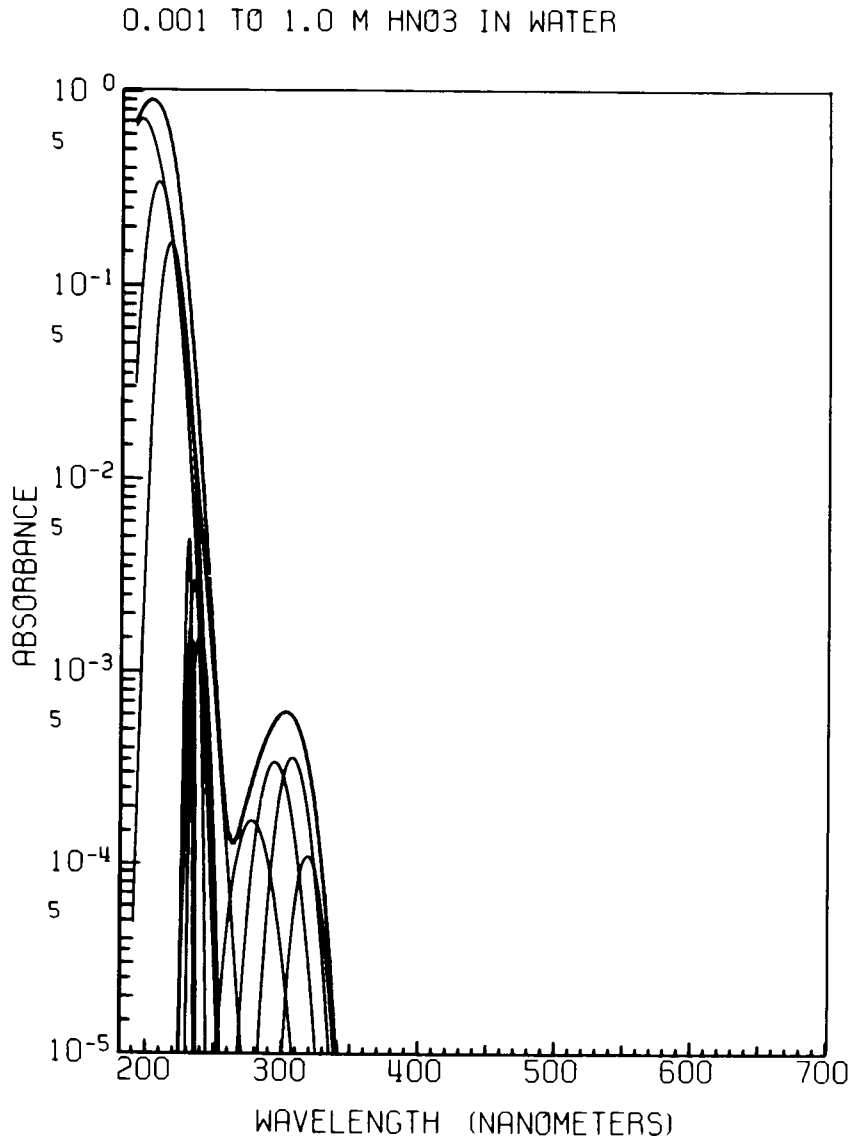


Fig. 8. Ultraviolet Spectrum of Aqueous 10^{-3} M to 1 M HNO_3 Solutions Resolved into Eleven Gaussian Bands (See Table 6).

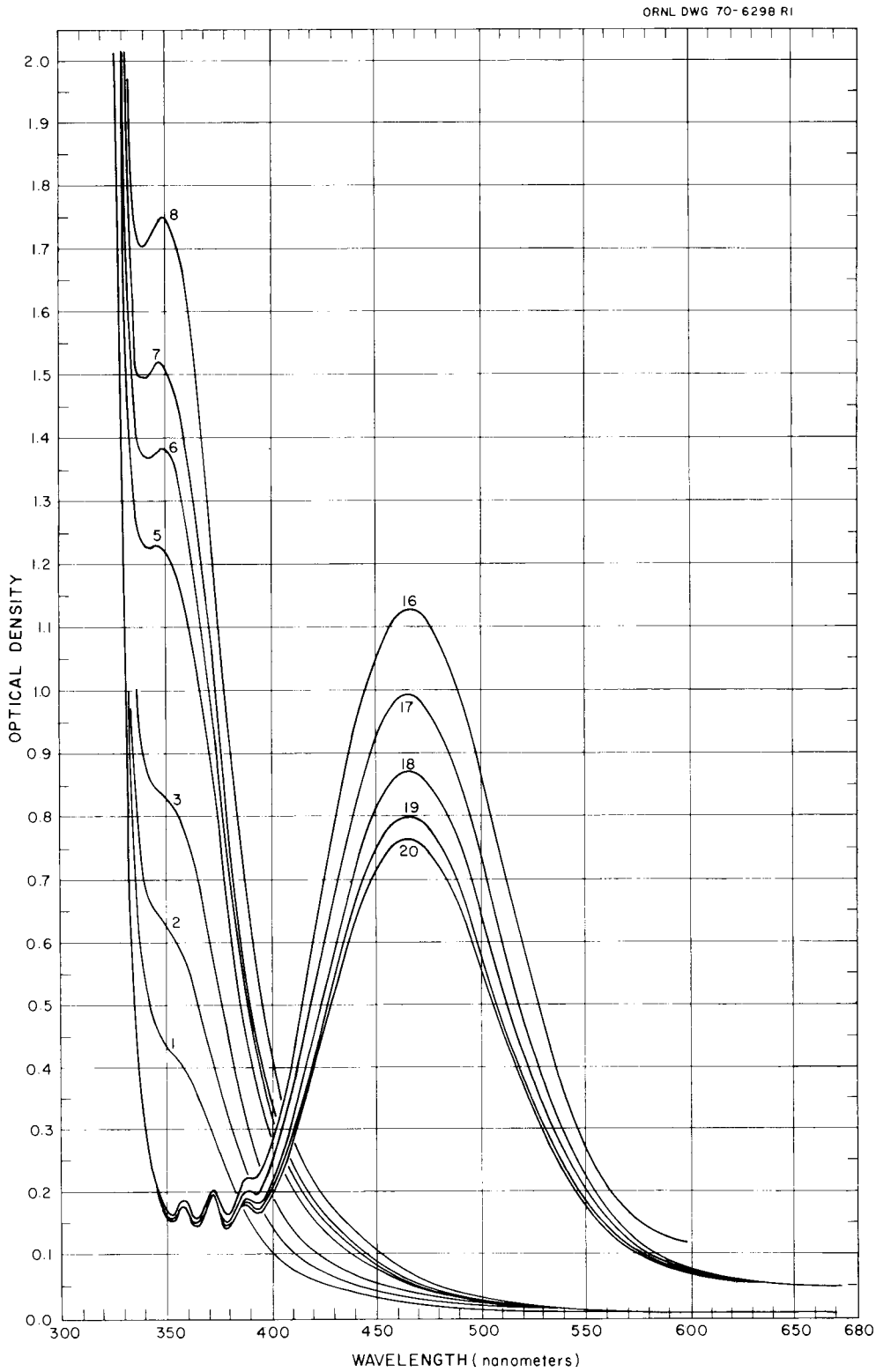


Fig. 9. Successive Spectra During the Oxidation of 10^{-2} *M* KI in 3 *M* HNO_3 to I_2, Including Precipitation of I_2 After Spectrum 16. Reaction times, in minutes, for the successive curves, are in parentheses as follows: 1(6), 2(12), 3(20), 5(40), 6(50), 7(60), 8(80), 16(195), 17(205), 18(220), 19(240), 20(270). Cell length was 0.5 cm.

ORNL DWG 71-10850

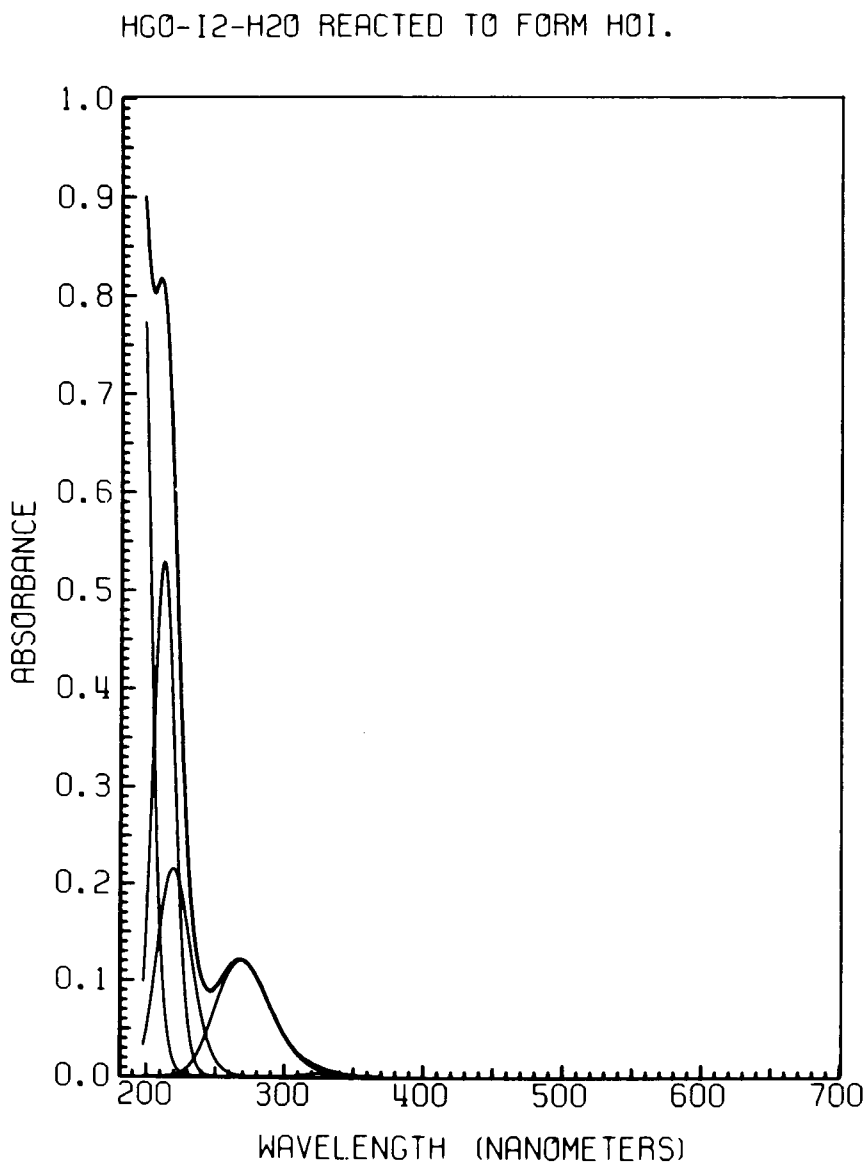
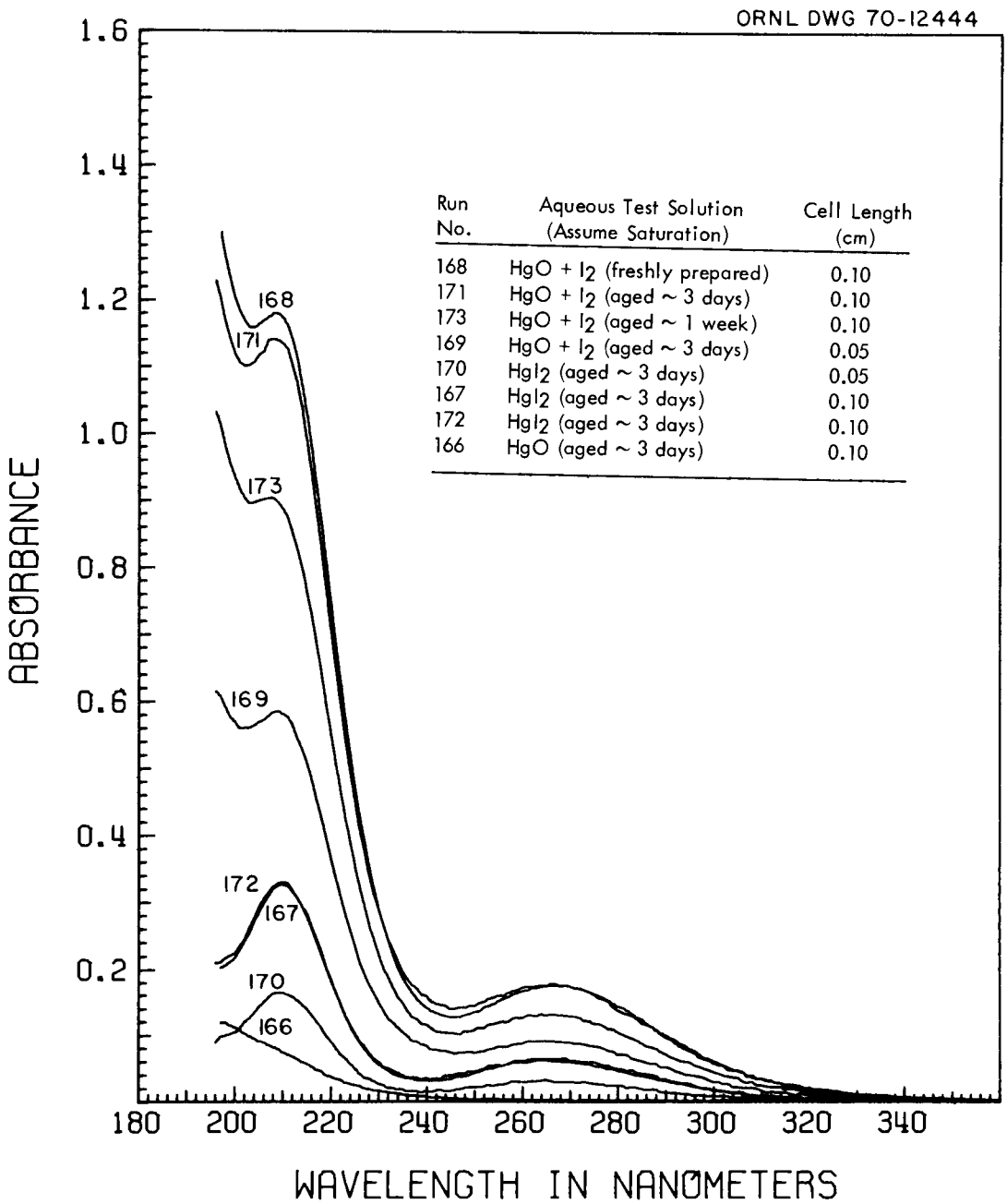


Fig. 10. Ultraviolet Spectrum of HOI (?) - the Filtrate from $HgO-I_2$ in Water - Resolved into Five Gaussian Bands (See Table 7).



Run No.	Aqueous Test Solution (Assume Saturation)	Cell Length (cm)
168	$HgO + I_2$ (freshly prepared)	0.10
171	$HgO + I_2$ (aged ~ 3 days)	0.10
173	$HgO + I_2$ (aged ~ 1 week)	0.10
169	$HgO + I_2$ (aged ~ 3 days)	0.05
170	HgI_2 (aged ~ 3 days)	0.05
167	HgI_2 (aged ~ 3 days)	0.10
172	HgI_2 (aged ~ 3 days)	0.10
166	HgO (aged ~ 3 days)	0.10

Fig. 11. Ultraviolet Spectra of Filtrates from HgO, HgI_2, and $HgO-I_2$ in Water After Various Periods of Aging to Show Changes of Intensities (See Table 8).

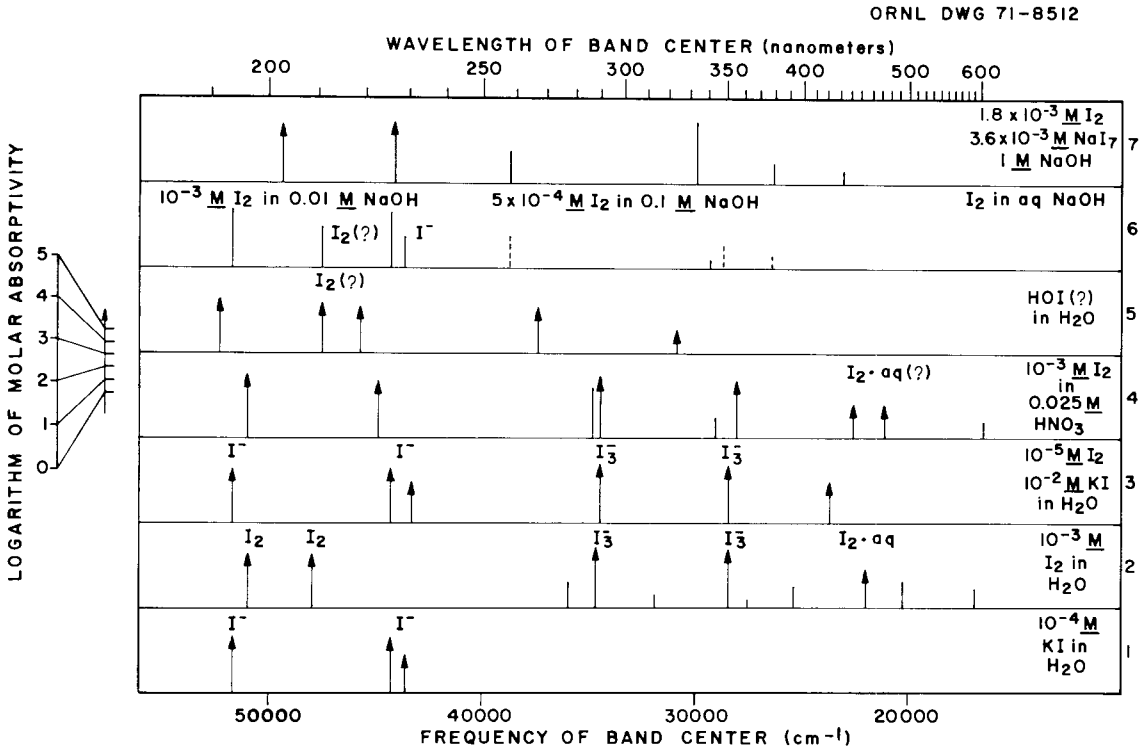


Fig. 12. Line-Spectrum Representation of Solutions with Some Assigned and Some Unassigned Chemical Species. Arrowheads imply relatively certain knowledge of chemical species and concentration; in these cases, the molar absorptivity is given by the scale on the left. Absence of arrowhead implies lack of knowledge of species or concentration, or both. Dashes represent bands whose intensities decrease with time. The length shown probably is a reasonable representation of molar absorptivity at t = 0 under our experimental conditions.

ORNL DWG 71-10851

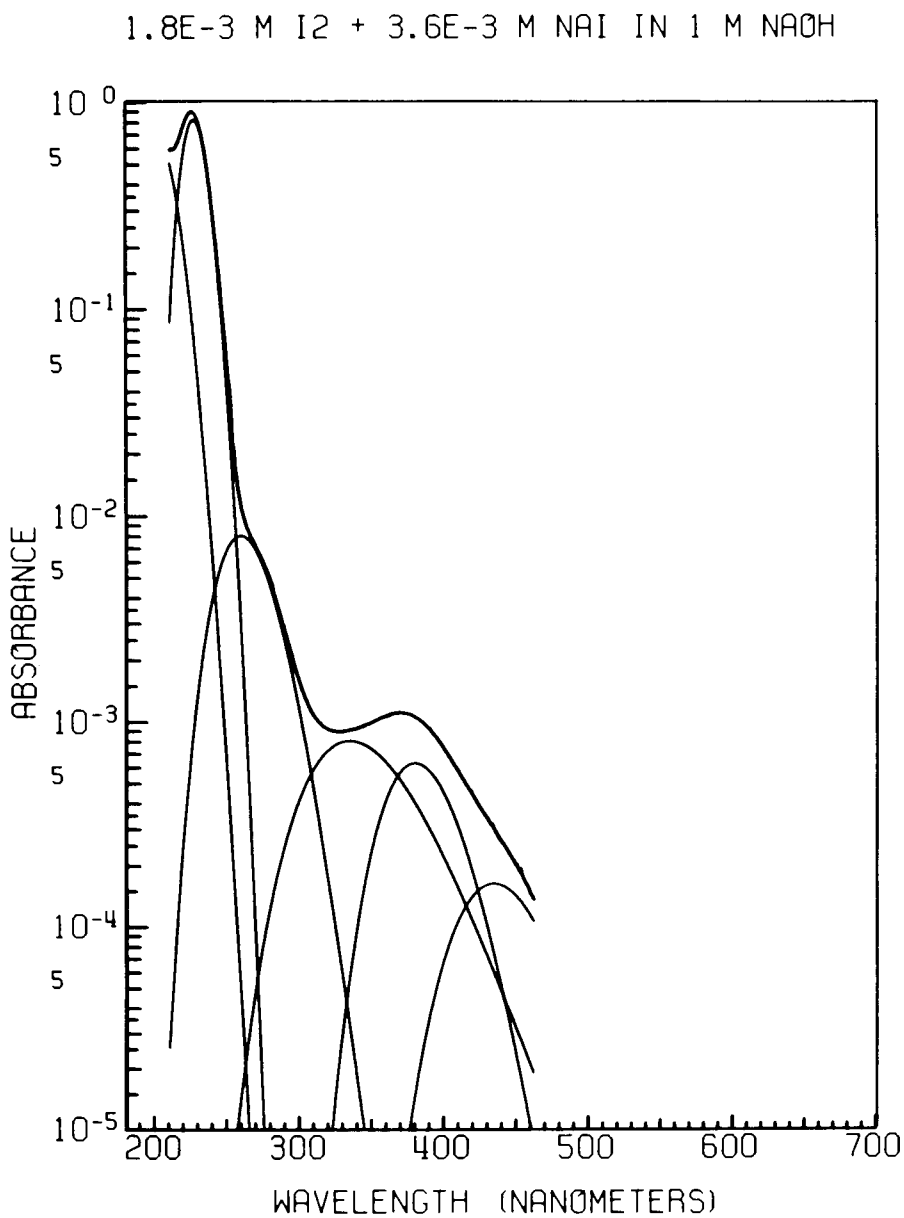


Fig. 13. Visible-UV Spectrum of 1.8×10^{-3} M I_2--3.6×10^{-3} M NaI in 1 M NaOH Resolved into Six Gaussian Bands (See Table 11).

ORNL DWG. 71-8694 R1

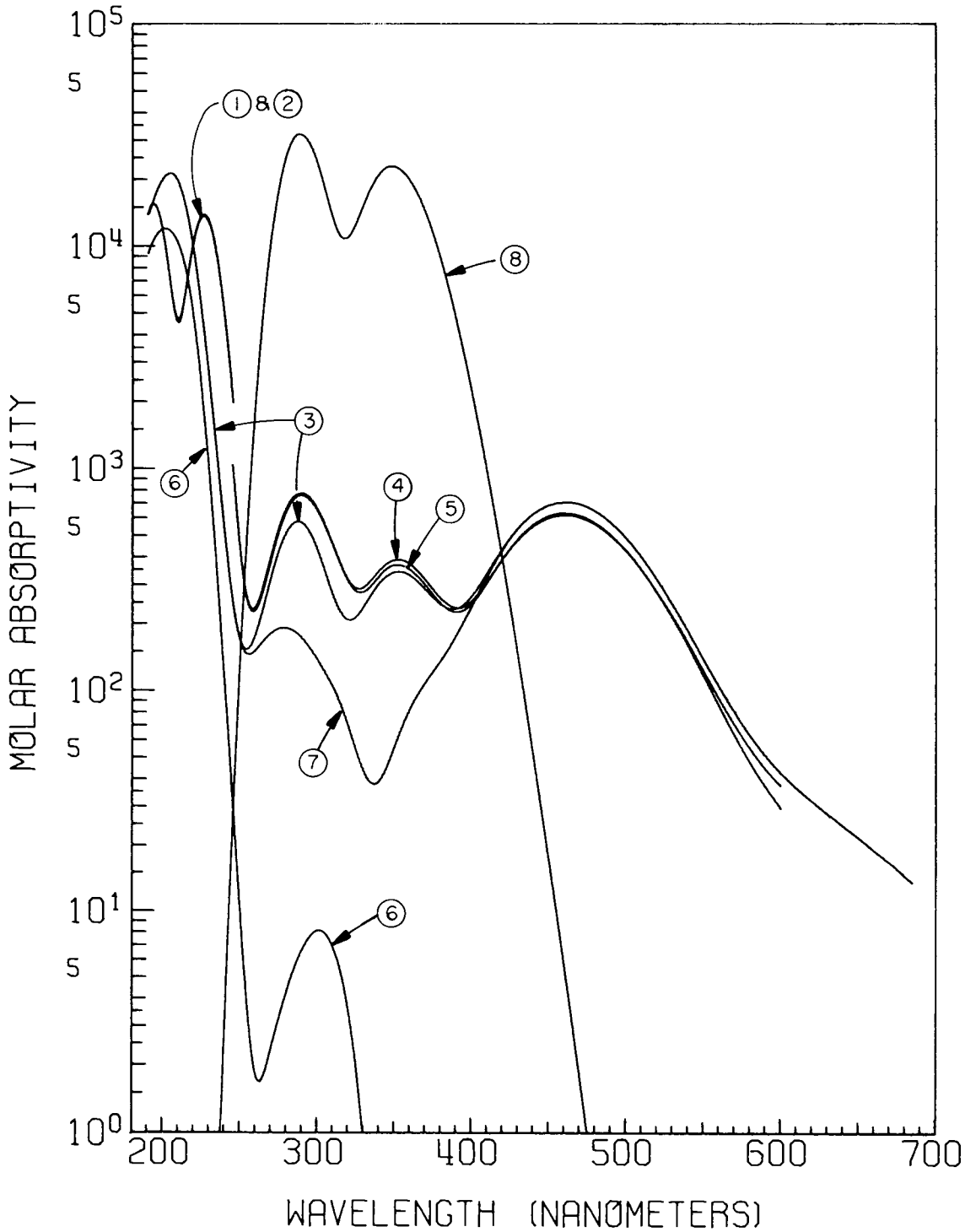


Fig. 14. Molar Absorptivities (Reference Spectra) of Some Iodine and Nitric Acid Solutions, Including the Calculated Spectrum of I_3^- and of I_2 without I_3^- (See Table 12). Identification of curves: 1 and 2, KI in H_2O; 3, I_2 in H_2O; 4 and 5, 0.001 *M* I_2 in 0.025 *M* HNO_3; 6, HNO_3 in H_2O; 7, hypothetical I_2 free of I_3^-; 8, I_3^-.

ORNL DWG. 71-8696 R1

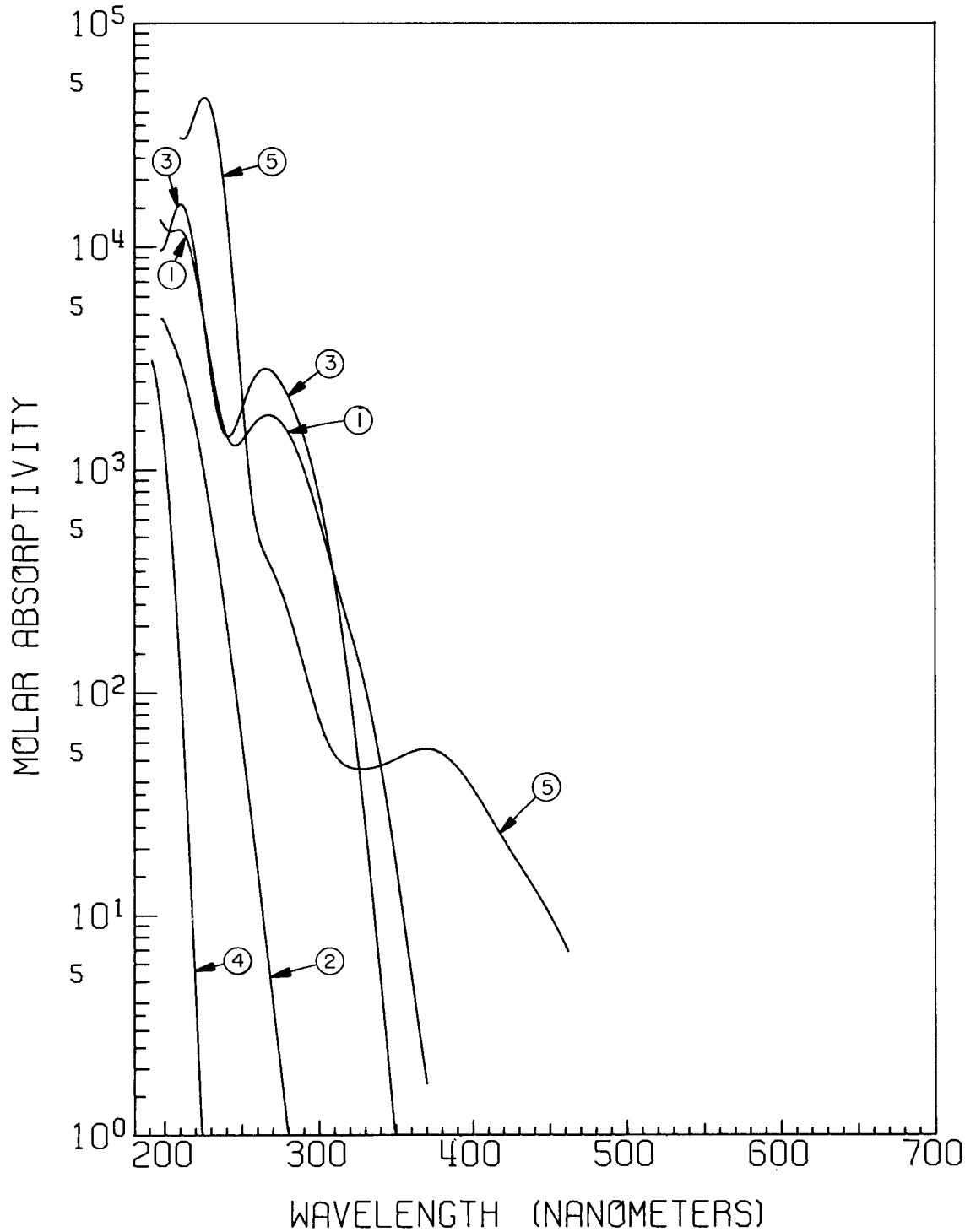


Fig. 15. Molar Absorptivities (Reference Spectra) of Some Solutions Containing HOI (?), IO^-, and Related Species (See Table 13). Identification of curves: 1, filtrate from HgO + I_2 in H_2O (HOI?); 2, filtrate from HgO in H_2O; 3, filtrate from HgI_2 in H_2O; 4, NaOH in H_2O; 5, 0.0018 *M* I_2, 0.0036 *M* NaI in 1 *M* NaOH.

ORNL DWG. 71-8695 R1

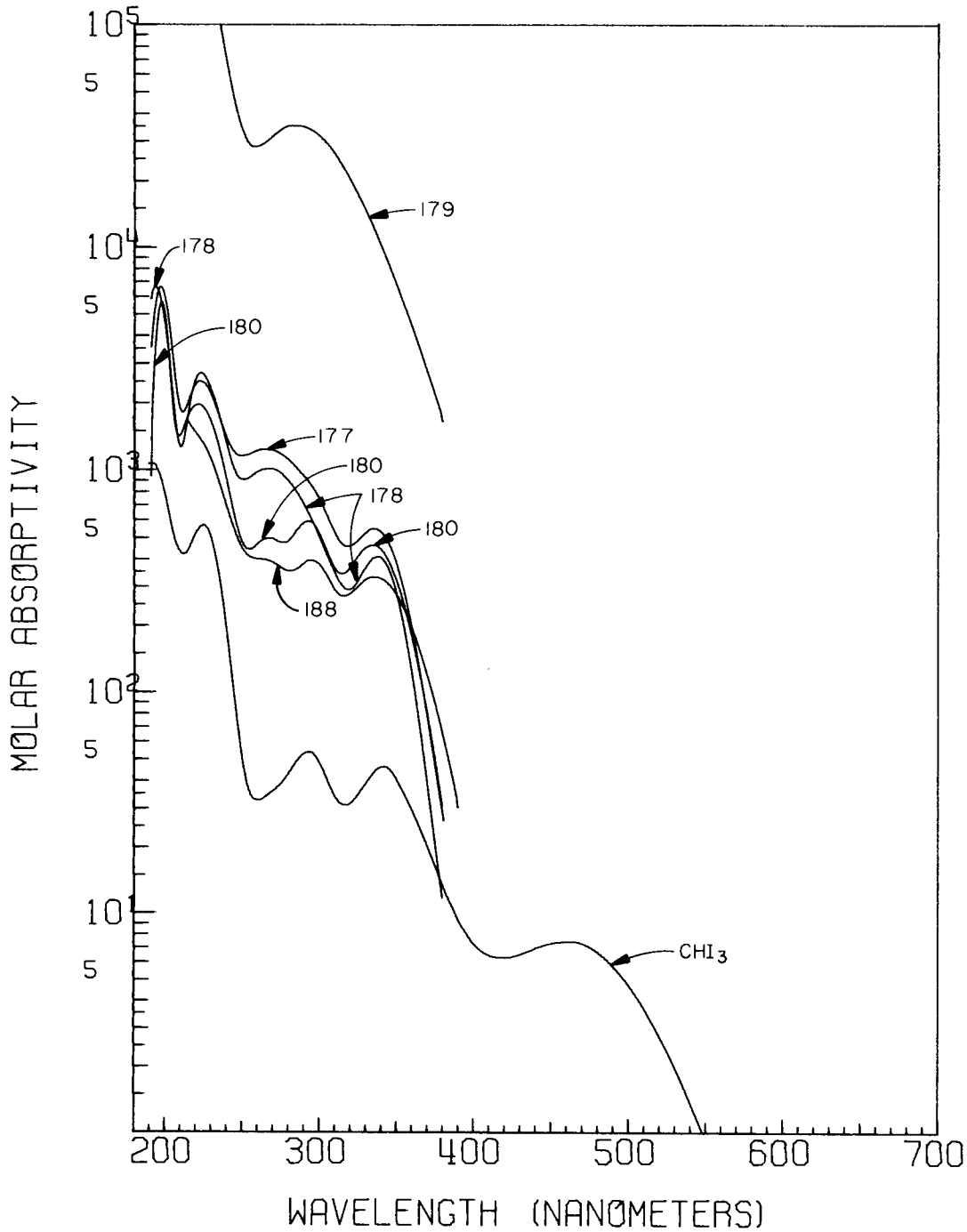


Fig. 16. Molar Absorptivities of Water Solutions of Iodoform (CHI_3) and of Iodine-Containing Species Vaporized by Nitrogen Sparging of Basic Nitrate Solutions. Run 177, J. M. Schmitt's preparation 510C, fresh; 178, 510C aged 24 hr at 25°C; 180, 510C aged 24 hr at 5°C; 179, preparation 512, fresh; 188, preparation 516, fresh. Runs 177, 178, and 180 clearly show the presence of some CHI_3.

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