Critical Review of Ultraviolet Photoabsorption Cross Sections for Molecules of Astrophysical and Aeronomic Interest

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This paper is devoted to a critical review of photoabsorption cross sections for molecules of aeronomic and astrophysical interest at wavelengths less than 3000 A. A discussion of the relative merits of various experimental techniques is given along with possible systematic and random errors that may be associated with them. The problems in data analysis associated with finite spectral bandwidths are reviewed, with special emphasis on the interpretation of published absorption cross sections. This review does not contain a complete set of cross-section-versus-wavelength values for each molecule; the prepared figures are used to compare the results of several determinations or to point out where difficulties of interpretation might arise. However, references to all papers believed to contain the more reliable data are given.

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I. INTRODUCTION

In 1958, K. Watanabe published a review of ultraviolet cross sections between 2900 A and 1 A for those molecules that are major and minor constituents of the earth's atmosphere. His review, which coincided with just over a decade of rocket experiments, has made an important contribution to the understanding of the basic absorption processes in the atmosphere [*Watanabe*, 1958]. Since 1958 there has been an extensive increase in the number of rocket and satellite experiments to study the earth's and planetary atmospheres, and also in the number of spectroscopic investigations in the ultraviolet of planetary constituents. It seems appropriate, therefore, that after a further decade of experimentation another review should be prepared. The intention of this review is to make a critical analysis of the available cross-section data, to assess their reliability, and to give the reader an idea of the limitations that must be placed on the interpretation and use of these data. *Hudson and Kieffer* [1970] have recently published a complete bibliography of photoabsorption cross section data; the references at the end of this review are to those papers that, in my opinion, contain the more reliable data.

II. MEASUREMENT TECHNIQUES

A. Total Photoabsorption Cross Sections

The total photoabsorption cross section σ_T of a gas is usually defined as follows

$$I_0(\lambda)/I(\lambda) = \exp n\sigma_T \ell \tag{1}$$

where $I_0(\lambda)$ and $I(\lambda)$ are the fluxes incident on and transmitted through the gas, n is the concentration in particles/cubic centimeter, and ℓ is the path length in centimeters. In many papers the absorption coefficient, k_T, is given; this is related to the cross section by

$$k_T = \sigma_T n_0$$

where n_0 is Loschmidt's number $(2.69 \times 10^{19}/cm^3)$.

A detailed description of many of the techniques developed for quantitative measurements of photoabsorption cross sections of gases has recently been published [*Samson*, 1967] and will not be explicitly dealt with in this review. Instead, emphasis will be given to a discussion of the relative merits of these techniques and to the systematic and random errors that may be associated with them.

As can be seen from equation 1, the parameters that must be known in order that a total photoabsorption cross section can be determined are

1. The ratio of I_0 to I.

2. The number density of the species under investigation, including the number density of contaminant species.

3. The length of the absorbing column.

The measurement of each of these quantities will have associated with it both a systematic and a random error. The policy of most experimenters engaged in ultraviolet measurements has been to quote a total error only; and, in general, the exact breakdown of this total between the two modes of error is not specified. Since the disagreement between published results is often outside these quoted total errors, it must be assumed that some of the possible systematic errors have been left out of these error analyses.

1. The ratio I_0/I. This ratio is best determined by double-beam spectrophotometric techniques in which the intensities $I_0(\lambda)$ and $I(\lambda)$ are measured simultaneously. Errors arising from short-term fluctuations in I or long-term drifts of I_0 can then be eliminated. Few such measurements have been made, and as a result the stability of the radiation source has been an important factor affecting the accuracy of published data. Although some radiation sources have been developed with extremely constant outputs, typical short-term fluctuations are observed varying from 2 to 5%, with long-term changes of up to 3%. The extent to which these fluctuations can affect the final error on σ_T depends on the method of data reduction and the values of the ratio I_0/I used in the experiment. The former point will be discussed further in the next section. The latter point is illustrated in Figure 1 where the error in σ_T arising from a systematic error in both I_0 and I of 1% of I_0 is shown as a function of I_0/I. The error arising from the random fluctuations in I_0 and I is statistical and should, presumably, be represented in the random errors quoted by the authors.

The two types of detectors most often used for quantitative work in the ultraviolet are photographic emulsions and photoelectric detectors (i.e., photomultipliers and photodiodes). Emulsions have the advantage of allowing the entire absorption spectrum to be recorded simultaneously, but they have the disadvantage that their calibration is not simple and that the photographic density is not a linear function of the incident photon flux. Errors in the determination of I_0/I can arise because of nonuniformity of the emulsion over the plate or film, the failure of the reciprocity law during the calibration procedures, incorrect development procedures, and uneven shrinkage on drying. Those experimenters who use photographic techniques usually take great care to try to minimize these sources of error.

Another cause of systematic errors in the determination of the ratio I_0/I from emulsions is scattered light within the spectrograph. In principle, the amount of scattered light can be determined using filters; but this procedure can be complicated in that during the intensity calibration of the emulsion the ultraviolet radiation and the scattered radiation are both reduced by the same amount, whereas during the experiment the intensity of the ultraviolet light is reduced, but the scattered light, which comes mainly from the visible portion of the spectrum, is not reduced. It should be noted that the latter statement does
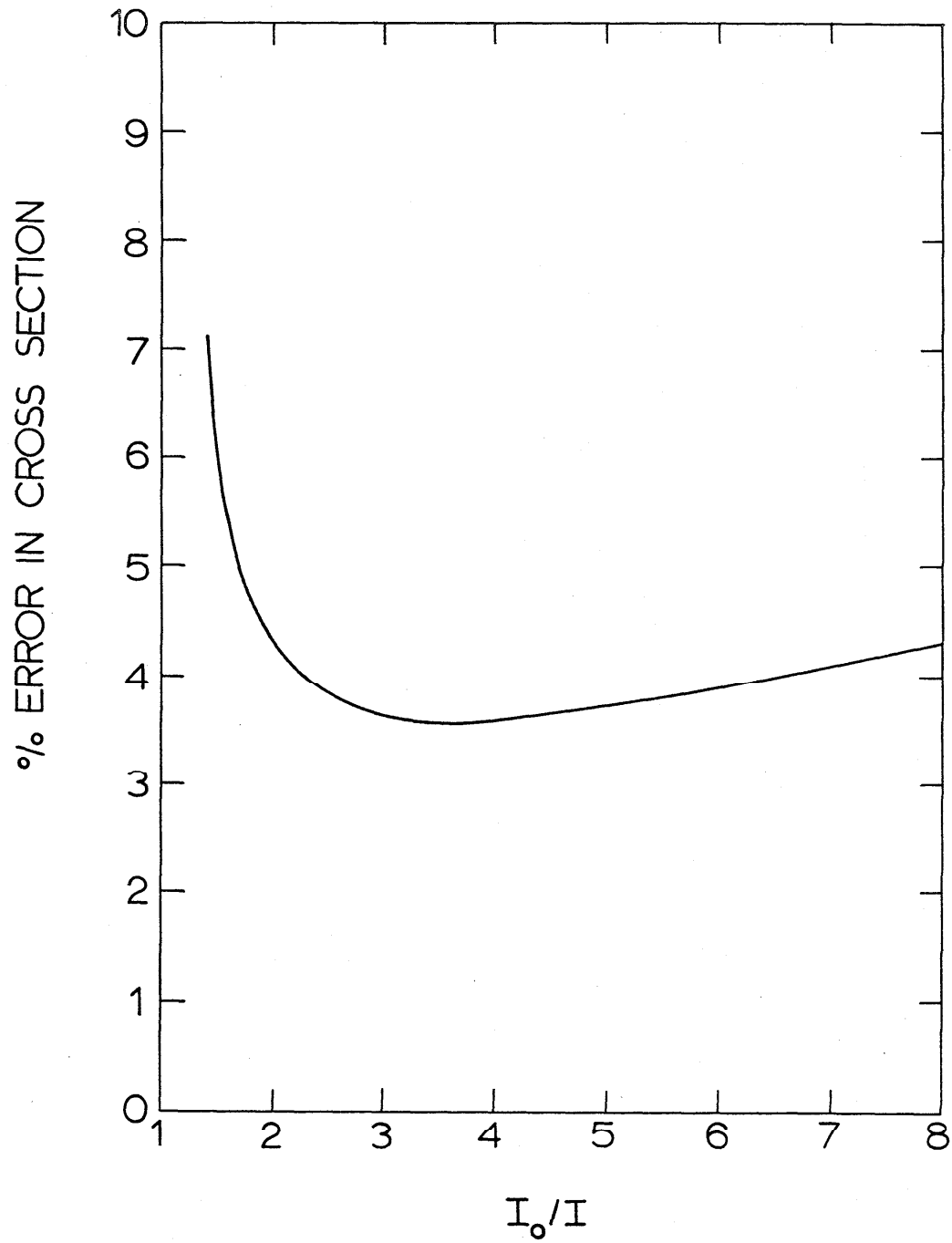
Fig. 1. Percent error in the cross section versus I_o/I.

not depend on the scattering properties of gratings, but on the fact that most light sources have their highest photon output in the visible region. The over-all systematic error in the ratio I_0/I that could arise in photographic measurements is difficult to assess; but a conservative estimate for the error in I_0 and I can be made of $\pm 1\%$ of I_0, giving rise to an error in σ_T (from Figure 1) of at least $\pm 3.5\%$.

Both photomultipliers and photodiodes, if used properly, show a linear response between their current output and the incident-photon flux over a wide range of values. Most of the photomultipliers used in the determination of absolute cross sections have windows of quartz or pyrex. The ultraviolet radiation below the window cutoff is then measured by observing, with the photomultiplier, the visible light output from a material (such as sodium salicylate) that fluorcsccs on exposure to vacuum ultraviolet radiation. Thus for reliable measurements of I_0/I one must be assured that the fluorescent efficiency of such a material is constant with time. Changes in the fluorescent efficiency of sodium salicylate have been noted, the usual change being a slow decrease of the efficiency with time; but exposure to some reactive gases can decrease the efficiency within minutes [Samson, 1967]. Such changes have a pronounced effect on the determination of the ratio I_0/I, especially if the change is reversible. It might seem that the use of simple photodiodes, which detect the photoemission of electrons from a metallic surface, would not suffer from this difficulty. However, in the typical experiment using such devices, the metal surface has been placed inside the absorption chamber, where it is immersed in the gas being studied. In this situation, changes in the photoelectric yield might well arise.

Waclawskii et al. [1967; personal communication, 1969] have investigated the effects of absorbed gases on the photoelectric yield of tungsten between 600 A and 1600 A. The sample was cleaned, by heating under high vacuum, before exposure to the gases, which included O_2, N_2, H_2, CO, and H_2O. They found changes in the photoelectric yield of as much as a factor of 6, changes that were specific for the particular gas investigated. They also found evidence that the photoionization of the absorbate contributed to the observed yield for coverages of the order of a monolayer. However, such effects might be smaller if the surface were not cleaned to begin with, i.e., were already covered by a monolayer of air, since the ambient gas would then have to replace the oxygen or nitrogen on the surface. Of course reactive gases, or those gases that tend to stick to metals (such as water vapor), might easily produce a larger and reversible change in the photoelectric yield.

Three other effects can also cause systematic errors in the measurements using photoelectric devices. These are nonlinearity in the electrometer-recorder combination used to measure the photoelectric currents, scattered light from the spectrograph, and fluorescent light from the absorption cell. In the papers reviewed, accounts are seldom given of the calibration of the electrometer-recorder combination, and it is difficult to believe that this has been carried out to any better than $\pm 1\%$ of full scale. The amounts of scattered light and fluorescent light can be determined by using filters. Scattered light is usually found to be less than 2% of the incident intensity, and corrections are made for its effect.

Fluorescence is normally important only if short absorption cells are used, where corrections as high as 10% have had to be made. If these corrections have been made correctly, it is estimated that they should contribute less than $\pm 0.25\%$ to the total systematic error in I_0/I. It seems likely then that the total systematic error in the determination of I_0/I is $\geq 1.25\%$, implying (from Figure 1) a systematic error in σ_T of $\pm 4\%$.

If measurements of the ratio I_0/I are made in a spectral region where the gas ionizes, then the double–ion-chamber method can be used. In this method two identical ion chambers are placed in tandem, and simultaneous measurements of the ion currents collected by the two chambers are made with the gas in the cell. The ratio of the ion currents can then be substituted for I_0/I in equation 1, where ℓ is now the distance between the front of the first and the front of the second chamber. *Samson and Cairns* [1964, 1965] have made extensive use of this method. They measure the current from the two ion chambers with separate electrometers, each calibrated to an accuracy of 1% of full scale. This implies a systematic error of at least $\pm 3.5\%$ in their determination of σ_T.

As indicated, the minimum systematic error that it seems reasonable to assign to the measurement of σ_T from the measurement of the ratio I_0/I is $\pm 3.5\%$.

2. The number density of the absorbing gas. The number density of the absorbing gas has, in almost all cases, been determined from direct measurements of the gas pressure and temperature. The temperature can be measured accurately (to better than $1°K$, i.e., 0.3%); however, the pressure measurement is less certain. Most experimenters use a McLeod gage as a primary standard. In principle this gage should be fairly accurate; some models are manufactured to tolerances that give a stated accuracy of $\pm 1\%$ for the measurement of a pressure of 10^{-2} torr if the mercury meniscus level is read with a precision of ± 0.25 mm. Contamination of the internal surfaces of the gage and the mercury surfaces will reduce this accuracy, and a further uncertainty arises if effects due to 'mercury pumping' into the cold trap associated with the gage are not minimized [*Gaede*, 1915; *Ishii and Nakayama*, 1962]. *Carr* [1964] has concluded that an accuracy of 1% can be achieved with McLeod gages at pressures lower than 0.1 torr only if the gage is baked before use, corrections are made for the presence of the cold trap, and variable compression measurements are made with permanent gases. Without such precautions, systematic errors as large as 10% can be made. Most experimenters quote errors from pressure measurements of $\pm 5\%$, but no distinction is usually made between systematic and random errors in their papers.

In some experiments the pressure has been determined by observing the attenuation of light by a gas at a wavelength for which the absorption cross section is 'known.' The systematic error on this determination is the sum of the total error for the 'known' absorption cross section and the systematic error in the determination of the ratio of I_0/I, and it is likely to be much larger than the error that would have been made with a McLeod gage. Larger systematic errors must also be assigned to those experiments in which secondary standards, such as thermocouples and ion gages, are used.

It is very important, especially when measuring small absorption cross sections, to know the number density of contaminant species, both in the absorption cell and, where applicable, in the body of the spectrograph. Experimenters have normally taken care to use pure samples of the gas they are investigating and to keep the spectrograph pressure below 10^{-5} torr; however, only a few analyze the impurity content. A possible source of contaminants is introduced when the absorption cell is placed between the light source and the spectrograph. With this arrangement, the gas under investigation is irradiated by the total undispersed flux from the source, and it is quite conceivable that large concentrations of excited species, dissociation products, or the results of the interaction of these products with the gas under study can accumulate in the cell. These products essentially become an impurity and lower the accuracy of the final data. The same arguments, of course, apply to those experiments in which the spectrograph is filled with the gas under study; but in this case the volume is much larger and the equilibrium densities of excited species should be much smaller.

In summary it can be said that the pressure determination probably constitutes the most common and largest source of error in photoabsorption measurements. Possible systematic errors in this determination could be between 1 and 10%.

3. The length of the absorbing column. The length of most absorption cells has generally been ≥ 10 cm and has been measured accurately (to better than ± 1 mm). Difficulties can arise, however, in windowless cells when there is a net gas flow into the spectrograph through the slit, producing a pressure gradient in the cell. Most experimenters have minimized this gradient by a careful design of their gas inlet systems, by using small slit areas, and by using absorption cells of large cross section. Formulas are available [*Dushman and Lafferty,* 1962] to calculate the rate of flow of a gas through a slit, and this flow can then be used to calculate the pressure differential in a typical absorption cell. Calculations indicate that for slit areas ≤ 100 μm by 1 cm, and for cell lengths ≥ 10 cm $\times$ 3 cm^2, the pressure differential from one end of the cell to the other will be less than 1%. This calculation assumes that the gas inlet is at the end of the cell farthest from the slit; if the gas inlet is close to the slit, the pressure differential is much less.

All experimenters but one claim to have reduced the effect of a pressure gradient to negligible proportions. This claim is based upon laboratory experiments that compared the absorption by molecular oxygen at 1450 A in a cell that could be used in either a windowed or a windowless configuration. Such a measurement will have associated with it both a systematic and a random error, which from previous discussions will not be less than $\pm 5\%$. In none of the papers reviewed was this additional source of error discussed.

4. Conclusion. From the discussion given above it seems reasonable to state that the sum of the systematic errors that would be expected in the determinations of σ_T is $>5\%$. This is of the same order as the error some experimenters quote for their total error. In general, the discussions of errors in the papers that describe measurements of ultraviolet cross sections are scanty. One can even find some papers where no estimate of errors is given. But even where errors are given, how does one interpret them? If a paper shows a continuous

curve of cross section versus wavelength and ascribes an error of ±5% to the cross section, does this error refer to (1) the error on each point used to draw the curve, (2) the spread of these points about the curve shown, or (3) the systematic error on the measurement, i.e., the fact that the whole curve could be raised or lowered by a factor of 1.05? These questions cannot be answered by reference to the papers alone, and this makes the task of the reviewer that much more difficult.

It is hoped that the above remarks on errors will make experimenters cautious and will cause them to give complete and reliable estimates of both random and systematic errors.

B.   Partial Absorption Cross Sections

The processes that contribute to the total photoabsorption cross section include photon excitation, photodissociation, photon scattering, photoionization, dissociative ionization, etc. In turn some of these processes can leave the product ion, molecule, or atom in several different excited states, and one may talk about partial photoionization cross sections, etc. For the main part, absolute measurements of these partial cross sections have not been made, but rather the ratio of these quantities to the total absorption cross section and the error to be assigned to these partial cross sections will include the error in σ_T. Thus the errors that will be discussed in this section are those that arise in addition to those described in the previous section.

1.   Photoexcitation cross sections.   Absorption measurements in the ultraviolet have been made with insufficient instrumental resolution for quantitative determinations of photoexcitation cross sections, although measurements have been made of oscillator strengths.

2.   Photodissociation cross sections.   Relatively few quantitative measurements have been made of photodissociation cross sections in the ultraviolet below 3000 A. Those that have been made have been limited to a few discrete wavelengths above 1100 A. The available data up to 1964 were reviewed by *McNesby and Okabe* [1964], and the reader is referred to their paper for details. Photodissociation is measured in terms of the quantum yield, Φ, where

$$\Phi = \frac{\text{number of particles produced}}{\text{number of photons absorbed}}$$

The photodissociation cross section σ_D is related to Φ by

$$\sigma_D = \Phi \sigma_T$$

The number of particles produced is usually determined from chemical analysis, and the flux of incident photons is determined by an absolute calibration technique. Typical errors for Φ quoted in the literature vary between 10 and 20%.

Apart from these isolated measurements photodissociation continua have been simply inferred from the shapes of absorption continua, or, where there is band structure, by connecting the minimum cross sections with a smooth curve. In section 5 it will be shown that this is not usually a valid procedure.

3. Photon-scattering cross sections. Photon scattering occurs in all gases at all wavelengths. Few absolute measurements of scattering cross sections exist for molecules at wavelengths shorter than 2000 A. However, the relative measurements that are available, together with those values obtained from both theoretical calculations and empirical extrapolations of refractive index measurements, indicate that these cross sections are typically of the order of 10^{-24} cm^2 at 1200 A, i.e., about 6 orders of magnitude smaller than most photoexcitation, dissociation, and ionization cross sections. The contribution of scattering to the total attenuation cross section can therefore be neglected except in the neighborhood of resonance lines and possibly in gases at high pressures where quasi-molecules might exist.

4. Photoionization cross sections. Many measurements of photoionization cross sections have been reported, but most of these involve the determination of a quantity, η, the photoionization yield. The photoionization cross section σ_i is then given by

$$\sigma_i = \eta \sigma_T$$

where η is defined as the number of ions formed per absorbed photon.

The determination of η depends on measurements of the number of ions produced and of the absolute photon flux. For wavelengths below 1023 A, the absolute flux is usually determined by measuring the ion current produced in a noble gas, whose photoionization yield is assumed to be 1. In some experiments, this technique has been used to calibrate a secondary standard, such as a piece of platinum; however, this calibration has an error associated with it, typically of $\pm 15\%$. For wavelengths above 1023 A, calibrated thermopiles are used to determine the absolute flux at a few wavelengths, and these are used to calibrate a secondary standard such as sodium salicylate, whose quantum efficiency is assumed to vary slowly with wavelength. It has been estimated [*Hinteregger*, 1965] that the absolute calibration of such systems is usually no better than $\pm 20\%$.

Other experimenters have measured η by totally absorbing the incident radiation first in the gas being investigated and then in a noble gas. The yield η is then given by the ratio of the ion currents. Great care has to be taken to ascertain that all of the ions formed are collected, that no electrons reach the ion collector, that photons cannot strike the ion collector and hence cause spurious currents, and that the collection voltage is such that electrons produced in the photoionization process cannot produce more ions in the gas. The total error quoted for the measurement of η by this process is usually $\pm 5\%$. In view of the fact that these measurements do not involve a pressure determination, most of this quoted error must arise from the systematic error in the measurement of the ratio of the ion currents.

It will be found that η is also referred to (in literature in this field) as the photoionization efficiency; however, one must be careful to distinguish between η and the quantity, photoionization efficiency (PE), as used in papers reporting mass spectrometric measurements. In this case the definition of PE is

$$ PE \;=\; \frac{\text{numbers of ions produced/sec}}{\text{flux in transmitted photons/sec}} $$

In these measurements the amount of absorption is small (less than 1%) and thus from equation 1

$$ PE \;=\; \frac{I_0(\lambda) \cdot n \cdot \ell \cdot \sigma_i(\lambda)}{I_0(\lambda)} \;=\; n\ell\sigma_i(\lambda) $$

Thus, the determination of PE will provide a direct determination of the partial photoionization cross section for a particular ion if the product $n\ell$ is known and if the collection and detection efficiencies of the mass spectrometer are known. They seldom are. Consequently, most experimenters publish relative values of PE, i.e., relative partial photoionization cross sections. The accuracy of these values depends on the method used to determine the absolute or relative photon flux, and also on the kinetic energy of the photoionization products (e.g., in dissociative ionization), as this could alter the collection efficiency of the mass spectrometer. For this reason it is difficult to estimate quantitative systematic errors for these determinations.

In recent years, considerable progress has been made in the study of the states of excitation of ions produced by photoionization. This study is generally accomplished by measuring the kinetic energies of the charged particles or by studying the fluorescence, if any, of the ions. These techniques, with a discussion of the possible sources of error, have recently been presented in a review by *R. I. Schoen* [1969].

III. ANALYSIS OF THE ABSORPTION DATA

The area that has probably received least attention in the derivation of accurate absorption cross sections has been that of data reduction. One of the most significant questions regards the use of equation 1 in reducing absorption data, or alternatively, the physical significance of the quantity σ_T in equation 1. The term 'physical significance' should be stressed, since any spectrograph that is used in absorption studies has a finite spectral bandwidth, and, as a consequence, the quantity σ that is measured is not necessarily a physical quantity, but in general represents a number that is not only characteristic of the atom or the molecule that is being studied, but is also characteristic of the instrument that was used in the experiment.

Let the flux incident on an absorption cell from the exit slit of a monochromator be defined as A_0, and the flux transmitted through the cell be defined as A. A_0 is a function of the wavelength at the center of the bandwidth, λ', and the bandwidth of the instrument, $\Delta\lambda$, and is given by

$$ A_0(\lambda', \Delta\lambda) \;=\; \int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda)G(\lambda)\cdot T(\lambda)\cdot d\lambda \tag{2} $$

In this equation, $S(\lambda)$ is the source function, that is, the flux that is incident on the entrance slit of the monochromator, $G(\lambda)$ is the slit function, and $T(\lambda)$ is

the transmission function of the monochromator. In general, $T(\lambda)$ is a slowly varying function of the wavelength and can be taken outside the integral.

The transmitted intensity, A, is then given by

$$A(\lambda', \Delta\lambda, N) = \int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda)G(\lambda) \cdot T(\lambda) \cdot \exp\left[-N\sigma_T(\lambda)\right] d\lambda \tag{3}$$

where $N = n\ell$. The ratio of A_0/A is given by

$$\frac{A_0(\lambda', \Delta\lambda)}{A(\lambda', \Delta\lambda, N)} = \frac{\displaystyle\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda) \cdot G(\lambda) \cdot d\lambda}{\displaystyle\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda) \cdot G(\lambda) \cdot \exp\left[-N\sigma_T(\lambda)\right] \cdot d\lambda} \tag{4}$$

It can be seen that the σ_T of equation 1 will only be equal to $\sigma_T(\lambda')$, the cross section at the center of the bandwidth, if $\sigma_T(\lambda)$ is a constant over the bandwidth. As in general this is not the case, the cross section that is obtained from equation 1 will be an average cross section, and hence it is better to replace the σ_T in equation 1 by the quantity $\bar{\sigma}_T$, where

$$\frac{A_0}{A} = \exp N\bar{\sigma}_T\{\lambda', \Delta\lambda, N, S(\lambda), G(\lambda), f[\sigma_T(\lambda)]\} \tag{5}$$

and $f[\sigma_T(\lambda)]$ is the functional form of σ_T versus wavelength.

The particular considerations discussed above apply especially where there is band structure in the absorption spectrum of a molecule. To interpret the cross-section data that have been published, some relationship must be found between $\bar{\sigma}_T$ and $\sigma_T(\lambda')$, and for this one needs to know $S(\lambda)$, $G(\lambda)$, and $f[\sigma_T(\lambda)]$. $G(\lambda)$ depends only on the slit width and the diffraction grating parameters, but because many instruments apparently have not been properly focused, the calculation of $G(\lambda)$ from the information given in the pertinent literature is difficult. For most ultraviolet measurements the wavelength of the incident radiation is much less than the slit width, and thus if a spectrometer is well-focused, with exit and entrance slits of equal width, the shape of $G(\lambda)$ versus λ will be triangular. If unequal slit widths are used, then the shape becomes trapezoidal.

Figure 2 shows values of $\ln(A_0/A)$ calculated from equation 4, versus $N\sigma(\lambda')$, at the peak of an isolated line with a Lorentz line shape, assuming a continuum light source ($S(\lambda)$ = constant) and a triangular slit function. There are several plots shown, each one corresponding to a different value of a parameter, α, where

$$\alpha = \Delta\lambda/\Delta L \tag{6}$$

ΔL is the Lorentz line width (full halfwidth). If $\bar{\sigma}_T(\lambda', \Delta\lambda, N)$ were equal to $\sigma_T(\lambda')$, then a straight-line plot would be obtained with a slope of 1.0. For α less than 1.0, plots of $\ln(A_0/A)$ versus $N\sigma(\lambda')$ are linear to within $\pm 0.5\%$, but the slopes are all less than 1. For α greater than 2.0, the plots deviate from a straight line, and the cross section as calculated from equation 1 would decrease as N is increased. The dependence of $\bar{\sigma}_T$ on N is quite well known in the literature in this field, where it is referred to as 'apparent pressure effect,' 'pressure dependence,' etc. It should be noted, however, that $\bar{\sigma}_T$ depends on the column density rather
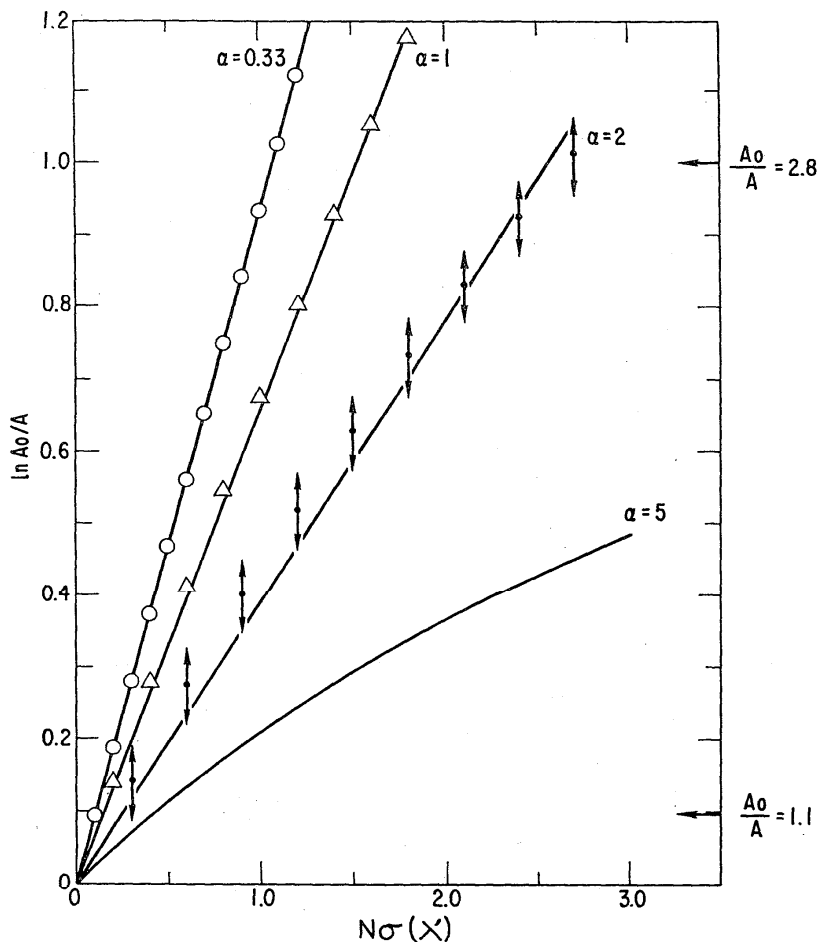
Fig. 2. Calculated values of ln A_0/A versus $N\sigma(\lambda')$ for four values of
$\alpha(\alpha = \Delta\lambda/\Delta L)$ assuming a Lorentz line shape.

than the pressure, i.e., the curves shown in Figure 2 depend on the product $n\ell$, not on n. Thus the use of the term 'pressure dependence' is unfortunate, especially since there are situations where $\bar\sigma_T$ is also a function of n, for example, in the pressure broadening of rotational lines.

Values of $\bar\sigma_T$, at peaks, are treated in two ways in related published work. If $\bar\sigma_T$ is found to be independent of N, within the random errors of each measurement, e.g., the curves for $\alpha < 1$ in Figure 1, then the published cross section is either obtained by averaging the cross sections calculated at various values of N, or from a plot of $\ell nA_0/A$ versus N, which is then known as a Beer's law plot. If $\bar\sigma_T$ is dependent on N, then the value given is the cross section obtained by extrapolating curves of $\bar\sigma_T$ versus N to 'zero pressure,' i.e., $N = 0$. Essentially then, both methods of data reduction give the value of $\bar\sigma_T$ as $N \rightarrow 0$, and for this condition, it can be shown that

$$\bar\sigma_T(\lambda', \Delta\lambda) = \int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda) \cdot G(\lambda) \cdot \sigma(\lambda) \cdot d\lambda \tag{7}$$

A word of caution should be introduced at this time against placing too much reliance on the values of $\bar{\sigma}_T$ obtained by extrapolating curves of $\bar{\sigma}_T$ versus N to 'zero pressure.' As has been shown in Figure 1, errors in $\bar{\sigma}_T$ arising from the determination of the ratio A_0/A become very large as this ratio approaches 1, i.e., as N approaches 0. Thus the extrapolation, of necessity, gives most weight to the least accurate data, and any slight systematic error in A_0 or A will cause a large systematic error in the determination of $\bar{\sigma}_T$.

If the calculation that was made above assuming Lorentz line shapes and a triangular slit function is now repeated using equation 7, one can obtain the ratio of $\bar{\sigma}_T(\lambda', \Delta\lambda)$ to $\sigma(\lambda')$. This ratio is plotted in Figure 3 versus the ratio α. As in the previous case (see Figure 2), the ratio approaches 1 for small values of α, but even for $\alpha = 1$, i.e., when the line width is equal to the bandwidth, the value of the ratio is only 0.7. Thus the published absorption cross section for a line having $\alpha = 1$, for which 'Beer's Law' would have been obeyed, is in error by at least 40%, an error which is far outside most quoted experimental errors.

The calculations discussed above were made for a well-focused instrument with equal exit and entrance slit widths. As has been intimated earlier, this is not always the case; and one can postulate that, although groups may quote the same spectral bandwidth, their slit functions may be different. To illustrate the effect of the slit function on measured cross section, Table 1 compares the ratio of $\bar{\sigma}(\lambda', \Delta\lambda)$ to $\sigma(\lambda')$ obtained from equation 7 for Lorentz line shapes, for triangular and rectangular slit functions.

The same arguments that have been applied above to the absorption at the peaks of lines are equally applicable to the minima between lines. In this case, however, the value of $\bar{\sigma}(\lambda', \Delta\lambda)$ will be larger than $\sigma(\lambda')$. A discussion of the ratio between these two quantities for a triangular slit function is given by *Hudson and Carter* [1968a].

To illustrate this 'averaging effect' of a finite spectral bandwidth, measured cross sections obtained by three groups for the first autoionization line of argon at 786.5 A have been plotted in Figure 4. The values published by *Huffman et al.* [1963a] and by *Metzger and Cook* [1965] were obtained at a stated bandwidth of 0.5 A, whereas the data of *Hudson and Carter* [1968a] were obtained at 0.038 A. These three sets of data have been normalized at a point in the continuum where $\sigma(\lambda')$ is constant, i.e., where the measured $\bar{\sigma}(\lambda', \Delta\lambda)$ should be independent of $G(\lambda)$ and $\Delta\lambda$. That this normalization procedure is reasonable can be
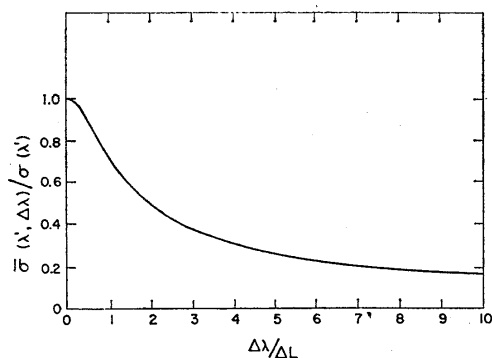

Fig. 3. Calculated values of $\bar{\sigma}(\lambda', \Delta\lambda)/\sigma(\lambda')$, for a Lorentz line shape and a triangular slit function, versus the ratio of the bandwidth to the Lorentz line width.

TABLE 1. Ratio of $\bar{\sigma}(\lambda', \Delta\lambda)$ to $\sigma(\lambda')$ for Triangular and Rectangular Slit Functions

$\alpha = \Delta\lambda/\Delta L$	$\bar{\sigma}(\lambda', \Delta\lambda)\sigma(\lambda')$ for Triangular Slit Function	$\bar{\sigma}(\lambda', \Delta\lambda)\sigma(\lambda')$ for Rectangular Slit Function
0.2	0.975	0.987
0.4	0.914	0.951
0.6	0.841	0.901
0.8	0.769	0.843
1.0	0.705	0.785
1.2	0.648	0.730
1.4	0.599	0.679
1.6	0.556	0.633
1.8	0.519	0.591
2.0	0.486	0.554

seen if one examines the spectrum at 785.7 A, where the cross section obtained at the highest resolution is varying linearly with wavelength. It can be shown that for this situation the average cross section obtained will be within a few percent of the value of $\sigma(\lambda')$ [Hudson and Carter, 1968a], and the fact that all three curves meet at this point is indicative that the normalization procedure was a valid one. One thing that can be noted immediately is that the curves of Huffman et al. [1963a] and Metzger and Cook [1965] show different line shapes and peak absorption cross sections even though both measurements were made with instruments having the same quoted spectral bandwidth.

Both of these groups give details of their spectrometers and the slit widths that were used, and hence one can obtain the theoretical bandwidths for their instruments. The theoretical bandwidth for Huffman et al. is 0.38 A, and that for Metzger and Cook is 0.54 A. Huffman (personal communication, 1969) states that the difference between the theoretical value of 0.38 and the measured value of 0.50 for his instrument was due to slight misalignment of the spectrograph; thus, one would expect the slit function to be trapezoidal. The slit function of Metzger and Cook is probably triangular. Figure 5 compares the measured line shapes of Huffman et al. and Metzger and Cook with theoretical calculations obtained from equation 7 using the line shape obtained by Hudson and Carter and the slit functions shown in Figure 5. The agreement between the measured and theoretical line shapes is good, illustrating the need for accurate slit functions before an attempt is made to compare peak absorption cross sections obtained by different groups.

The arguments made above leave no doubt that the cross sections obtained at 0.038 A give the closest estimate of the physical line shape for the particular transition in argon; and, indeed, the shape that is obtained does agree well with recent theoretical calculations by Mendez [1968]. The line shapes obtained at wider bandwidths will be correct, to within the quoted errors, for the particular slit function and bandwidth used in the experiment, and if a spectrometer with the same slit function and bandwidth is employed, then the attenuation by argon of a continuum light source can be calculated by using these quoted cross sections in equation 1. But it should be noted that in order to use these data, one
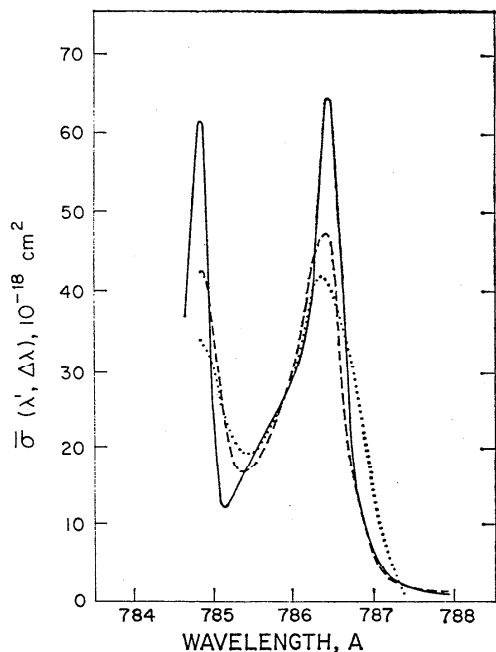
Fig. 4. Experimental line shape for the transition from the ground state to the $(3s)^2(3p)^5\,^2P_{1/2}\,9d$ state of argon; solid line, Hudson and Carter [1968a]; dotted line, Metzger and Cook [1965]; dashed line, Huffman et al. [1963a].
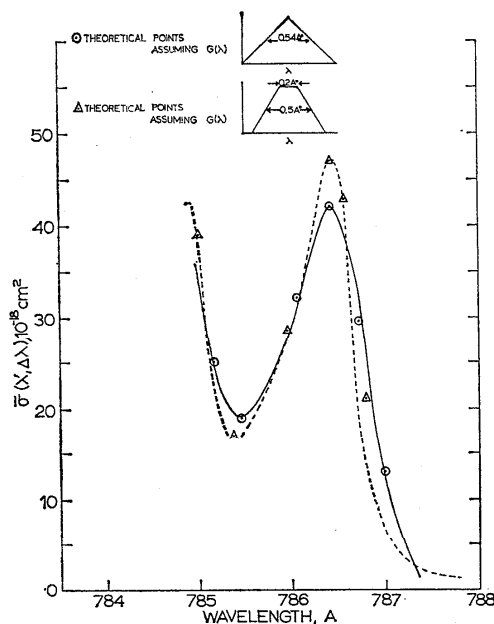
Fig. 5. Comparison of experimental line shapes for the autoionization line at 786.5 A, versus calculated points assuming slit functions shown above; dashed line, Huffman et al. [1963a]; solid line, Metzger and Cook [1965].

has to specify the instrument; that is, the cross section that has been published is as much a function of the spectrometer as it is of the argon atom. Provided one understands this limitation, one can use these low-resolution data. But, if, for example, one wishes to know the attenuation of an emission line centered at the peak of the argon absorption line, then the poor-resolution data will yield the wrong result. The application of these arguments to the absorption of solar line emission by atmospheric molecules must be quite apparent.

The above arguments regarding the bandwidth dependence of the total absorption cross sections will apply equally well to measured ionization cross sections. For an instrument of finite bandwidth, an average quantity $\bar{\eta}(\lambda', N, \Delta\lambda)$ can be defined, which, from the definition of the photoionization yield η, will be given by

$$\bar{\eta}(\lambda', N, \Delta\lambda) = \frac{\displaystyle\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda)G(\lambda)\eta(\lambda)\{1 - \exp[-N\sigma_T(\lambda)]\}\,d\lambda}{\displaystyle\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda} S(\lambda)G(\lambda)\{1 - \exp[-N\sigma_T(\lambda)]\}\,d\lambda} \tag{8}$$

and this quantity can be a function of N, $\Delta\lambda$, $S(\lambda)$, and $G(\lambda)$. Thus the measured ionization cross section $\bar{\sigma}_i(\lambda', \Delta\lambda, N)$, given by

$$\bar{\sigma}_i(\lambda', \Delta\lambda, N) = \bar{\eta}(\lambda', N, \Delta\lambda)\cdot\bar{\sigma}_T(\lambda', N, \Delta\lambda) \tag{9}$$

can also be a function of $\Delta\lambda$, N, $S(\lambda)$, and $G(\lambda)$.

Similarly

$$\text{PE}\,(\lambda',\,\Delta\lambda)\;=\;N\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda}S(\lambda)G(\lambda)\sigma_i(\lambda)\,d\lambda\Big/\int_{\lambda'-\Delta\lambda}^{\lambda'+\Delta\lambda}S(\lambda)G(\lambda)\,d\lambda \qquad (10)$$

and the published values of PE will also be subject to a bandwidth dependence.

One is, therefore, presented with a considerable problem when trying to compare values obtained by different authors for cross sections obtained at peaks and minima, for not only does one have to compare the quoted systematic errors arising from the experimental procedures, but one must also estimate, if possible, the systematic errors that might arise from bandwidth considerations. The situation is further complicated when experimenters use the same instrumental bandwidth but not the same functional form for $G(\lambda)$. In many cases such a comparison appears to be unfruitful. One thing evident from this analysis is that, in the vicinity of bands, errors from the data analysis alone can be much greater than any other systematic error.

To the reviewer it seems clear that the terms 'atomic cross section' and 'molecular cross section,' from their definitions, should apply to cross sections that are characteristic of the atom or molecule only, and that cross sections that are also characteristic of the measuring instrument should not be referred to as atomic or molecular. The reviewer feels that both editors and referees should insist in the future that experimenters demonstrate that the cross sections in their papers do indeed have physical significance.

IV. WAVELENGTH ERRORS

The solar emission spectrum below 1600 A consists principally of sharp lines. To calculate attenuation profiles for these lines the wavelengths of the absorption features must be known accurately (the accuracy needed will depend on the widths of the emission lines). Typical accuracies quoted for the wavelengths of absorption features in the papers reviewed varied from 0.1 to 0.5 A.

It is difficult to ascertain the exact nature of this error, for one effect of poor-resolution studies is to shift the peaks of asymmetric features to shorter or longer wavelengths (see, for example, Figures 4 and 5). Thus there need be no exact correlation between the wavelengths of bandheads, etc., which have been obtained from high-resolution photographic studies, and the wavelengths obtained from the absorption cross section measurements.

V. INTERPRETATION AND USE OF PUBLISHED CROSS SECTION DATA

A. Effect of Finite Spectral Bandwidths

The averaging effect of instrumental bandwidths discussed in the previous section plays an important role in the interpretation that many experimenters place on measured absorption curves. To illustrate this point, Figure 6 shows results obtained by *Huffman et al.* [1964b] at wavelengths shorter than the ionization edge of carbon monoxide. It should be stressed that these data are used because they represent one of the few examples of experimenters' giving

detailed experimental results. Included are results that were obtained at four different pressures, indicating the reproducibility of the results.

Figure 6 is typically interpreted as showing bands overlying a continuum. If one assumes such a continuum and assumes that the bands have a Lorentz profile, then a theoretical fit to the experimental data can be made, as is shown in Figure 7a. This figure contains two curves; the top curve is of $\sigma(\lambda')$, the bottom that of $\bar{\sigma}(\lambda', \Delta\lambda)$, assuming the bandwidth of 0.5 A quoted by Huffman et al. and a triangular slit function. The crosses on the bottom curve are the experimental data. However, another possible interpretation of the experimental curve is that it is made up entirely of overlapping bands and that there is no continuum. A theoretical fit can be made using this assumption, and the curves of $\sigma(\lambda')$ and $\bar{\sigma}(\lambda', \Delta\lambda)$ are shown in Figure 7b. The fit to the experimental results is also good.

Thus there are at least two interpretations of the same experimental result, which lead to quite different curves of $\sigma(\lambda')$ versus λ'. From the nature of the solutions obtained one can, of course, postulate that many more interpretations can be made ranging between the two. Clearly, the use of insufficient resolution has not yielded a unique answer; and in order to distinguish between these interpretations, one needs additional information. Usually, the only additional information that exists is that energetically an ionization continuum is possible, a fact that is often quoted to support the assumption of a continuum overlaid by bands. But the fact that a continuum is energetically possible does not necessarily mean that it need be measurable, since the extent and intensity of the continuum must depend upon the relative transition probabilities between the
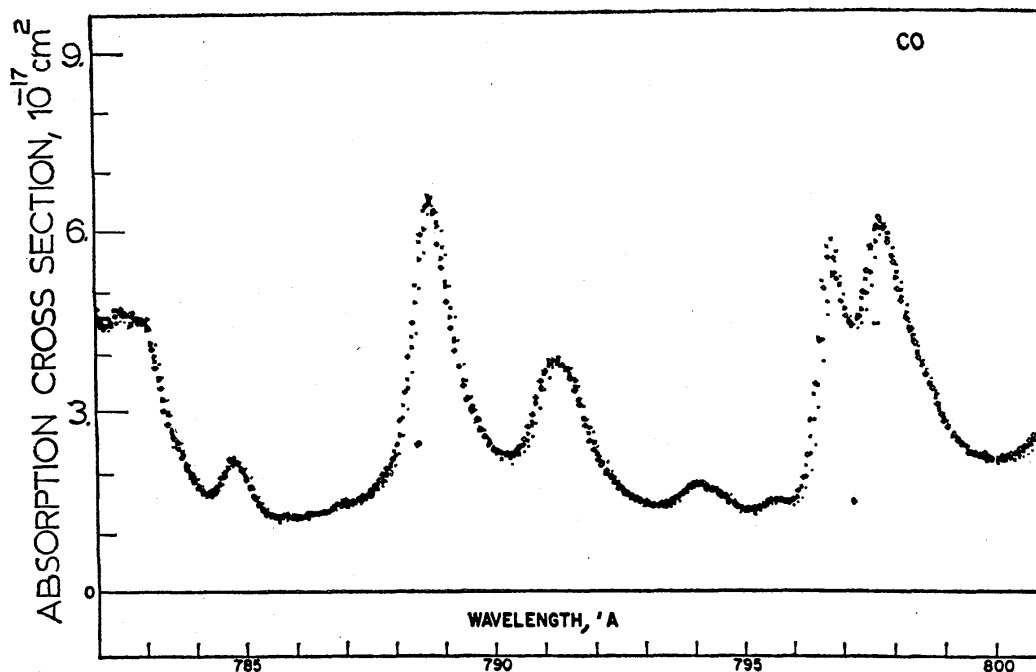

Fig. 6. Measured absorption cross section for carbon monoxide between 782 and 801 A. Taken directly from paper by *Huffman et al.* [1964b] except for label change on ordinate.
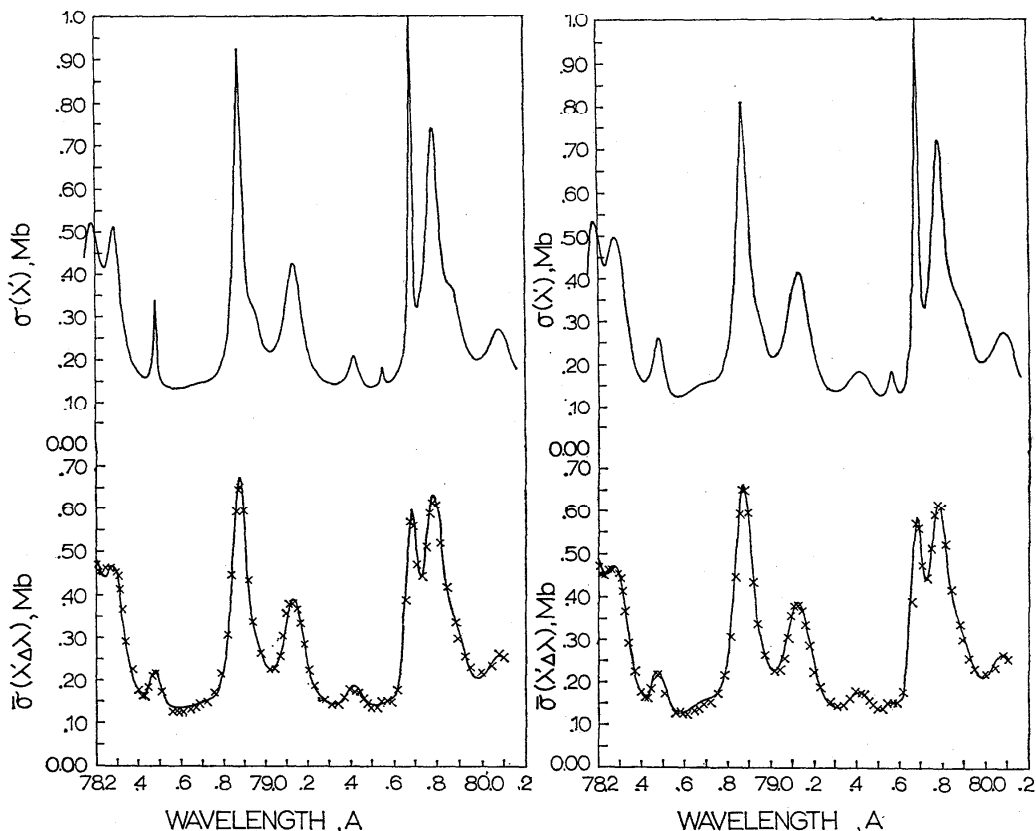
Fig. 7. Comparison of theoretical fit and measured absorption cross section for CO between 782 and 801 A. The curves shown in Fig. 7a assume bands overlying a continuum; those in Fig. 7b assume bands only. The crosses are the experimental data of *Huffman et al.* [1964b].

upper and lower states. Until that has been calculated, one can draw no conclusions about an underlying ionization continuum. An example where lines without an accompanying continuum have been measured is available in the autoionization spectrum of barium and strontium [*Hudson et al.*, 1969].

This double interpretation that one can place on experimental absorption cross sections in the vicinity of bands is also illustrated in Figure 8. This figure shows the absorption spectrum of sulphur dioxide (SO₂) obtained by *Warneck et al.* [1964]. It should be noted that the parameter plotted was labeled absorption intensity, not molecular cross section. This label was chosen as the authors realized that the cross sections they obtained would be bandwidth-dependent. It is a pity that this nomenclature was not adopted by other experimenters. The authors show two apparent continua; the first extends from 1700 to 2350 A and the second from 2350 to about 3100 A. There is, in this interval, a theoretical dissociation limit at 2280 A that is associated with the process

$$SO_2 + h\nu \rightarrow SO + O(^3P) \tag{11}$$
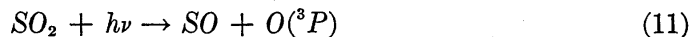
The authors conclude that the continuum above 2280 is not compatible with

any known dissociation energy of SO_2. Thus, although it gives the appearance of a continuum, it must really be due to 'the restrictive spectral resolution used in the experiment and the effect of considerable overlapping of the individual bands.' However, they also conclude that the apparent continuum below 2280 A is a true continuum. Yet the measured absorption spectrum at 3000 A and that around 2100 A are sufficiently similar that if one can postulate that the 3000 A continuum is not real, then one must postulate that the continuum below 2280 A need not be real. This is not to say that dissociation does not take place; dissociation might then be due to predissociation of the overlapping bands with a consequent broadening of the rotational lines that will accentuate the appearance of an apparent continuum. Predissociation in band absorption
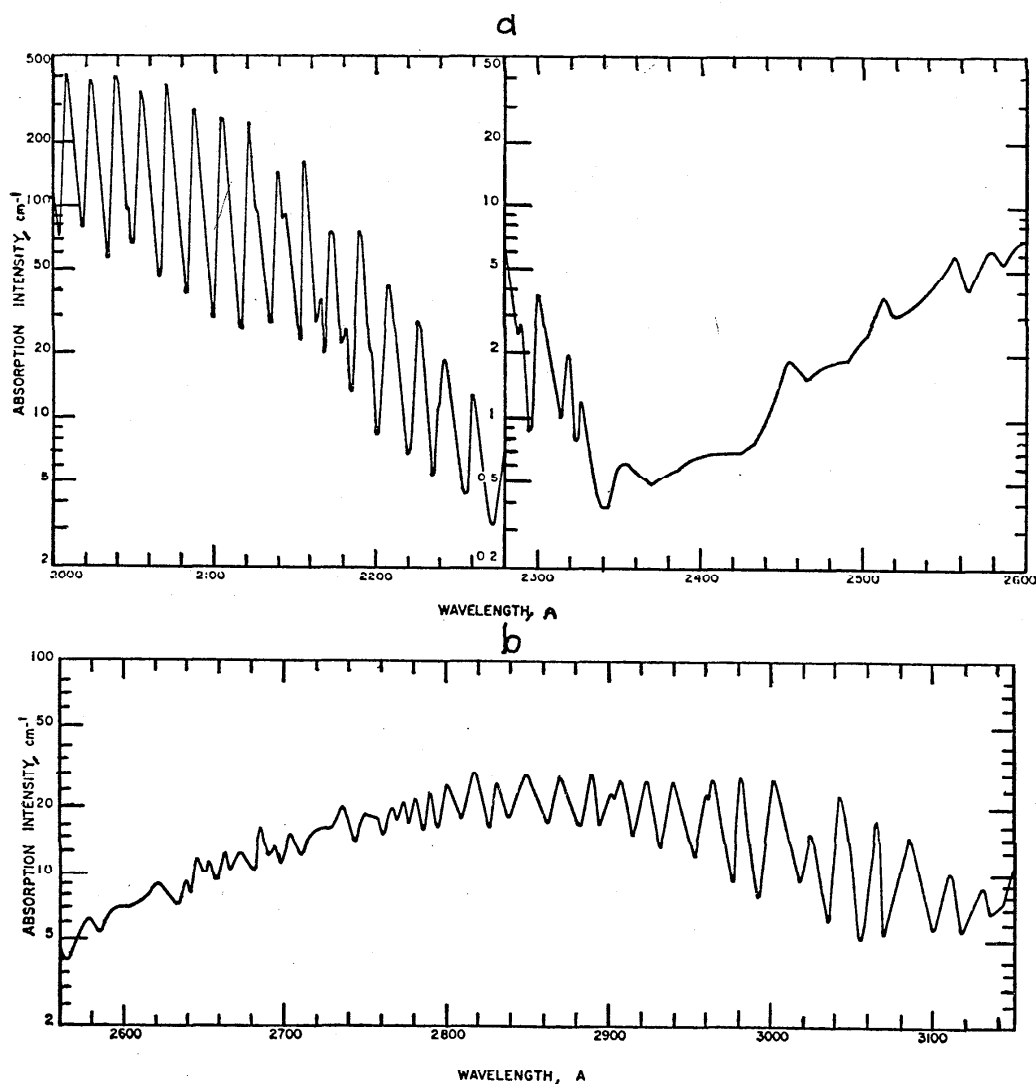

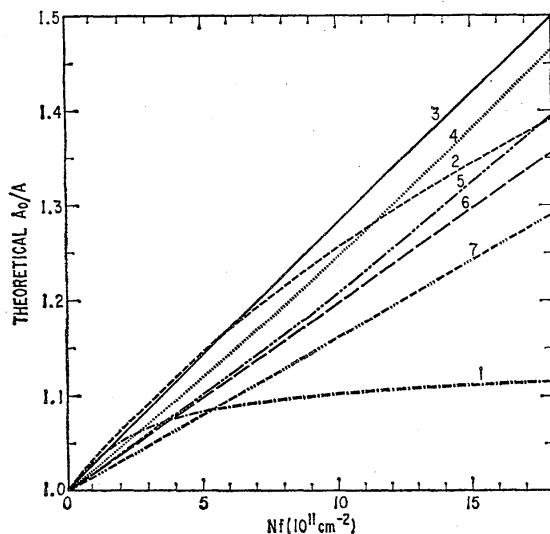Fig. 8. Absorption intensities of SO_2 between 2000 and 3100 taken from *Warneck et al.*
[1964].

Fig. 9. Theoretical A_0/A versus Nf for ΔL's of
(1) 0.121 cm^{-1}, (2) 0.294 cm^{-1}, (3) 0.63 cm^{-1}, (4)
1.3 cm^{-1}, (5) 1.9 cm^{-1}, (6) 2.3 cm^{-1}, and (7) 3.1
cm^{-1}. Taken from *Hudson and Carter* [1968b].

rather than dissociation through a continuum will, in many cases, alter the final energy state of the dissociated product; and in studies of planetary atmospheres, a knowledge of these energy states is important in the calculation of equilibrium conditions.

Another area in which an understanding of bandwidth effects can alter the interpretation of data is in attempts to infer the relative intensities of bands by their peak absorption cross sections. Figure 9, taken from a recent paper by *Hudson and Carter* [1968b], shows calculations made for their particular spectrograph, of ln A_0/A versus Nf (f is the oscillator strength of the line) for lines having a Voigt profile. Each curve corresponds to a different line width, with curve 1 corresponding to a pure Doppler broadened line. It is immediately apparent that the same value of ln A_0/A can be obtained over a wide range of oscillator strengths, if the line width is allowed to vary.

A common phenomenon in molecular spectroscopy is to find a Rydberg series ending on an excited state of the ion. Frequently this phenomenon is accompanied by an apparent increase in the intensity of the series as it crosses the first ionization edge. However, exactly the same effect would be produced if the rotational lines of the Rydberg bands became wider as they crossed the limit, i.e., if the Rydberg series became preionized. With reference to Figure 9, such an effect would correspond to moving along curve 1 toward the origin and at a given value of Nf moving up to one of the other curves, thus suddenly increasing the peak value of ln I_0/I.

In summary then, anyone attempting to use ultraviolet absorption cross sections should realize that there are limits that can be placed on the use of the data, and that the interpretations that experimenters have made about their

published curves need not necessarily be the only interpretations. In section VI of this review, such limits will be discussed for the individual molecules.

B. *Effect of Atmospheric Temperature*

It should be stressed that, apart from one measurement on molecular oxygen [*Hudson et al.,* 1966], the cross sections that will be discussed in this review have been obtained at room temperature (300°K), whereas the temperature of planetary atmospheres can vary between 100 and 2000°K. Thus even if the cross-section data were obtained with sufficient resolution to give band profiles that were independent of bandwidth, the question still arises about the applicability of these data to calculations of atmospheric attenuation profiles.

The tendency in most papers that report calculations of these attenuation profiles has been to ignore the effect of temperature. With our present knowledge of band profiles for atmospheric species perhaps this is justified, but one sometimes wonders whether the reasoning behind the neglect is not that at 1000°K only 5 to 10% of the molecules are in the first excited vibrational state and thus one should, at most, expect a 5 to 10% change in the molecular absorption profile. That this reasoning is not necessarily correct is illustrated in Figure 10, which is taken from a recent paper by *Hudson and Carter* [1968*b*]. The figure shows absorption profiles for molecular oxygen in the Schumann-Runge system at three temperatures, 300, 600, and 900°K. The column density N was a constant at each temperature. At 600°K only 2% of the oxygen molecules are in the first vibrational level, yet one is obviously seeing much more than a 2% effect. The reason is that the transition probabilities for the $V'' = 1$ transitions are much larger than for the $V'' = 0$ transitions. Unfortunately this strong V'' dependence tends to mask the change in the shape of each band due to changes in the rotational population.

VI. REVIEW OF PUBLISHED ULTRAVIOLET CROSS SECTIONS

In preparing this review all papers that are listed in the bibliography published by *Hudson and Kieffer* [1970] have been considered by the reviewer. Therefore this review should be current up to October 1969.

Except in a few isolated cases, published ionization cross sections are not reviewed. It was felt that because σ_T and η are the fundamental quantities measured, it was more meaningful to compare these quantities than the derived quantity σ_i. This has meant that in some instances the reviewer has had to convert values of σ_i back to values for η. This review does not contain a complete set of cross-section–versus–wavelength values for each molecule. The prepared figures are used solely to compare the results of several determinations or to point out to the reader where difficulties of interpretation might arise.

Table 2 lists those papers from which cross-section data were taken for this review. As well as listing the authors and the species studied, the table contains a summary of the experimental techniques, including the pressure measurement, the instrumental bandwidth, and the author's estimate of the experimental errors. It will be noted that there are many blanks under the column headings. The reader may assume that where such a blank occurs, no account of the mea-
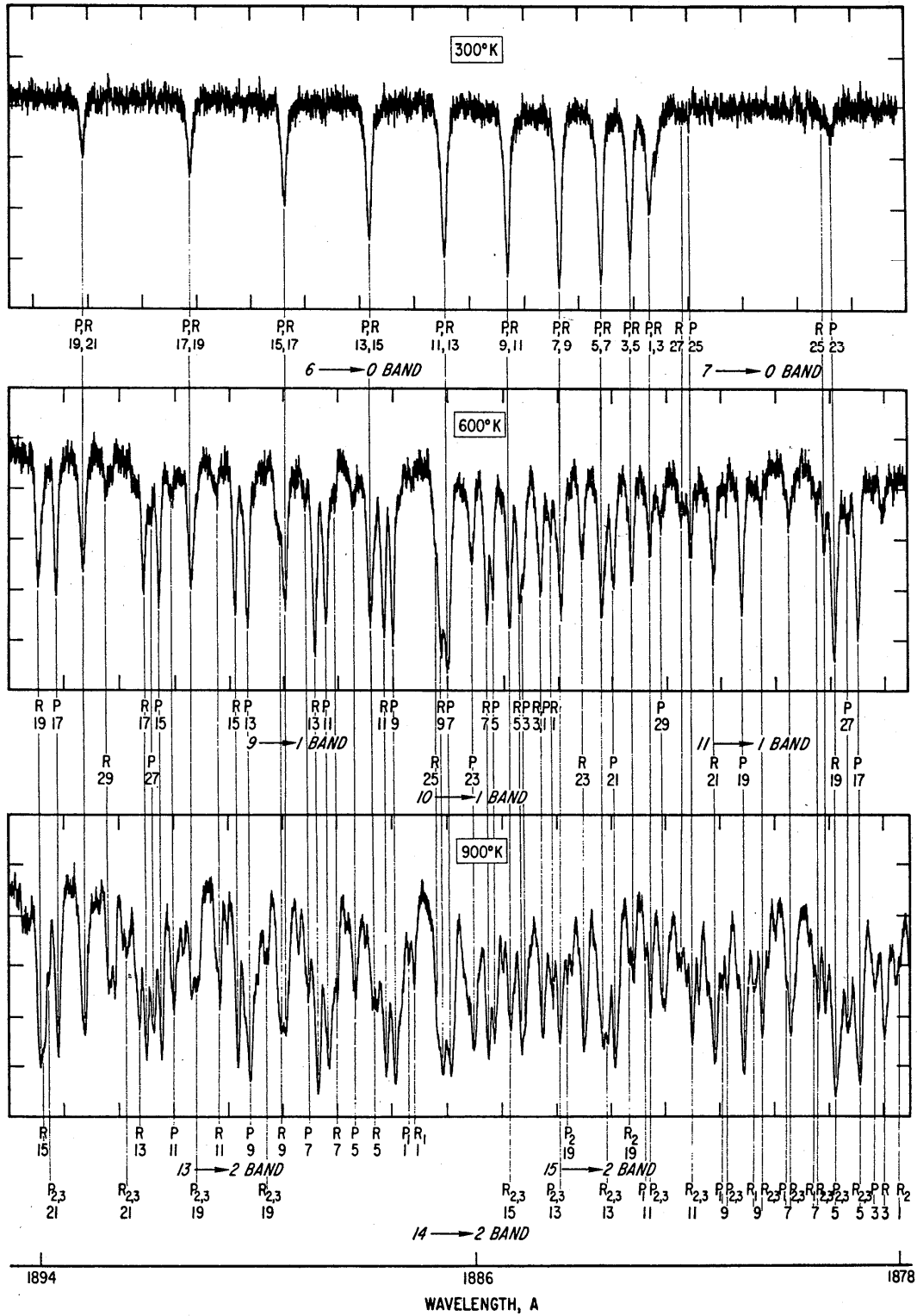
Fig. 10.   Absorption by molecular oxygen between 1878 and 1894 A at 300, 600, and 900°K.
Taken from *Hudson and Carter* [1968*b*].

TABLE 2. Summary of Experimental Parameters for Papers Discussed in the Review

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, Å	Errors	Remarks
Ditchburn and Young [1962]	O_2	Photographic; 1850–2500 A; continuum source			Constant error of 1.0×10^{-24} cm^2	
Blake et al. [1966]	O_2	Photomultiplier or ion chamber; 1250–2350 A; continuum and line source	Oil and mercury manometers, McLeod gage	1–2	5%, 2000–2400 A and 1250–1750 A	Used double beam technique
Thompson et al. [1963]	O_2, CO, CO_2, H_2O, N_2O, NH_3, NO, SO_2, CH_4	Photomultiplier; 1850–4000 A; light source not discussed				Discussed purification of gases
Watanabe et al. [1953a]	O_2	Photomultiplier; 1050–1900 A; continuum and line source	McLeod gage	0.85	About 5%; wavelength error 1–2 A	Checked impurity content of O_2 with mass spectrometer
Goldstein and Mastrup [1966]	O_2	Photographic; 1270–1745 A; continuum source	NRC Alphatron gage calibrated against McLeod gage	0.4	Random error, 5%; systematic error, 5%; wavelength error, ±1 A	
Metzger and Cook [1964b]	O_2	Photomultiplier; 1050–1800 A; continuum and line source	Thermocouple gages calibrated against McLeod gage, directly	0.5	Not explicitly given, but envelope of scatter on published curves gives ±5%	Impurity content of O_2 checked with mass spectrometer
Hudson et al. [1966]	O_2	Photomultiplier; 1580–1950 A; continuum source	McLeod gage	<1750 A Δλ=0.75 >1750 A Δλ=0.075	Random error, 10%; systematic error, 1%	Cross section measured at 300, 600, 900°K
Watanabe [1958]	O_2	Photomultiplier; 1160–1280 A; line emission source		0.2 and 0.1		Contained in review article; unpublished data of Watanabe, Mottl, and Sakai
Watanabe and Marmo [1956]	O_2, N_2	Photomultiplier and ion chamber; 850–1500 A; line emission source	Used 'known' cross section of O_2 at 1450 A	0.85	5% for absorption measurement; yield measurement, 10%; wavelength error, 0.1–0.5 A	
Cook and Metzger [1964a]	O_2, N_2	Platinum photodiode; ion chamber; 600–1000 A; continuum light source	Micromanometer, thermocouple, or ion gage, calibrated against McLeod gage	0.5	Cross section, 10% between 670 and 950 A, 15% outside this range; yield, 5%	Used unequal entrance and exit slits

TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Huffman et al. [1964a]	O_2	Photomultiplier; 580–1060 A; continuum light source	McLeod gage	0.5	10% for wavelength >722 A; 15% for wavelength <722 A	Values of observed coefficients increased by factor of 1.15, to account for pressure gradient in absorption cell
Samson and Cairns [1964]	O_2, N_2	Photomultiplier; double ion chamber; 303–1038 A; line emission source		0 7	5%	
Samson and Cairns [1965]	O_2, N_2, H_2	Photomultiplier; double ion chamber; 209–537 A; line emission source		0.7	10%	
Matsunaga and Watanabe [1967]	O_2	Photomultiplier; ion chamber; 580–1070 A; continuum source 580–1070 A; line emission source 900–1070 A	Micromanometer	0.3 and 0.2	Cross section, 10% >670 A, 15% <670 A; yield 10% <990 A, 20% >990 A	
R. D. Hudson and V. L. Carter (personal communication, 1968)	O_2	Photomultiplier; 830–836 A; continuum source	Relative measurement	0.038	Scatter of points around curve less than 5%	Data normalized to value of 10.5 mb at 835 A
Wainfan et al. [1955]	O_2, N_2, CO_2, H_2O, H_2, CH_4	Photomultiplier; double ion chamber; 473–991 A; line emission source		10	Total error given at each wavelength; includes errors from light intensity, current recording system, and pressure measurement	
Lee [1955]	O_2	Photographic; 200–1320 A; line emission source	McLeod gages		10–15%	
Dibeler and Walker [1967]	O_2, CO_2, COS, CS_2	Mass spectrometric; 600–1500 A; continuum and line emission sources	Relative measurement	2 or 1	Apart from systematic errors (not given) uncertainty in PE quoted as 1%; wavelength error 1A	Purity of gases checked with mass spectrometer
Nicholson [1963]	O_2, NO	Mass spectrometric; 885–1360 A; line emission source	Relative measurements	4.4	Cause of errors discussed but no numbers given	
Comes et al. [1968]	O_2	Mass spectrometric; gold photo cathode; 450–700 A; line and continuum sources	Relative—used molecular beam	2.5 A	Error bars given at each point measured	Dissociative ionization cross section normalized to O_2^+ ionization cross section at longer wavelengths

TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Huffman et al. [1963b]	N₂	Photomultiplier; 580-1000 A; continuum light source	McLeod gage	0.5	±10% 630-796 A; ±20% 580-630 A; wavelength error ±0.1 A	Results corrected by factor of 1.15 for pressure gradient in absorption cell
Hudson and Carter [1969a]	N₂	Photomultiplier; 828-887 A; continuum light source	Relative measurement	0.04		These data published in report
Itamoto and McAllister [1961]	N₂	Photomultiplier; 850-1000 A; line emission source	Micromanometer calibrated using O₂ and CO; absorption at 1435, 1121, and 'known' cross sections	0.2	Random error of 5%, plus systematic error of 10%	
Cook and Ogawa [1965]	N₂	Platinum photodiode; ion chamber; 734-805 A; continuum light source	Thermocouple gage calibrated against McLeod gage	0.2		
Henke et al. [1967]	O₂, N₂, C₂H₆, H₂S	Proportional counter; 8-114 A; line emission sources	Mercury or oil manometer		Random error, 0.5%; number density, 0.25%; sample impurity, 0.5%	
Comes and Lessman [1964]	N₂	Mass spectrometric; 420-800 A; line emission source	Relative measurement	2 and 4		Purity of gas checked by use of gas analysis
Wilkinson and Johnston [1950]	H₂O, CH₄, CO₂, C₂H₄	Photographic; 1400-2000 A; line and continuum source		1		Purity of gas checked with mass spectrometer; pressure during a run observed to vary by 10%
Watanabe and Zelikoff [1953]	H₂O	Photomultiplier; 1060-1860 A; line and continuum source	Alphatron gage calibrated against McLeod gage	1	Some possible sources discussed, but no numbers given	
Johannin-Gilles et al. [1956]	H₂O	Photographic; 1600-1750 A; line emission source	From vapor pressure relationship with liquid water		Sources of error discussed, but no numbers given	
Watanabe and Jursa [1964]	H₂O	Photomultiplier; ion chamber; 850-1110 A; line emission source	Relative measurements	1	Cross section, 20%	Results normalized to data of Watanabe and Zelikoff [1953]; impurity content checked with mass spectrometer
	H₂S	1060-2100 A; line and continuum source	Micromanometer and Alphatron gage			

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TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Laufer and McNesby [1965]	H_2O, CH_4	Photomultiplier; 1100–1800 A; line and continuum source	Oil manometer	6.6		
Metzger and Cook [1964a]	H_2O, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6	Platinum photodiode; ion chamber; 600–1000 A; continuum light source	Ion and thermo couple gages calibrated against McLeod gage or micromanometer	0.5	Errors discussed, but no numbers given except yield (10%)	
Dibeler et al. [1966]	H_2O, NH_3	Mass spectrometric; tungsten photodiode; 600–1250 A; continuum and line emission sources	Relative measurements	2	Estimated error in photon flux given as 3%	
Brehm [1966]	H_2O, O_2, C_2H_2, C_2H_4, CH_4	Mass spectrometric; photomultiplier; 830–1200 A; line emission source	Relative measurements	0.5, 0.2		
Comes and Wellern [1968]	H_2	Photomultiplier; ion chamber; 790–860 A; continuum source		0.5	Wavelength accuracy, 0.2 A	
Cook and Metzger [1964b]	H_2	Platinum photodiode; ion chamber; 600–1000 A; continuum light source	Thermocouple and ionization gages calibrated against McLeod gage	0.5	Cross section, 10–15%; yield, 5%;	
Bunch et al. [1958]	H_2, C_2H_6	Photographic emulsion and photomultiplier; 433–1334 A; line emission source	McLeod gage			
Comes [1967]	H_2	Mass spectrometric; photomultiplier; 760–810 A; continuum source	Relative measurement	0.4		
Dibeler et al. [1965b]	H_2	Mass spectrometric; tungsten photodiode; 700–815 A; continuum light source	Relative measurement	2		
Watanabe et al. [1953c]	CO	Photomultiplier; 1060–2100 A; line and continuum source	McLeod gage	0.85		
Huffman et al. [1964b]	CO	Photomultiplier; 600–1000 A; continuum source	McLeod gage	0.5	Cross section, 10%; wavelength, 0.1 A;	Observed cross sections raised by factor 1.15 to correct for pressure gradient in absorption cell
Cook et al. [1965]	CO	Platinum photodiode; ion chamber; 600–1000 A; continuum source	Thermocouple gage calibrated against McLeod gage	0.2–0.5		

TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Cairns and Samson [1965, 1966]	CO, CO_2	Photomultiplier; double ion chamber; 200–1040 A; line emission source	McLeod gage	0.7	Cross section, 5% at wavelengths >340 A, otherwise 10%; yield, 5%	
Marmo [1953]	NO	Photomultiplier; 1100–2300 A; line and continuum source	McLeod gage, mercury manometer, ion gage	0.85	Discusses effect of N_2O impurity on the results	
Walker and Weissler [1955c]	NO, N_2O	Photomultiplier; double ion chamber; 600–1400 A; line emission sources	McLeod gage	5		
Watanabe [1954]	NO, NH_3	Photomultiplier; ion chamber; 1070–1340 A; line emission source	Alphatron gage and oil manometer	1	Cross section, 5–10%; yield, 10%	
Watanabe et al. [1967]	NO	Photomultiplier; ion chamber; 580–1350 A; line and continuum sources	Micromanometer calibrated against McLeod gage	0.2, 1060 to 1350 A; 0.4, 860 to 1100 A; 0.3, 580 to 590 A		
Metzger et al. [1967]	NO	Platinum photodiode; ion chamber; 600–950 A; continuum light source	Micromanometer, or thermocouple gage calibrated against McLeod gage	0.2, 0.5	Cross section, 10%; yield, 20%	
Weissler et al. [1959]	NO, O_2, N_2, CO, CO_2, N_2O, NO_2	Mass spectrometric; photomultiplier; 430–1570 A; line emission source	Relative measurement	8		
Reese and Rosenstock [1966]	NO	Mass spectrometric; tungsten photodiode; 600–1360 A; continuum light sources	Relative measurements	2		
Inn et al. [1953]	CO_2	Photomultiplier; 1050–1800 A; line and continuum source	McLeod gage	0.85		Purity of gas checked with mass spectrometer
Nakata et al. [1965]	CO_2	Photomultiplier; ion chamber; 580–1670 A; line and continuum source	Micromanometer calibrated against McLeod gage	0.2 above 1000 A; 0.3 below 1000 A	Cross section, 10% >670 A; 15–20% <670 A; yield, 10%	
Cook et al. [1966]	CO_2	Platinum photodiode; ion chamber; 600–1000 A; continuum light source	Thermocouple gage calibrated against McLeod gage	0.2 to 0.5	Cross section, 10% 650–950 A; 15% outside this range; yield, 5%	

TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Inn and Tanaka [1953]	O_3	Photomultiplier; 2000–3500 A; continuum source	H_2SO_4 manometer		Cross section, 5%; wavelength error, ±1 A	
Griggs [1968]	O_3	Photomultiplier; 2000–3600 A; continuum source	H_2SO_4 manometer		Scatter of results less than ±1.5% between 2000 and 3000 A; up to 6% outside this range	
Hearn [1961]	O_3	Photomultiplier; 2500–3400 A; line emission source	Pyrex spiral manometer calibrated against McLeod gage		Full discussion of errors given for each point	
DeMore and Raper [1964]	O_3	Photomultiplier; 2000–3100 A; line emission source	Conversion of O_3 to O_2; O_2 pressure measured with gas buret calibrated against McLeod gage		4%	
Tanaka et al. [1953]	O_3	Photomultiplier; 1050–2200 A	H_2SO_4 manometer		10%	
Ogawa and Cook [1958]	O_3	Photographic; 526–1305 A; line emission source	Relative measurement	8.5	Less than 20% from normalization procedure; other errors given for each line	Results normalized at 1215 A taken from Tanaka et al. [1953]
Watanabe and Sood [1965]	NH_3	Photomultiplier; ion chamber; 580–1700 A; continuum and line emission sources	Micromanometer calibrated against McLeod gage	0.2, 850–1700 A 0.3, 580–1000 A	Cross section, 10%; no error given for yield	
Tannenbaum et al. [1953]	NH_3	Photographic emulsion and photomultiplier; 1600–3000 A; continuum light source			5–10%	
Walker and Weissler [1955a]	NH_3	Photomultiplier; double ion chamber; 600–1200 A; line emission source			Cross section, 5 to 10%; yield, 10%	
Romand and Mayence [1949]	N_2O	Photographic emulsion; 1400–2500 A; line and continuum source	Manometers			
Zelikoff et al. [1953]	N_2O	Photomultiplier; 1080–2100 A; line and continuum source		0.85		NO_2 purity checked with mass spectrometer
Cook et al. [1968]	N_2O	Platinum photodiode; ion chamber; 600–1000 A; continuum source	Diaphragm-type transducer and thermocouple gage calibrated against McLeod gage	0.5	Absorption cross section 10% at 650–950 A, 15% outside this range; yield 20% at 650–950 A, 30% outside this range	

TABLE 2. (continued)

Authors	Species	Experimental Arrangement	Pressure Measurement	Bandwidth, A	Errors	Remarks
Dibeler et al. [1967]	N_2O, NO_2	Mass spectrometer; tungsten photodiode; 600–1300 A; line and continuum sources	Relative measurement	2		
Nakayama et al. [1959]	NO_2	Photomultiplier; 1080–2700 A; line and continuum source	Micromanometer and silicone oil manometer	0.2	10–20% at wavelengths below 1800 A; higher at longer wavelengths	
Hall and Blacet [1952]	NO_2, N_2O_4	Photomultiplier; 2400–5000 A	Silicone manometer or mercury manometer	2–5	Errors discussed but no figures given	
Frost et al. [1962]	NO_2	Mass spectrometer; photomultiplier	Relative measurement	6		
Ditchburn [1955]	CH_4	Photographic emulsion; 350–1600 A; line and continuum sources	McLeod gage		Relative values of points estimated to be accurate to ±10%; systematic error given as ±7%	
Sun and Weissler [1955]	CH_4, NH_3	Photographic emulsion; 374–1300 A; line emission source	McLeod gage		Systematic error from pressure measurement given as 5%	
Rustgi [1964]	CH_4	Photomultiplier; 170–1000 A; line emission source	Thermocouple gage calibrated against McLeod gage	1		
Schoen [1962]	CH_4, C_2H_6, C_2H_4, C_2H_2	Mass spectrometer; ion chamber; photomultiplier; 450–1550 A; line emission source	McLeod gage	8	Absolute calibration of detector has error of 15%; other errors given in captions of figures	
Lukirskii et al. [1964]	CH_4	Proportional counter; 23–250 A; line emission source			Error on cross section, 5%	
Dibeler et al. [1965a]	CH_4, CD_4	Mass spectrometer; tungsten photodiode; 600–1000 A; continuum light source	Relative measurement	2	Error shown in figure for each point	
Chupka [1968]	CH_4	Mass spectrometer; nickel photodiode; 600–1000 A; continuum light source	Relative measurement	1.6 and 0.4	Probable error of each point equal to or less than diameter of point in figure	
Cook and Ogawa [1939a, b]	CS_2, COS	Platinum photodiode; ion chamber; 600–1000 A; continuum light source	Thermocouple and ionization gage calibrated against McLeod gage	0.5		Impurity level checked with mass spectrometer

TABLE 2. (continued)

Authors	Species	Experimental Arrangements	Pressure Measurement	Bandwidth, A	Errors	Remarks
Golomb et al. [1962]	SO_2	Photomultiplier; 1050–2170 A; line and continuum source	Micromanometer	1	For wavelength above 1350 A, error is 10% where structure is displayed and less elsewhere	Purity of sample checked with mass spectrometer
Warneck et al. [1964]	SO_2	Photomultiplier; 1849–3150 A; continuum and line sources	Silicone oil manometer and dial gage	1		
Matsunaga and Watanabe [1967]	COS	Photomultiplier; ion chamber; 1070–1700 A; line and continuum source	Calibrated micromanometer, silicone oil manometer	0.5	Absorption cross section, 10%, 1410–1700 A; 10–20%, 1070–1410 A	
Nakayama and Watanabe [1964]	C_2H_2	Photomultiplier; ion chamber; 1050–2000 A; line and continuum source	Micromanometer and silicone oil manometer	1	Absorption cross section, 10–20%	
Moe and Duncan [1952]	C_2H_2	Photographic emulsion; 1050–1520 A; line emission source		0.5	About 15% maximum	
Botter et al. [1966a]	C_2H_2	Mass spectrometer; photodiodes of tungsten, gold, and aluminum; 600–1100 A; continuum and line sources	Relative measurement			
Zelikoff and Watanabe [1953]	C_2H_4	Photomultiplier; 1065–2000 A; line and continuum source	McLeod gage and mercury manometer	0.85	5%	Purity of sample checked with mass spectrometer
Walker and Weissler [1955b]	C_2H_2, C_2H_4	Photomultiplier; ion chamber 687–1200 A; line emission source	McLeod gage		Absorption cross section, 10%; yield, 10%	
Botter et al. [1966b]	C_2H_4	Mass spectrometer; tungsten photodiode; 600–1200 A; line and continuum sources	Relative measurement	1	Wavelength, ±0.5 A	
Person and Nicole [1968]	C_2H_4	Photomultiplier; ion chamber; nickel photodiode	Capacitive manometer	1	Absorption cross section, 4%; yield, ~10%	Error on yield reviewer's estimate, since yield was relative to nitric oxide yield of Watanabe et al. [1967]

surement or error was given in the paper. Where the authors have referred to a previous paper, the latter has been used to fill in the appropriate column. Whenever possible, additional papers that contain photographs of the absorption spectra under review have been referred to in the text.

Most of the figures shown in this review were prepared by the Information Center at the Joint Institute for Laboratory Astrophysics. Almost all of the data reproduced in these figures were presented in the original literature in graphical form. In this case blown-up photographs of the figures were made, and the data were digitized by means of a Gerber data-reduction system. Once the digitized data had been obtained they were permanently stored on magnetic tape. The review figures were then photocomposed from these tapes on a DD280 cathode ray tube display.

A. Molecular Oxygen, O_2

The absorption spectrum of molecular oxygen between 1750 and 2600 A is characterized by the absorption bands of the Schumann-Runge system ($B^3\Sigma_u^-$ → $X^3\Sigma_g^-$) between 1750 and 2000 A and the weak Herzberg dissociation continuum ($A^3\Sigma_u^+$ → $X^3\Sigma_g^-$), which, according to the theoretical calculations of *Jarmain and Nicholls* [1967], extends from 1850 to 2600 A. The absorption cross section for this continuum is of the order of 10^{-23} cm^2, and consequently long path lengths and pressures of the order of 1 atmosphere are necessary for measurable absorption. Under these conditions the total column density of O_2 can be measured to an accuracy of better than ±1%. However, impurities such as ozone (arising from the interaction of the product atoms with the molecular oxygen) will now play an important role in the accuracy of the measurements.

The continuum has been investigated by two groups: *Ditchburn and Young* [1962] and *Blake et al.* [1966]. Ditchburn and Young used photographic detection and placed the absorption cell between the spectrograph and the light source. Path lengths of 5, 10, and 30 meters were used with pressures varying from 0.2 to 5 atmospheres. Great care was taken to insure that ozone was not formed in the absorption cell. As is pointed out by Ditchburn and Young, the fact that they see little absorption at 2500 A, where the ozone absorption cross section is at its maximum, would seem to indicate that the formation of ozone was not a problem in their experiment. The data of Blake et al. were obtained with a monochromator. They placed the absorption cell at the exit slit and used pressures ranging from 1 to 2 atmospheres. The results obtained by these two groups are compared in Figure 11, from which it can be seen that those of Blake et al. are 10 to 15% higher than those of Ditchburn and Young.

Both groups found that their measured cross sections increased linearly with pressure, a fact which they attributed to the formation of O_4 at the high pressures employed. In the wavelength interval between 2000 and 2040 A the strength of the Schumann-Runge bands corresponding to transitions from $V'' = 1, 2,$ and 3 is weak, but nevertheless does contribute significantly to the total absorption cross section. Figure 12 shows a theoretical plot of the absorption cross section, averaged over 1-A intervals, that arises from these transitions at zero optical depth, for the wavelength interval 2000 to 2100 A. The plot was
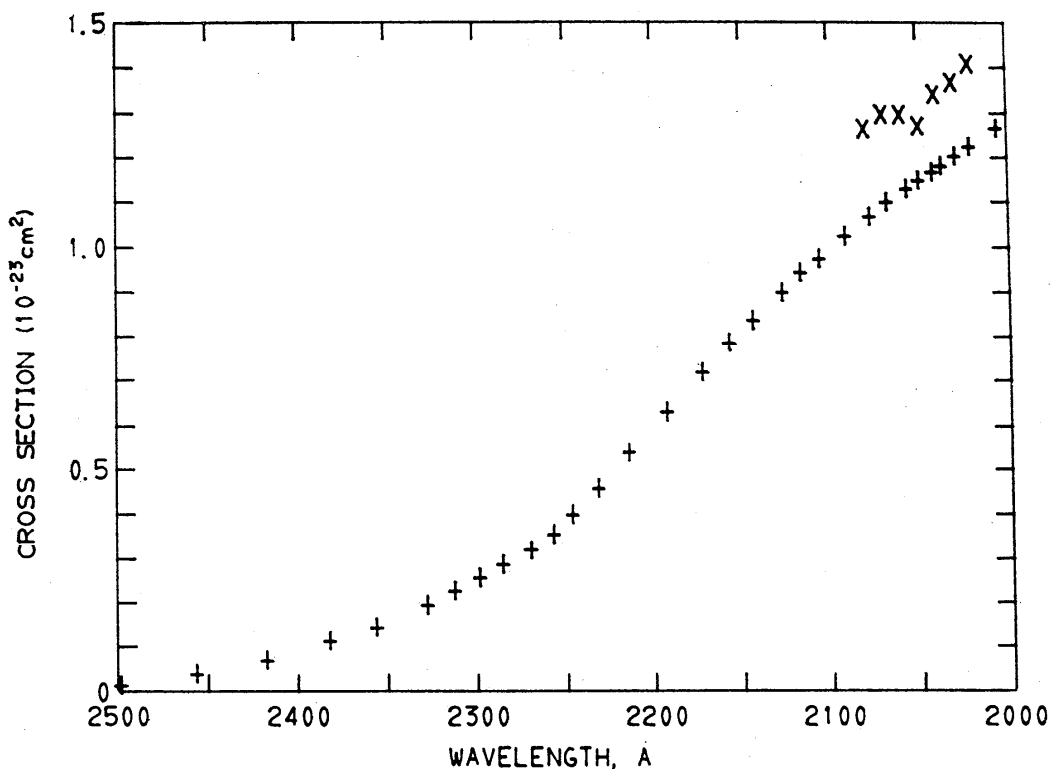
Fig. 11. Comparison of measured total absorption cross sections for O_2 between 2000 and 2500 A; +, *Ditchburn and Young* [1962]; ×, *Blake et al.* [1966].

obtained using the oscillator strengths for the $V'' = 0$ bands of *Bethke* [1959] and the relative Franck-Condon factors for the other bands of Jarmain and Nicholls (personal communication, 1967). The cross sections at 2000 A obtained by Ditchburn and Young and by Blake et al. vary from 1.2×10^{-23} at zero pressure (i.e., after extrapolating their measured cross sections to zero pressure) to 4×10^{-23} at a pressure of 2 atmospheres. Although the bands cannot account for the total measured absorption cross section, they do account for most of it; and the observed pressure effect is characteristic of pressure broadening of rotational lines. Thus the shape and magnitude of the Herzberg continuum must be considered in doubt at this time.

Absorption cross sections in the region of the Schumann-Runge bands, 1750–1950 A, have been obtained by *Blake et al.* [1966], *Thompson et al.* [1963], and *Watanabe et al.* [1953a] at an instrumental bandwidth of 1 A. High-resolution spectra of these bands [*Brix and Herzberg*, 1954; *Knauss and Ballard*, 1935; and *Hudson and Carter*, 1968b] have shown that the region consists of well-separated rotational lines, and therefore the data of these former three groups can at best be considered qualitative. The oscillator strengths for these bands, in absorption, have been obtained by *Bethke* [1959] and confirmed recently by *Hudson and Carter* [1968b]. The latter paper also reviews the evidence for predissociation in these bands.

The wavelength interval between 1750 and 1250 A consists of the strong

Schumann-Runge dissociation continuum ($B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$) and three diffuse bands or continua that are situated at about 1352, 1332, and 1293 A [*Tanaka*, 1952]. More than 10 measurements have been made in the Schumann-Runge continuum, using both photographic and photoelectric techniques. Until recently, there has been a constant discrepancy between the cross sections obtained by these two techniques. The discrepancy has, in part, been ascribed by either side to the differences in the means used to correct for scattered light, but it is also significant that until the recent work by *Goldstein and Mastrup* [1966] the photographic measurements have placed the absorption cell between the light source and the spectrograph. (See previous discussion.) Goldstein and Mastrup filled the spectrograph with the gas, which would be expected to produce less excited species or ozone in the absorption path; and their measurements are in essential
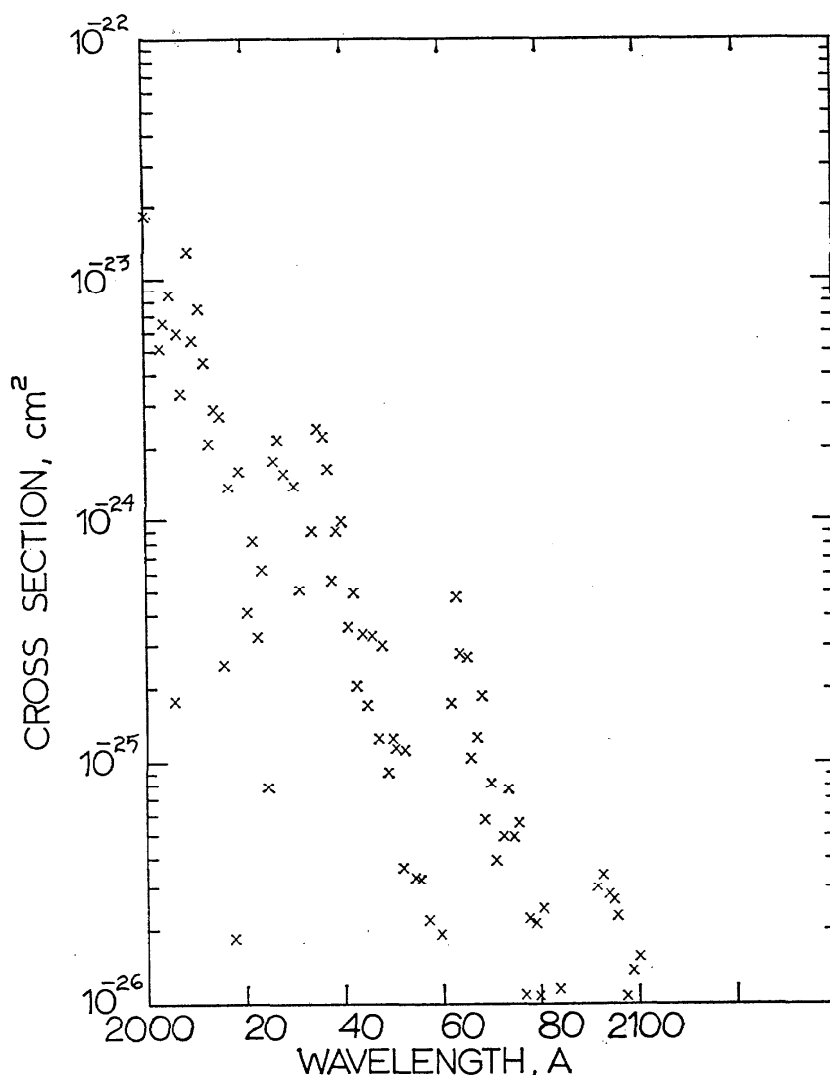
Fig. 12.   Estimate of the contribution of the Schumann-Runge bands to the total absorption by O_2 near 2000 A.

agreement with those obtained using photoelectric techniques. Figure 13 compares the photoelectric measurements of *Huffman et al.* [1964c] *Watanabe et al.* [1953a], *Blake et al.* [1966], and *Metzger and Cook* [1964b] with that of Goldstein and Mastrup, between 1350 and 1550 A.

As can be seen from Figure 13, these groups agree well within their quoted experimental errors at the peak of the absorption curve at 1440 A, while at 1500 A the spread of the results is outside the quoted errors. But the most significant feature of this figure is that it indicates the different shapes that these groups obtained for the Schumann-Runge continuum. If other measurements by other groups are included, then further discrepancies from one group to the next in the over-all shape of this particular transition can be found. Perhaps this discrepancy between these groups illustrates the problems that exist in absorption spectroscopy in the ultraviolet even where the systematic errors due to data analysis should be at a minimum.

Measurements of the Schumann-Runge continuum between 1800 and 1600 A are displayed in Figures 14 and 15. An additional paper, *Hudson et al.* [1966], is displayed along with those of *Watanabe et al.* [1953a], Blake et al., and Metzger and Cook. The resolution used by Hudson et al. for wavelengths below 1750 A was 0.75 A; for wavelengths above 1750 A a resolution of 0.075 A was used in order that the continuum could be measured between the rotational lines
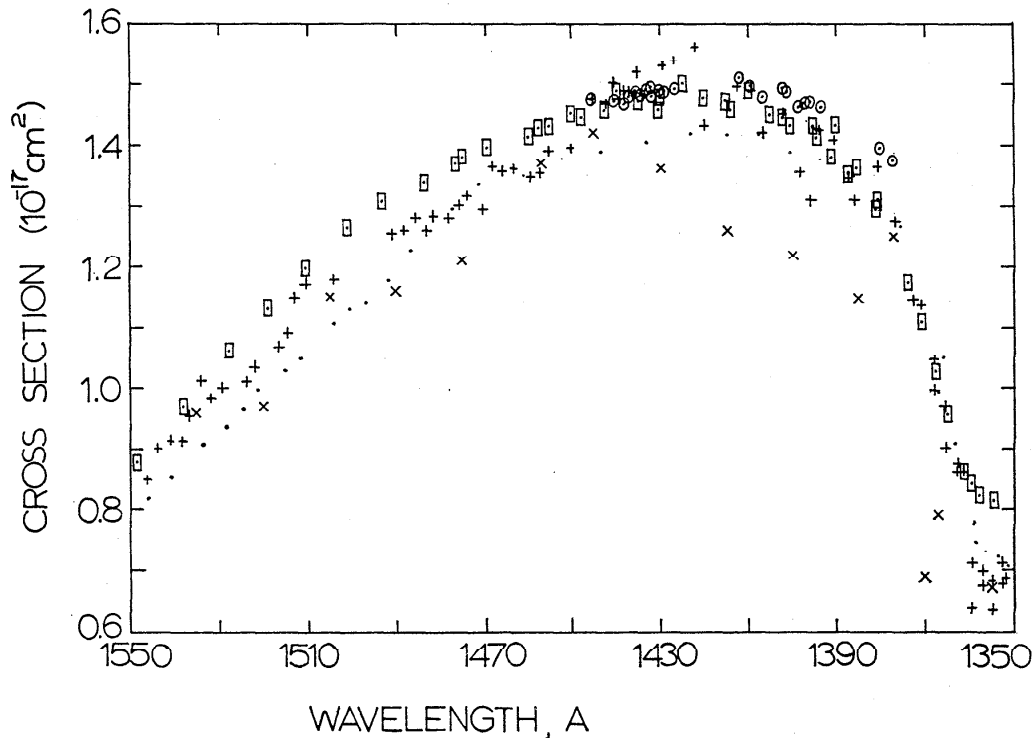

Fig. 13. Comparison of measured total absorption cross sections for O_2 between 1350 and 1550 A; dot, *Watanabe et al.* [1953a]; boxed dot, *Blake et al.* [1966]; +, *Metzger and Cook* [1964b]; circled dot, *Huffman et al.* [1964]; ×, *Goldstein and Mastrup* [1966].

of the Schumann-Runge band system. This paper presents cross sections obtained at 300, 600, and 900°K, although only the results obtained at 300°K are shown in Figures 14 and 15. The authors found a marked change in the absorption cross section as a function of temperature, indicating that the transition probabilities to the continuum from excited vibrational levels of the ground state are considerably higher than that from the ground vibrational state. Agreement between the results of *Watanabe et al.* [1953a] and *Hudson et al.* [1966] is extremely good over this entire wavelength interval, being within ±3%, well within the quoted errors of both experiments. The results of Metzger et al. are, in general, higher than those obtained by these two groups. In summary, it may be said that the cross section in the Schumann-Runge continuum between 1370 and 1800 A is probably known to within ±5% (excluding systematic errors), but that the shape of this continuum is not well known.

Figure 16 presents results obtained by Blake et al., *Watanabe et al.* [1953a], and Metzger and Cook between 1300 and 1370 A. This region includes three apparent continua centered at 1352, 1332, and 1293 A. High-resolution spectrograms taken by *Tanaka* [1952] show diffuse band structure in this wavelength interval, indicating that these continua could be the result of band overlap. The band centered at 1352 A has been associated with a dissociation process in molecular oxygen leading to two oxygen atoms, both of which are in ^1D states.
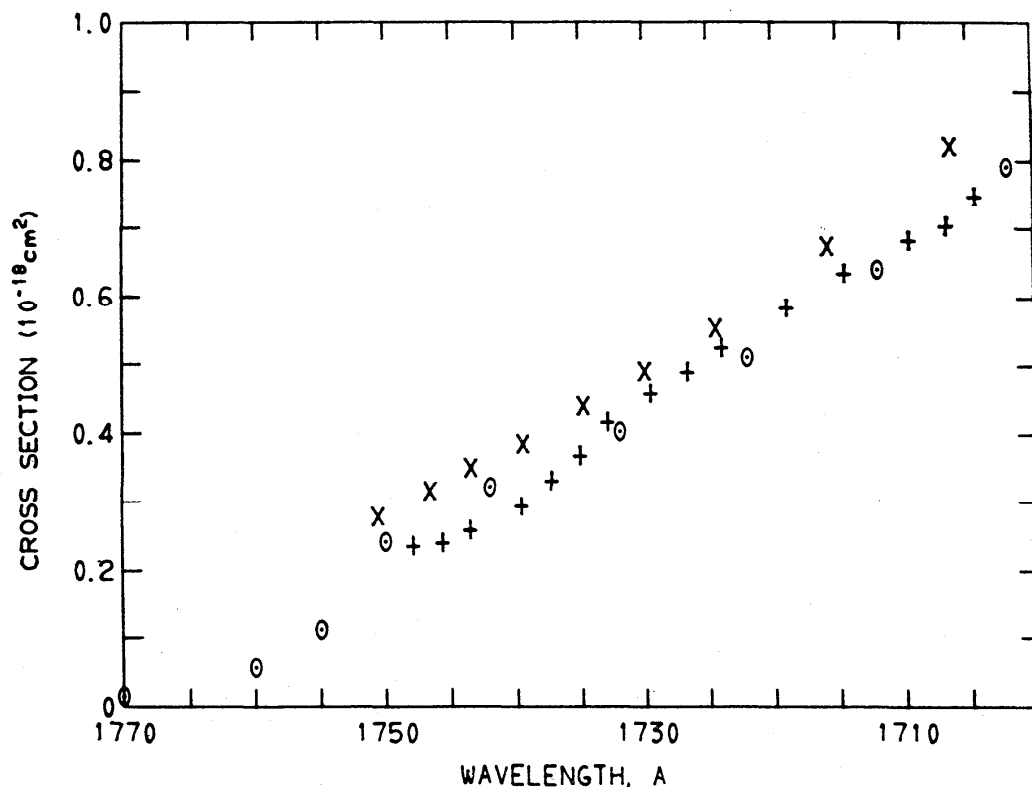

Fig. 14. Comparison of measured total absorption cross sections of O_2 between 1700 and 1770 A; +, *Watanabe et al.* [1953a]; ×, *Blake et al.* [1966]; circled dot, *Hudson et al.* [1966].
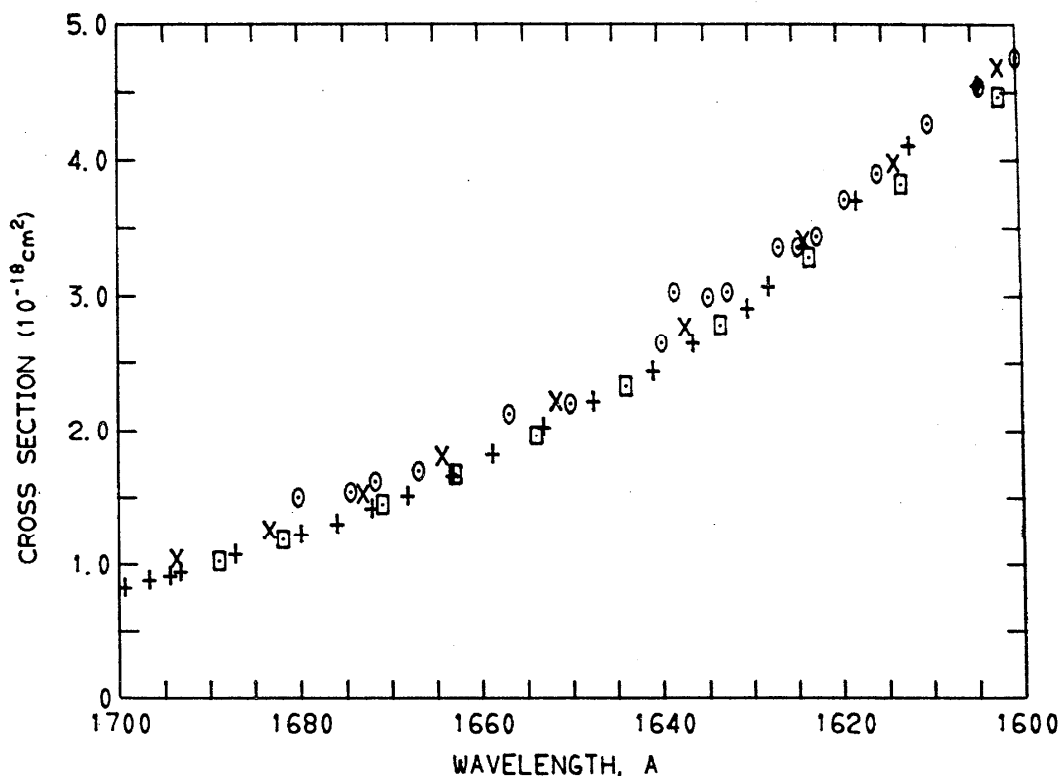
Fig. 15. Comparison of measured total absorption cross section data for O_2 between 1600 and 1700 A; +, *Watanabe, Inn, and Zelikoff* [1953]; ×, *Blake et al.* [1966]; circled dot, *Metzger and Cook* [1964b]; boxed dot, *Hudson et al.* [1966].

Of the other two weaker continua, at least one is thought to result in dissociation products of one normal oxygen atom and one metastable atom in the ^1S state. If these three structures are due to the overlap of diffuse bands, and the diffuseness is due to predissociation, it would seem that, as yet, no definite conclusion can be reached about the final state of the dissociation products. It will be noticed in Figure 16 that although the three measurements agree well for the continuum centered at 1332 A, there is disagreement around 1350 A. The disagreement is disturbing, since both Blake et al. and Metzger and Cook used continuum light sources, and one should expect reasonable agreement in the over-all shape of the absorption curve at this particular point. At the present moment, the disagreement is well outside the mutual experimental errors of these three groups.

The spectral region between 1025 A and 1300 A has been investigated in detail by *Watanabe et al.* [1953a] and *Watanabe* [1958], and at isolated points, namely at band minima and band maxima, by *Metzger and Cook* [1964b]. The absorption spectrum in this wavelength interval consists of a complexity of absorption bands with the possibility of a weak underlying continuum. The bands show structure under high resolution [see *Tanaka,* 1952; *Alberti et al.,* 1968], but the bands are diffuse, and the absorption cross sections measured have been found to be independent of N. As discussed previously, this does not
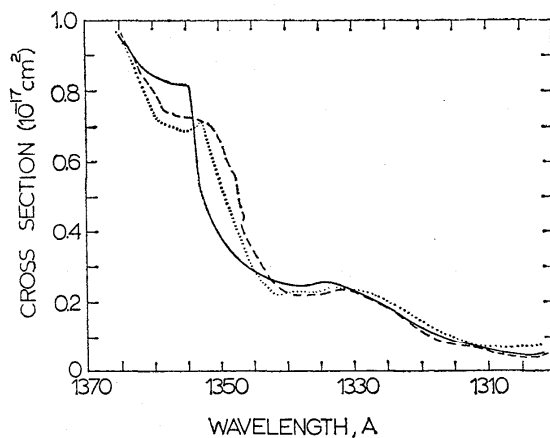
Fig. 16. Comparison of measured total absorption cross section data for O_2 between 1300 and 1370 A; solid line, *Blake et al.* [1966]; dashed line, *Watanabe, Inn, and Zelikoff* [1953]; dotted line, *Metzger and Cook* [1964b].

necessarily mean that the published peak values or minima values are correct. Between the bands there is a series of deep windows, one of which corresponds to Lyman α, 1215 A. The absorption cross section has been given special attention at this wavelength by many investigators, and in Table 3 these reported values are listed. The absorption cross section at Lyman α has been observed to increase with pressure, an effect ascribed to the formation of O_4 in the absorption cell; and the cross section quoted by the authors was obtained by extrapolating their measured cross section to zero pressure. The agreement between the various observers is good and well within their mutual experimental errors. Pressure broadening of the rotational line structure seen by *Tanaka* [1952], *Alberti et al.* [1968], and *Ogawa* [1968b], in the vicinity of Lyman α could also account for the pressure dependence of the cross section in this window; and thus the use of the cross sections in Table 3 may not necessarily give true absorption profiles for solar Lyman α in the earth's atmosphere. Figure 17 reproduces the

TABLE 3.   Measured Cross Section for O_2, at Lyman Alpha, 1215.6 A, Extrapolated to Zero Pressure

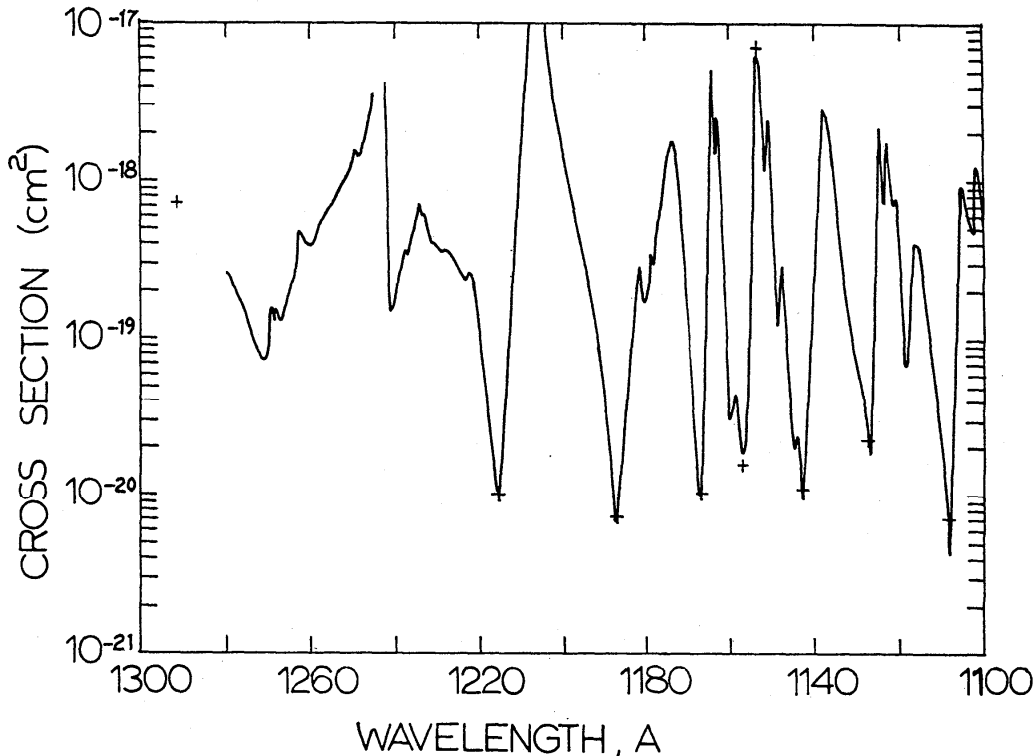| Investigators	Cross Section, 10^{-20} cm²	Method
Preston [1940]	1.04	Photoelectric
Watanabe et al. [1953a]	1.00	Photoelectric
Ditchburn et al. [1954]	0.84	Photographic
Lee [1955]	0.85	Photographic
Watanabe [1958]	1.00	Photoelectric
Metzger and Cook [1964b]	1.04	Photoelectric
Shardanand [1967]	1.08	Photoelectric
Ogawa [1968b]	1215.72–1.03	Photoelectric
	1215.63–1.13	

Fig. 17. Comparison of measured total absorption cross section data for O_2 between 1100 and 1300 A; solid lines, Watanabe [1958]; +, Metzger and Cook [1964b].

absorption cross section data of *Watanabe* [1958] and of *Metzger and Cook* [1964b] between 1100 and 1300 A. In view of its importance to the D and E regions of the earth's ionosphere, it would appear that more work in this particular spectral region could be useful.

The ionization edge of molecular oxygen is at 1027 A, and below this wavelength a complex band spectrum is observed down to 600 A [*Price and Collins*, 1935; *Tanaka and Takamine*, 1942; *Tanaka*, 1952]. These bands have been assigned to Rydberg series that converge to limits at 682.22 A and 610.49 A. In the region between 600 and 500 A, Rydberg series of neutral oxygen have been observed by *Codling and Madden* [1965]. These converge to limits at 500.84 and 504.71 A. Photographs of the absorption spectrum of molecular oxygen are reproduced in the papers cited above.

The six most recent photoelectric measurements of the total photoabsorption cross section of molecular oxygen, between 600 and 1025 A, are by *Watanabe and Marmo* [1956], *Cook and Metzger* [1964a], *Huffman et al.* [1964a], *Samson and Cairns* [1964], and *Matsunaga and Watanabe* [1967]. Of the results obtained with a continuum light source, the data of Matsunaga and Watanabe were obtained at the highest resolution, 0.3 A. The data obtained by Huffman et al. between 800 and 1000 A agree very well in the over-all shape of the absorption curve but are in general about 20% lower than those of Matsunaga

and Watanabe (see Figure 18). The data of Cook and Metzger are not in such good agreement with those of Matsunaga and Watanabe; a comparison of the cross sections at peaks and minima shows no constant discrepancy.

In the region between 600 and 800 A, the results obtained by *Huffman et al.* [1964a] are considerably higher than those obtained by Matsunaga and Watanabe, the discrepancy between the two sets of data becoming larger as one goes to shorter wavelengths (see Figure 19). This would indicate that over the spectral range from 600 to 1000 A there is a systematic error between these two measurements that depends upon wavelength. Where they can be compared, the results of Samson and Cairns agree best with those of Matsunaga and Watanabe. The data of Cook and Metzger are also in good agreement with those of Matsunaga and Watanabe at the minima, although the maxima are in general lower. However, the absorption curves of Cook and Metzger do not show the band structure seen by *Huffman et al.* [1964a] and by Matsunaga and Watanabe at wavelengths shorter than 670 A, although this structure is evident in the photographic studies of *Ogawa* [1968a]. This is apparently due to the weakness of their light source at wavelengths below 670 A.

The cross-section curves given in the above papers are all subject to band-
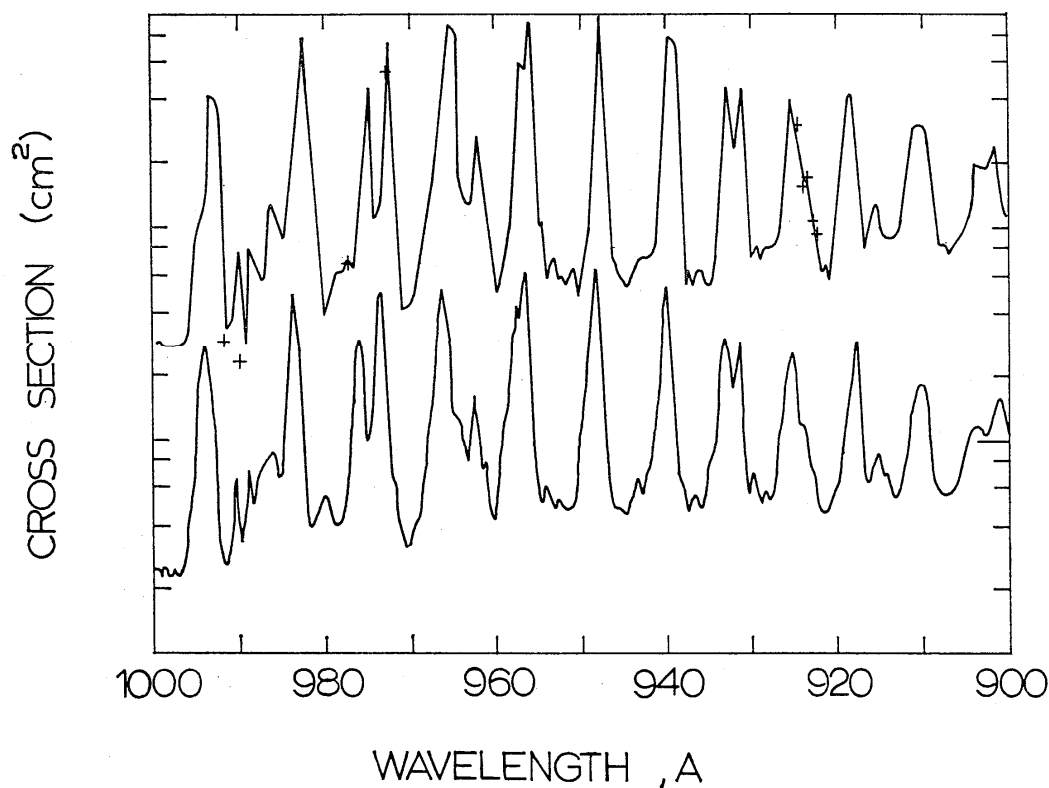
Fig. 18. Comparison of measured total absorption cross section data for O_2 between 900 and 1000 A; top curve, *Matsunaga and Watanabe* [1967]; bottom curve, *Huffman et al.* [1964a] divided by ten; +, *Samson and Cairns* [1964]. This computer plot is not scaled in integral units of ten, the maximum value of the ordinate being 5.60×10^{-17} cm^2.
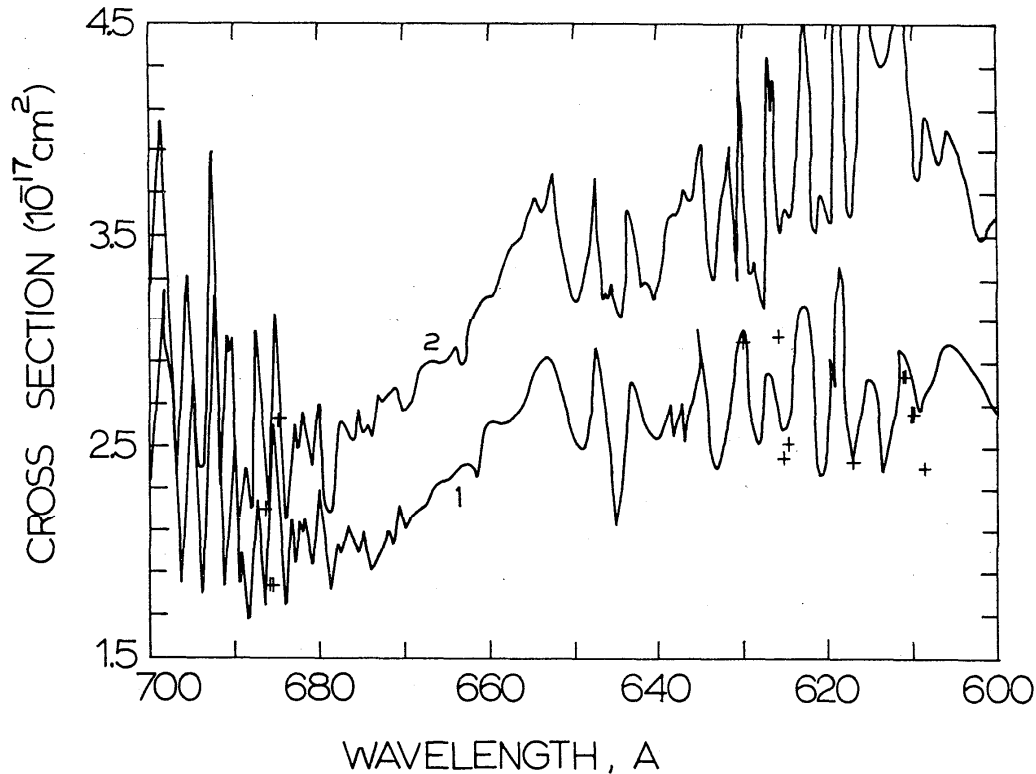
Fig. 19. Comparison of measured total absorption cross section data for O_2 between 600 and 700 A; curve 1, *Matsunaga and Watanabe* [1967]; curve 2, *Huffman et al.* [1964a]; +, *Samson and Cairns* [1964].

width dependence, as is illustrated in Figure 20. In this figure the band profile at 832 A obtained at 0.04 A bandwidth (Hudson and Carter, personal communication, 1968) is compared with that obtained from the curve published by Matsunaga and Watanabe and with the points given by Samson and Cairns. Also indicated on Figure 20 are positions of strong solar emission lines. It will be noticed at once that the continuous curve as given by Matsunaga and Watanabe would yield the wrong attenuation profiles for some of these lines. Table 4 compares results obtained at the peak of this band by several investigators. The agreement is reasonable, and one might be tempted to interpret this agreement as indicating that the cross section of molecular oxygen is well known at this wavelength. But, as is indicated in Figure 20, the band shape must also be known accurately, and the presently published data do not yield this information.

Measurements of the total absorption cross section between 200 and 600 A have been obtained largely with line emission sources, and the results of *Samson and Cairns* [1964, 1965] and *Wainfan et al.* [1955] are displayed in Figure 21. The agreement between the various results selected is good, but there appears to be a large amount of scatter between 500 and 600 A. Some of this scatter can be attributed to the Rydberg series of absorption bands seen by *Codling and Madden* [1965]. *Henke et al.* [1967] have obtained cross-section data between 8 and 114 A.
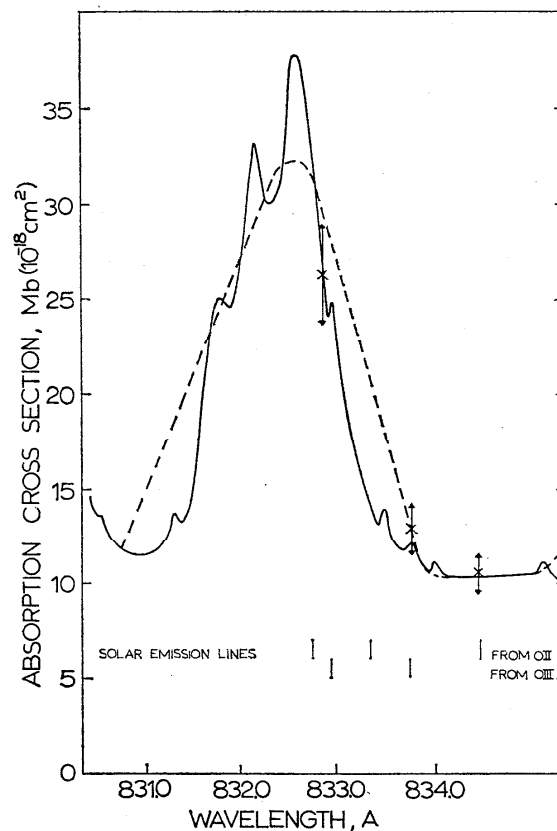
Fig. 20. Comparison of measured total absorption cross section data for O_2 between 830 and 836 A; sol;d line, R. D. Hudson and V. L. Carter (personal communication); dashed line, Matsunaga and Watanabe [1967]; ✕, Samson and Cairns [1964].

The photoionization yield, η, has been measured by several groups between 300 A and the photoionization limit at 1025 A. A comparison of the most recent results between 700 and 900 A is presented in Figures 22 and 23. Cook and Metzger [1964a] used a platinum plate in their ion chamber as a secondary standard, standardizing the photoelectric yield of the metal against an inert gas. This determination also required a pressure measurement. The data of Samson and Cairns and of Matsunaga and Watanabe were obtained using the total-absorption technique, which does not require a secondary standard or a

TABLE 4. Cross Section for O_2 at the Peak of the Absorption Band at 832.70

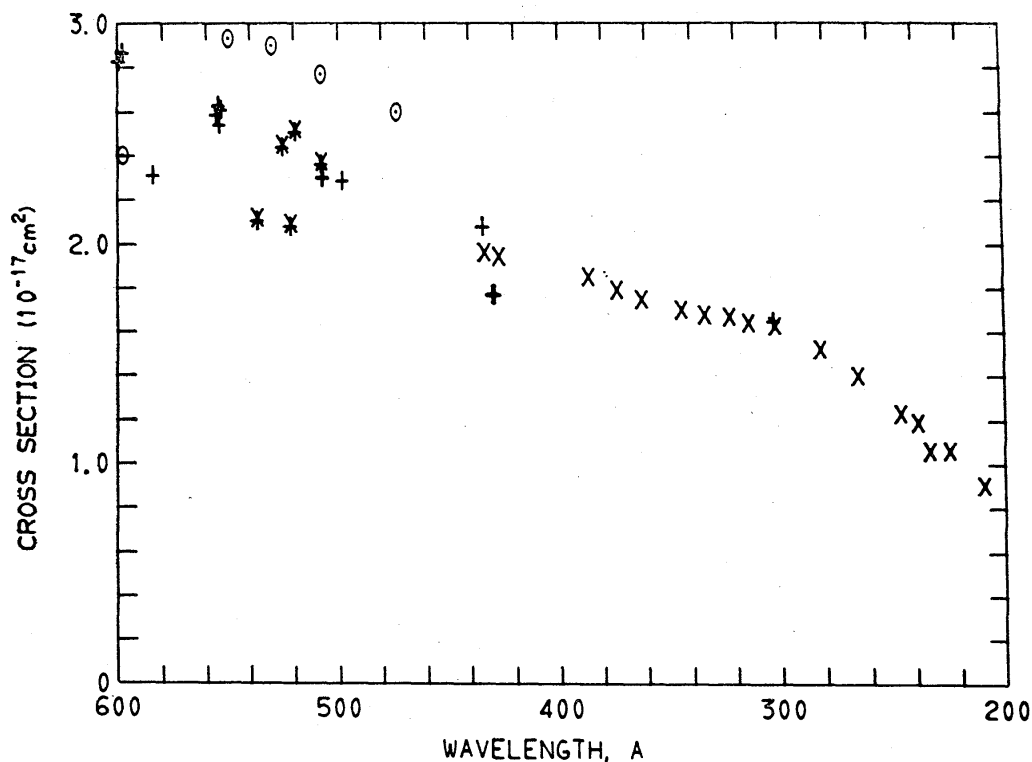| Investigators	Cross Section, $Mb(10^{-18}\ cm^2)$,
Weissler and Lee [1952]	24.9
Huffman et al. [1964a]	36.4
Cook and Metzger [1964a]	35.32
Matsunaga and Watanabe [1967]	32.70

Fig. 21. Comparison of measured total absorption cross section data for O_2 between 200 and 600 A; +, *Samson and Cairns* [1964]; circled dot, *Wainfan et al.* [1955]; ×, *Samson and Cairns* [1965].

pressure measurement and should be more accurate. *Cairns and Samson* [1965] estimate the accuracy of their yield to be ±5%, as do Matsunaga and Watanabe. *Cook and Metzger* [1964a] estimate a higher experimental error of ±10%, although they do not report whether this error includes the error in the determination of the photoionization yield of their secondary standard.

In the regions of band structure (680 to 900 A) the yield shows considerable structure indicating that the bands do not completely preionize, but probably predissociate as well. As was indicated in the introduction, $\bar{\eta}(\lambda', \Delta\lambda)$ can also be bandwidth-dependent, and in general one would expect the published results to be upper limits for the particular bands. A comparison of the measurements between 600 and 700 A indicate excellent agreement between the data of Samson and Cairns, Matsunaga and Watanabe, and Wainfan et al., whereas the results of Cook and Metzger are consistently lower.

Between 700 and 900 A the yield appears to drop to a value of about 50%, and Matsunaga and Watanabe have postulated an underlying dissociation continuum at this point corresponding to the process

$$O_2 + h\nu \rightarrow O^3P + O^3S$$
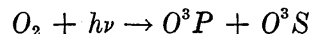
However, this region is also overlaid by bands, and by analogy with the example given for carbon monoxide in subsection 5.1 one can postulate that no con-

tinuum is involved, but rather that the predissociation lifetime of the bands is becoming shorter, giving rise to an apparent dissociation continuum due to band overlap. Because of the importance of excited atomic species in atmospheric processes, this possibility should be explored further.

The photoionization curve published in the paper by Matsunaga and Watanabe should represent a reasonable value for the photoionization cross section of molecular oxygen, bearing in mind the possibility of bandwidth dependence. In the region below 600 A the consensus of results indicates that the photoionization efficiency is 1; thus the photoabsorption cross section as shown in Figure 21 will be numerically equal to the photoionization cross section.

Photoionization efficiency curves, as defined in mass spectrometric measurements, have been obtained by *Dibeler and Walker* [1967] and by *Nicholson* [1963]. Unfortunately, both of these measurements were obtained at much poorer resolution than the results of Matsunaga and Watanabe, and it is difficult to compare these three sets of experimental data. In general, the relative ionization-cross-section curves in the two former papers are consistent with the results in the latter paper.

Dibeler and Walker did observe the onset of dissociative ionization at 719 A, this dissociative ionization leading to the production of an O^+ and an O^- ion.
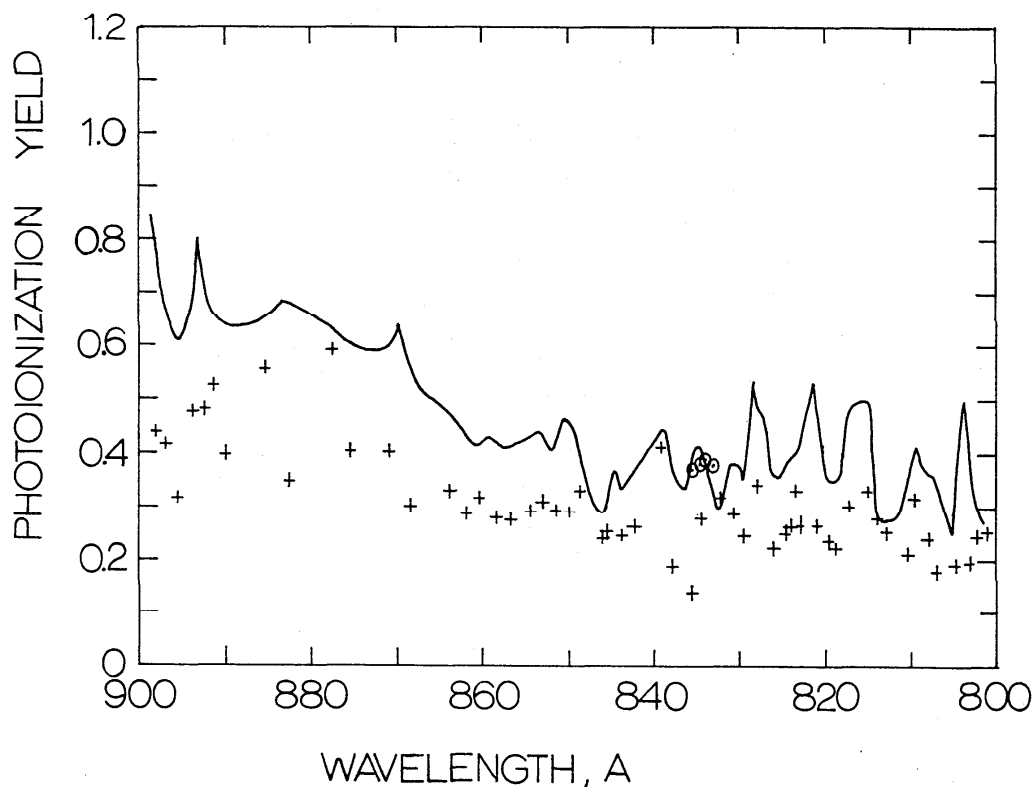

Fig. 22. Comparison of measured photoionization yield data for O_2 between 800 and 900 A; +, *Cook and Metzger* [1964a]; circled dot, *Samson and Cairns* [1964]; solid line, *Matsunaga and Watanabe* [1967].
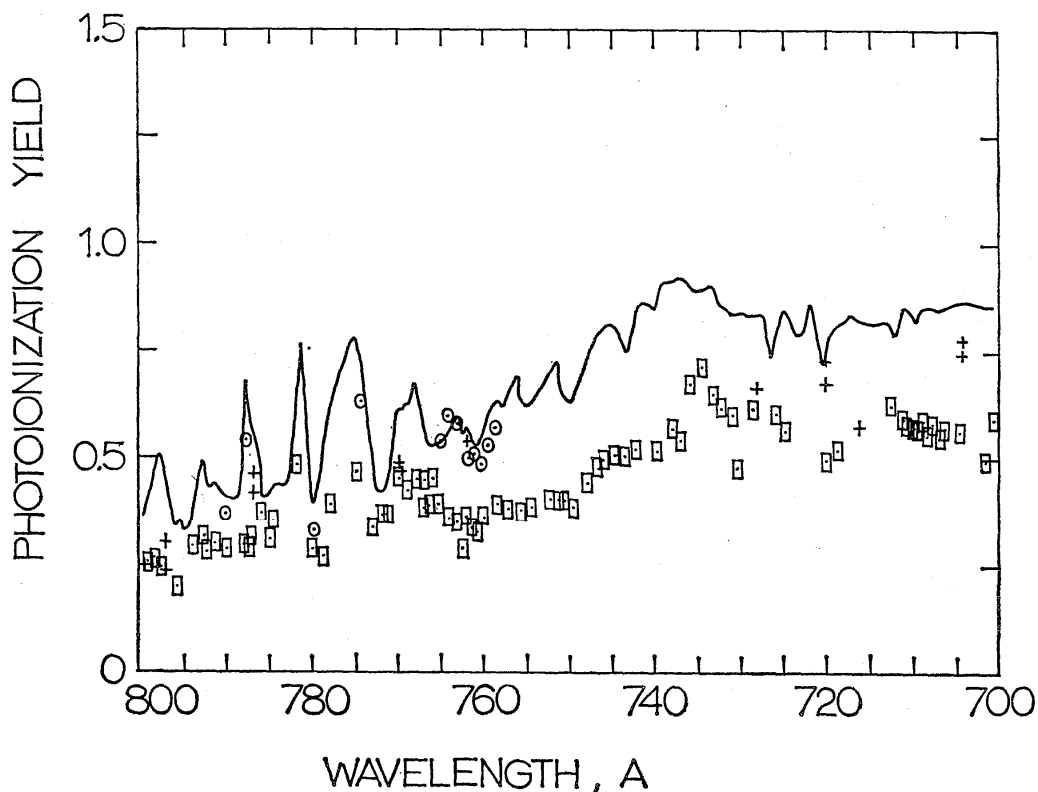
Fig. 23. Comparison of measured photoionization yield data for O_2 between 700 and 800 A; solid line, *Matsunaga and Watanabe* [1967]; boxed dot, *Cook and Metzger* [1964a]; circled dot, *Samson and Cairns* [1964]; +, *Wainfan et al.* [1955].

They observe this dissociation process to be much weaker than the production of the O_2^+ ion, but as mentioned earlier, part of this discrepancy could be due to the finite kinetic energy that the atomic ions will possess. These curves also show some structure indicating preionization into the dissociative continuum.

Comes et al. [1968], using a molecular beam technique, have also investigated the production of O^+ from O_2 and have published dissociative ionization cross sections. Unfortunately, it would appear that the production of energetic O^+ ions at wavelengths shorter than 720 A should affect the cross-section measurements of these workers as well; thus the accuracy of their results is not known. Their results are more likely, however, to be too low than too high, and more likely to be in error at shorter wavelengths than at the longer wavelengths. Evidence for the production of excited states in O_2^+ by the use of photoelectron spectroscopy and by the study of the fluorescence from the excited molecules has recently been summarized by *Schoen* [1969], and the reader is directed to his review for a detailed discussion of these experimental results.

B. Molecular Nitrogen, N₂

The absorption spectrum of molecular nitrogen between 2000 A and 100 A can be characterized by weak absorption bands between 1000 A and 2000 A,

strong band structure between 660 A and 1000 A, and an ionization continuum extending from 100 A to 800 A.

The absorption bands of N_2 observed above 1000 A arise from forbidden transitions from the ground state $X^1\Sigma_g^-$ to the $a^1\Pi_g$ state (the Lyman-Birge-Hopfield bands), the $C^3\Pi_u$ state, and the $w^1\Delta_u$ state. These bands have been studied photographically at high resolution by *Sponer* [1927], *Birge and Hopfield* [1928], *Tanaka* [1955], and *Tanaka et al.* [1964]. The strongest system is the Lyman-Birge-Hopfield system. The bands appear to be sharp, although for the 7-0 band and above, there is evidence for predissociation [*Herman-Montagne*, 1945; *Herzberg and Herzberg*, 1948]. Several experimenters have measured absorption coefficients, at poor resolution, above 1000 A [*Ditchburn et al.*, 1954; *Watanabe et al.*, 1953c; *Weissler et al.*, 1952; and *Preston*, 1940]. Their conclusions are that, apart from the bands where quantitative measurements were not possible, any underlying continuum must have a cross section of less than 2×10^{-22} cm^2. The oscillator strengths for the bands have recently been measured by *Ching et al.* [1967] and *Shemansky* [1970].

Between 660 A and 1000 A, molecular nitrogen has a complex spectrum of strong bands. *Worley* [1943, 1953] and *Ogawa and Tanaka* [1962] ordered these bands into Rydberg series and into 13 short vibrational progressions. Recent
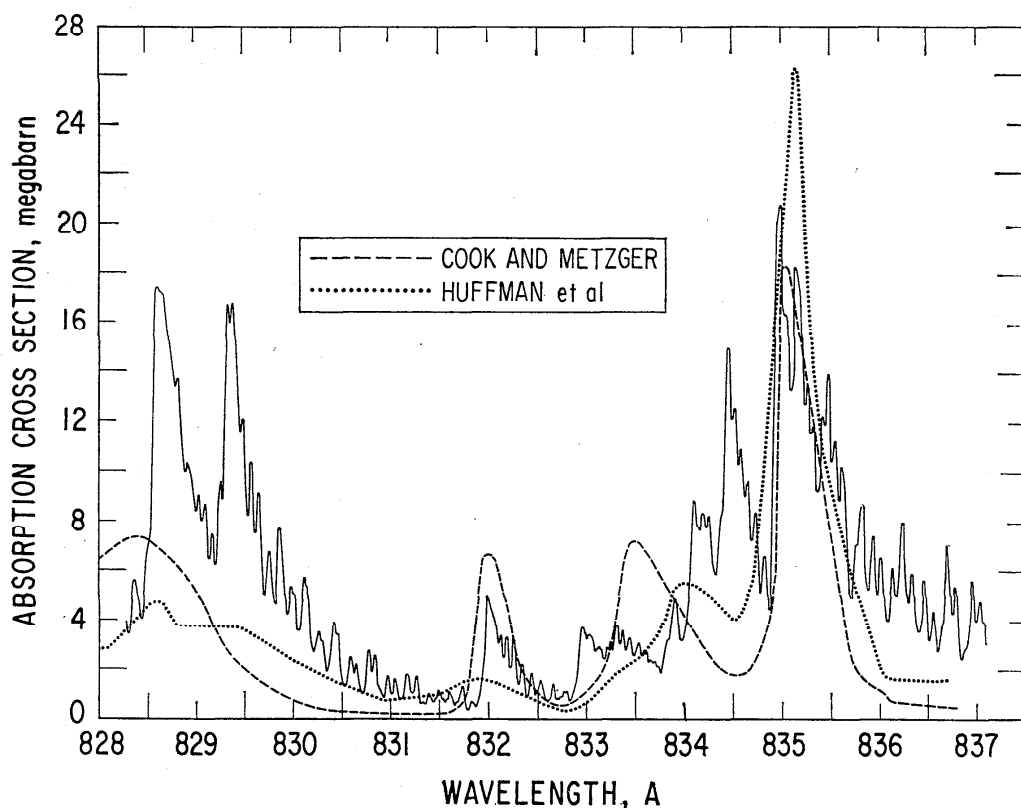

Fig. 24. Comparison of measured total absorption cross section data for N_2 between 828 and 837 A; solid line, *Hudson and Carter* [1969a]; dotted line, *Huffman et al.* [1963b]; dashed line, *Cook and Metzger* [1964a].

analysis by *Dressler* [1969] has reordered these bands, however, into two excited valence states, b' $^1\Sigma_u^+$ and b $^1\Pi_u$, whose levels show strong interaction with the levels of Rydberg states, C' $^1\Sigma_u^+$ and C $^1\Pi_u$, of the configuration $(N_2^+S)3p\sigma_u$, $3p\pi_u$. All of the spectra obtained with high-resolution spectrographs show clearly resolved rotational structure. Bandwidth dependence of measured cross sections is to be expected under these circumstances and is seen in a comparison of experimental results. Such a comparison, taken from a recent paper by *Hudson and Carter* [1969a], is shown in Figure 24. It should be stressed that the data of Hudson and Carter, obtained at a bandwidth of 0.04 A, are for $\bar{\sigma}(\lambda', \Delta\lambda, N)$, not $\sigma(\lambda')$.

The wavelength interval from the ionization edge, at 795.8 A, to 1000 A has been investigated by *Huffman et al.* [1963b] and by *Cook and Metzger* [1964a], who used a continuum light source, and by *Watanabe and Marmo* [1956], *Itamoto and McAllister* [1961], and *Samson and Cairns* [1964], who used a line emission source. In view of the strong bandwidth dependence of the measured absorption cross sections between 800 A and 1000 A, it has not been considered fruitful to attempt to compare the different sets of data. It is recommended that, where possible, the data of Samson and Cairns should be used; otherwise the data of *Cook and Metzger* [1964a] and of *Huffman et al.* [1963b] have equal
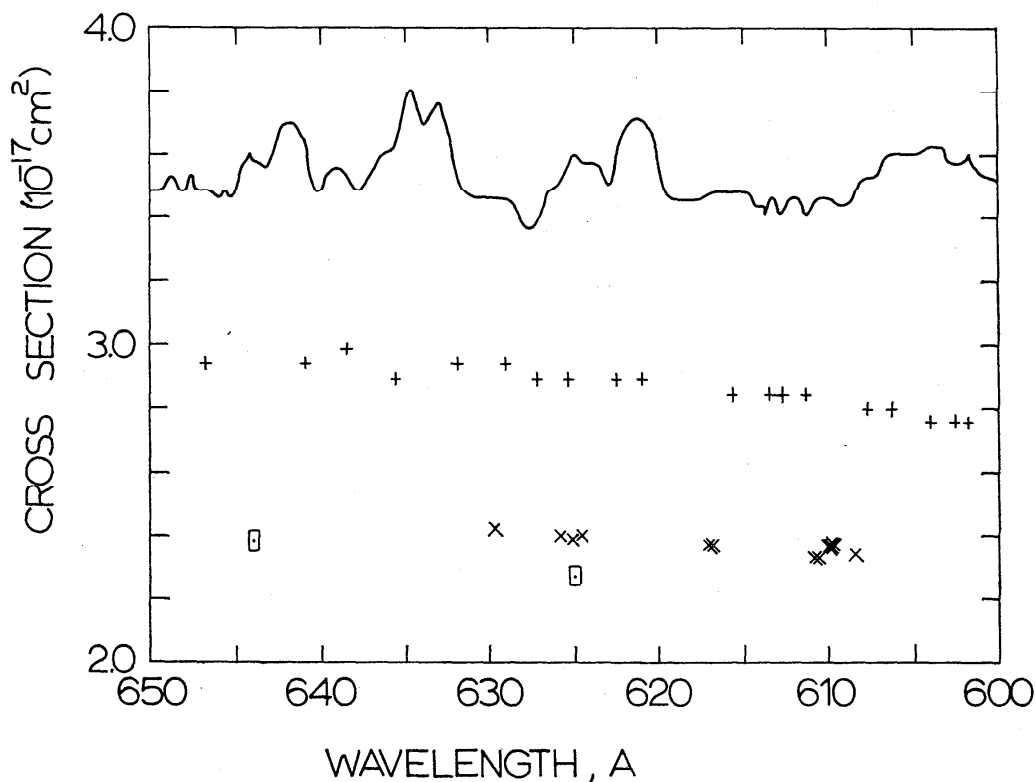

Fig. 25. Comparison of measured total absorption cross section data for N_2 between 600 and 650 A; $+$, *Cook and Metzger* [1964a]; $\times$, *Samson and Cairns* [1964]; solid line, *Huffman et al.* [1963b]; boxed dot, *Wainfan et al.* [1955].

weight. The latter group has available (R. Huffman, personal communication, 1969) more detailed cross section curves than those published in their paper (R. Huffman, personal communication, 1969).

The strong bandwidth dependence found for the measured cross sections is almost certainly the cause of the discrepancy between the intensity distribution among the bands obtained from these optical results and the electron energy-loss spectra of Lassettre et al. [1965, 1966] and Geiger and Stickel [1965]. The recent high-resolution (0.04 A) absorption data of Lawrence et al. [1968] between 958 and 972 A is, on the other hand, in excellent agreement with the energy-loss spectra. The reviewer concurs with these authors that until further high-resolution absorption studies are made, the band oscillator strengths obtained from the energy-loss spectrum should be preferred over the optical results.

No investigations have been made of the dissociation of N_2 between 800 A and 1000 A, although both Hudson and Carter [1969a, b] and Lawrence et al. [1968] have inferred predissociation in bands at 972 and 828 A from anomalously broad line widths. The presence of a dissociation continuum under the bands is not clearly evidenced. The high-resolution spectra of Hudson and Carter [1969a] would set an upper limit to such a continuum at 830 A of 5×10^{-19} cm^2. Previous estimates have been 2–4 $\times$ 10^{-19} cm^2, between 850 and 1000 A [Watanabe and Marmo, 1956; Cook and Metzger, 1964a].

The first ionization limit of N_2 is at 795.8 A. From this wavelength to 600 A the absorption spectrum appears to consist of bands on an underlying continuum. Most of the bands in this region are diffuse [Worley, 1943, 1953; Ogawa and Tanaka, 1962]. Wainfan et al. [1955], Huffman et al. [1963b], Cook and Metzger [1964a], Cook and Ogawa [1965], and Samson and Cairns [1964], who have made absorption measurements in this spectral region, do not report finding any 'apparent pressure effects.' As was pointed out in section IV, this does not imply that the cross sections are not bandwidth dependent. Between 660 and 720 A there are a series of Rydberg lines with their accompanying 'apparent emission series' (i.e., preionization features with $q = 0$ [Fano, 1961]), and in Table 5, the results obtained for these maxima and minima by Huffman et al. [1963b] and by Cook and Metzger [1964a] are compared. The agreement is not good.

Figure 25 compares the total absorption-cross-section data obtained by these

TABLE 5. Comparison of Cross Sections for N_2 Between 660 A and 720 A

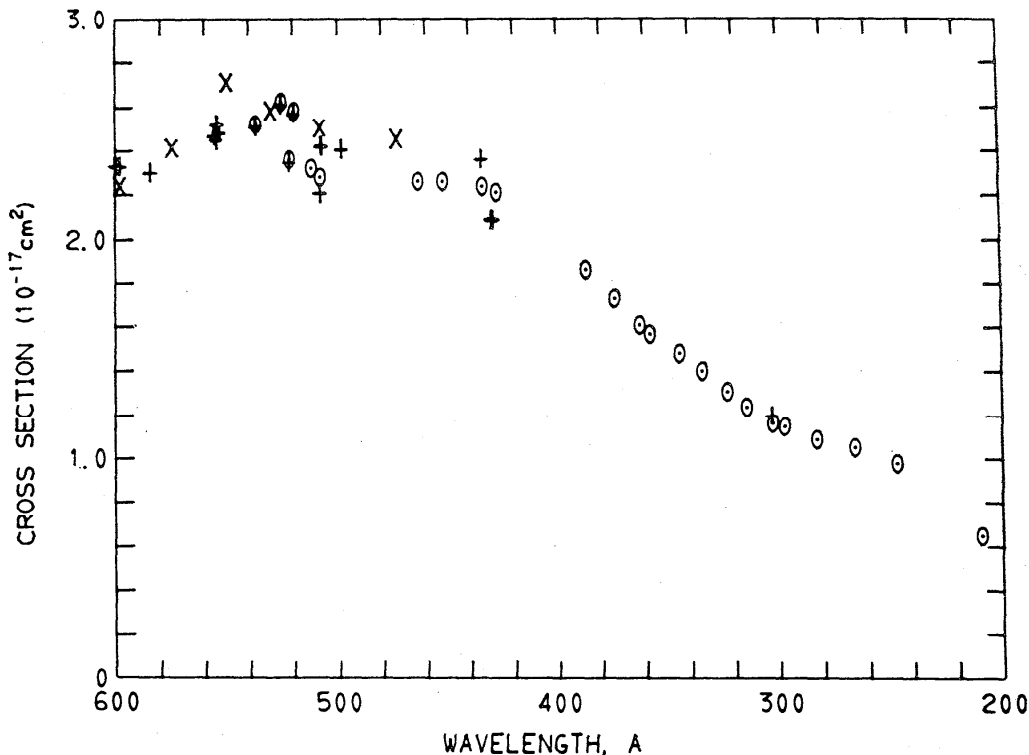| Wavelength, A (nominal)	Cross Section, Mb(10^{-18} cm^2)	
	Huffman et al. [1963b]	Cook and Metzger [1964a]
723.4	82.2	49.1
715.3	16.7	23.0
694.9	61.7	35.3
690.9	19.8	20.8
681.9	48.3	29.0
679.7	19.6	21.6
675.1	42.0	25.7
674.1	24.7	21.6

Fig. 26. Comparison of measured total absorption cross section data for N_2 between 200 and 600 A; +, *Samson and Cairns* [1964]; ×, *Wainfan et al.* [1965]; circled dot, *Samson and Cairns* [1965].

two groups with those of *Wainfan et al.* [1955] and *Samson and Cairns* [1964], between 600 A and 660 A. There appears to be a distinct difference between the results obtained with the use of line emission sources and those obtained with the use of continuum sources. The helium continuum source is generally weaker in this region, and great care has to be taken to account for the effects of the fluorescence from N_2^+ that has a sharp onset at 660 A. *Huffman* [1969] has reported that the step in the cross section that was reported by *Huffman et al.* [1963b] at 660 A is probably not real, a fact that the reviewer assumes to be the result of an overcorrection for this fluorescence. The over-all view of the cross section for N_2 between 600 A and 800 A is, then, one of confusion.

The cross-section curve below 600 A appears to be continuous, except for the region between 480 and 555 A, where *Codling* [1966] observed discrete structure photographically. This previously unresolved structure was identified by Codling as due to a state of neutral N_2, and is observed to be preionized. Figure 26 compares absorption data obtained by *Samson and Cairns* [1964, 1965] and *Wainfan et al.* [1955] between 200 A and 600 A. The results of both groups agree well within their quoted errors. *Henke et al.* [1967] have measured cross sections for molecular nitrogen between 10 A and 114 A.

The photoionization yield, η, has been measured between 300 and 800 A by

Wainfan et al. [1955], *Samson and Cairns* [1964], *Cook and Metzger* [1964a], and *Cook and Ogawa* [1965]. Wainfan et al., using a calibrated thermopile, measured the absolute photon flux entering their ionization chamber, whereas Samson and Cairns used the total-absorption technique as described in section III. Both Cook and Metzger and Cook and Ogawa used a platinum photodiode as a secondary standard, the photoyield of the platinum being determined in an inert-gas–filled ion chamber. Wainfan et al. estimate an error in the determination of the yield of about ±15%; Samson and Cairns estimate ±5%; Cook and Metzger estimate ±5% between 650 A and 800 A, and ±10% for wavelengths less than 650 A; and Cook and Ogawa give no estimate of the error.

Figure 27 compares the results obtained by these groups between 600 A and 700 A. The data of Samson and Cairns indicate a yield of 1 between 500 A and 640 A, falling to about 0.95 at 690 A. The data of Wainfan et al. are in essential agreement with this, except between 500 A and 580 A, where the Rydberg series of Codling and Madden are to be found. The data of Cook and Metzger are about 20% lower. Between 700 A and 800 A the yield fluctuates, especially at the band maxima, between 40% and 100%. These fluctuations have been shown to be dependent on the particular series to which the upper state belongs [*Cook and Ogawa*, 1965]. It should be noted that the efficiency measured by Cook and Ogawa
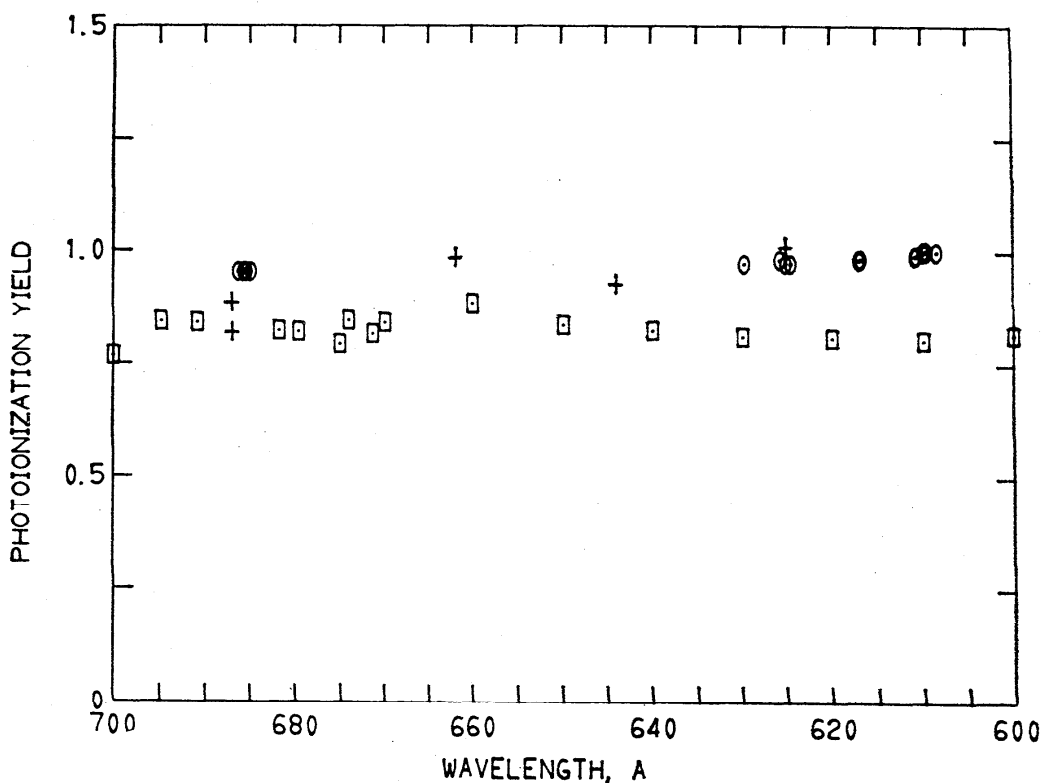

Fig. 27. Comparison of measured photoionization yield data for N_2 between 600 and 700 A; +, *Wainfan et al.* [1955]; circled dot, *Samson and Cairns* [1964]; boxed dot, *Cook and Metzger* [1964a].

is $\bar{\eta}$, which will be bandwidth-dependent; thus some of the fluctuation could be accounted for by different line widths of the bands in the series.

The error given by Cook and Metzger for their yield measurements does not appear to include the systematic error inherent in the calibration of the photoelectric yield of their platinum photodiode. It is likely, therefore, that their measured yield for N_2 below 650 A could be as high as 1.0. At this time it is felt that for the continuum from 10 A to 650 A an efficiency of 1 can be assumed, and the photoionization cross section will be numerically equal to the total photoabsorption cross section. Between 650 A and 800 A the data of Cook and Metzger and those of Cook and Ogawa must be used with some reservations.

Relative photoionization cross sections, using a mass spectrometer, have been obtained by *Comes and Lessmann* [1964]. Unfortunately, the instrumental resolution used was 2 A, and direct comparison cannot be made with other measurements.

C. Water Vapor, H_2O

The absorption spectrum of water vapor in the ultraviolet consists of continuous absorption between 1450 and 1860 A, diffuse bands between 1250 and 690 A, and continuous absorption below 690 A. The ionization edge is at 984 A, and the bands that overlie the ionization continuum lead to two limits at 860 A and 690 A.
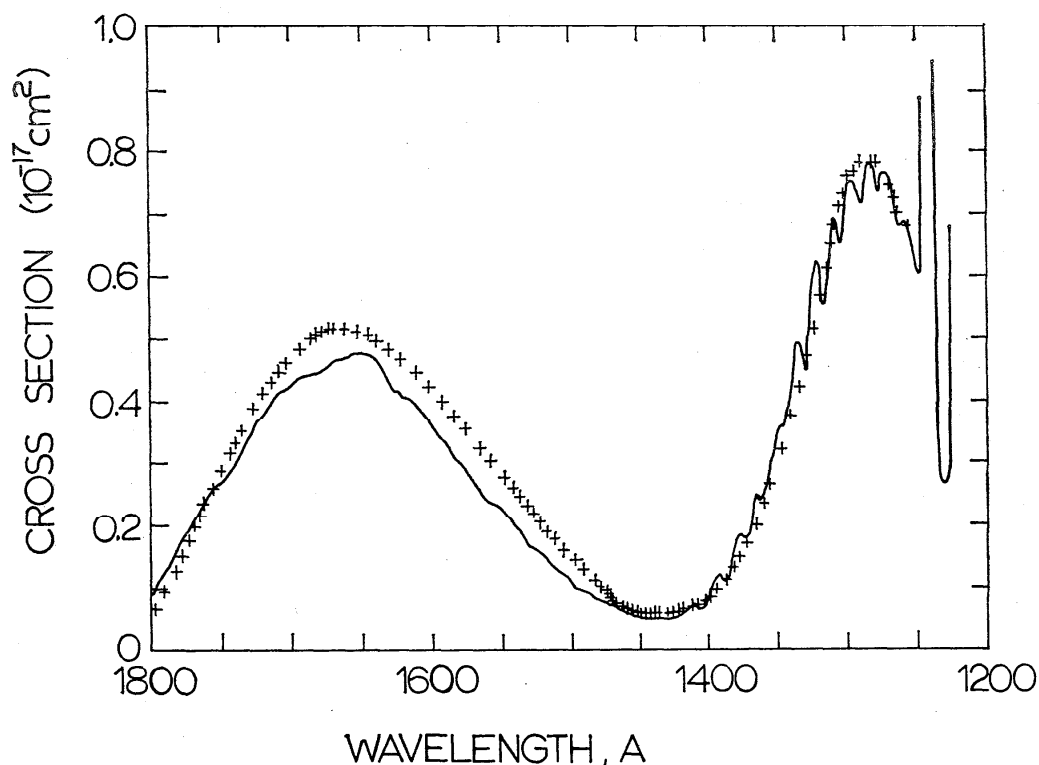

Fig. 28. Comparison of measured total absorption cross section data for H_2O between 1200 and 1800 A; solid line, *Watanabe and Zelikoff* [1953]; +, *Laufer and McNesby* [1955].

The continuous absorption between 1450 A and 1860 A has been measured by *Wilkinson and Johnston* [1950], *Watanabe and Zelikoff* [1953], *Johannin-Gilles et al.* [1956], *Watanabe and Jursa* [1964], and *Lauffer and McNesby* [1965]. Figure 28 shows the absorption cross section for water vapor between 1200 A and 1800 A obtained by *Watanabe and Zelikoff* [1953] and *Lauffer and McNesby* [1965]. The two sets of results agree within ±10%. Neither group explicitly states what the error in its measurements might be, but it seems reasonable to assign an error of at least ±10%, such that the agreement between these two curves can be considered good. Both Wilkinson and Johnston and Johannin-Gilles et al. observed band structure in this wavelength interval. However, neither Watanabe and Zelikoff nor Lauffer and McNesby find any such band structure within their experimental error of less than ±5%.

Between 1250 A and 1450 A *Watanabe and Zelikoff* [1953] observed broad diffuse bands in agreement with the photographic evidence obtained by *Price* [1936]. Lauffer and McNesby do not report seeing these bands, although the over-all shape of the curve they obtained is in quantitative agreement with the mean curve obtained by Watanabe and Zelikoff. It would seem that the data of Watanabe and Zelikoff are to be preferred in this spectral region. Below 1250 A, *Price* [1935] could distinguish rotational structure on his photographic plates, although the structure was too complicated to analyze. Apparent pressure effects
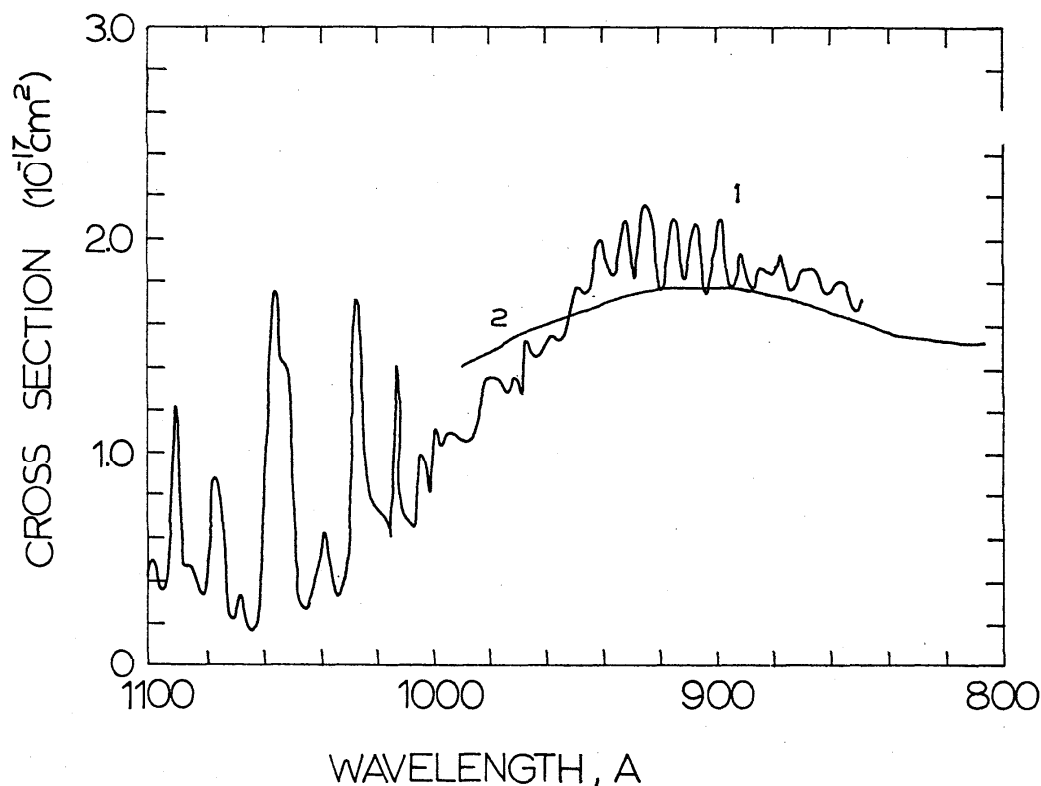

Fig. 29. Comparison of measured total absorption cross section data for H_2O between 800 and 1100 A; curve 1, *Watanabe and Jursa* [1964]; curve 2, *Metzger and Cook* [1964a].

are to be expected and are reported by Watanabe and Zelikoff between 1060 A and 1250 A.

Total absorption cross sections for wavelengths below 1060 A have been obtained by *Watanabe and Jursa* [1964] and *Metzger and Cook* [1964a]. Figure 29 compares the results obtained by these two groups. In the region of overlap between the data of Metzger and Cook and those of Watanabe and Jursa there is surprising disagreement. Metzger and Cook show a smooth curve between 860 A and 1000 A, in direct conflict with the band structure observed by Watanabe and Jursa. Because this band structure has been observed by *Henning* [1932] and *Hopfield* [1950], using photographic techniques, it is felt that the data of Watanabe and Jursa are more reliable in the wavelength region from 860 A to 1160 A. The reader is cautioned that the results given by Watanabe and Jursa may be subject to bandwidth dependence.

The photoionization yield for wavelengths shorter than 984 A has been investigated by *Watanabe and Jursa* [1964], *Metzger and Cook* [1964a], and *Wainfan et al.* [1955]. Watanabe and Jursa obtained photoionization yields of 30% at 984 A, 40% at 950 A, and nearly 50% in the region below 900 A. Metzger and Cook, on the other hand, obtained a photoionization yield of 15% at 984 A,
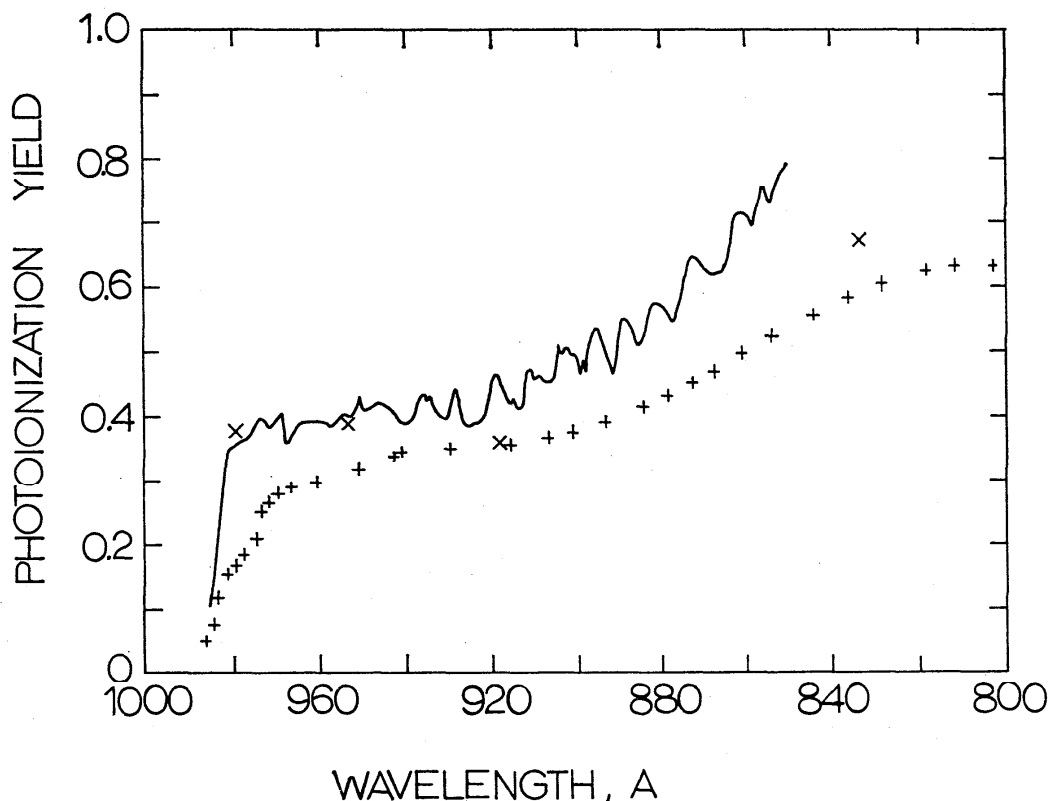

Fig. 30. Comparison of measured photoionization yield data for H_2O between 800 and 1000 A; solid line, *Watanabe and Jursa* [1964]; +, *Metzger and Cook* [1964a]; ×, *Wainfan et al.* [1955].

30% at 950 A, and 38% at 900 A. The three sets of data are compared in Figures 30 and 31.

The photoionization efficiency using mass spectrometers has been obtained by *Dibeler et al.* [1966] and by *Brehm* [1966]. If these two sets of relative ionization cross sections are normalized to the value obtained at 970 A by Watanabe, then the three curves of Watanabe et al., Dibeler et al., and Brehm are in very good agreement about the over-all shape of the curve in the region of overlap.

All three groups report band structure in this wavelength interval, indicating that the band structure observed by Watanabe and Jursa is preionized. Band structure has also been reported by *Dibeler et al.* [1966] between 800 A and 690 A, but again no bands were seen in this wavelength interval by Metzger and Cook. The other two measurements of photoionization cross sections did not extend to this wavelength region.

The fact that Metzger and Cook do not report bands between 984 and 860 A could be ascribed to the weakness of their helium continuum light source in this wavelength interval. But, as this emission continuum peaks at about 800 A, it is difficult to understand why Metzger and Cook did not observe the band structure reported by Dibeler et al. between 860 A and 690 A, especially as both groups used the same light source.

At 687 A Dibeler et al. observed the onset of dissociative ionization, giving rise to an OH^+ ion and a hydrogen atom. At the same time, the ionization efficiency for the molecular ion shows a marked decrease. Dibeler et al. suggest
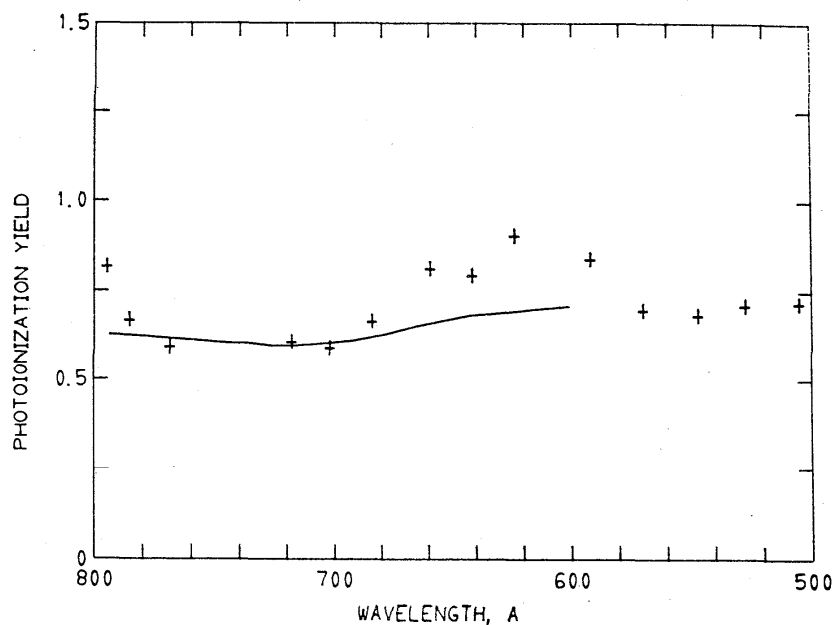

Fig. 31. Comparison of measured photoionization yield data for H_2O between 500 and 800 A; solid line, *Metzger and Cook* [1964a]; +, *Wainfan et al.* [1955].

that the OH⁺ ion could arise from the dissociation of the H_2O^+ ion, which energetically can then be left in the $^2B_2$ state at this wavelength.

D. Molecular Hydrogen, H_2

The absorption spectrum of molecular hydrogen is characterized by sharp absorption bands at wavelengths longer than 840 A; a dissociation continuum overlaid by absorption bands between 800 and 840 A; and an ionization continuum extending from 800 A down to 200 A (the present lower limit of the absorption measurements) that is also overlaid by bands between 740 A and 800 A. The absorption bands above 840 A exhibit sharp rotational lines, and no quantitative absorption cross sections are available. Haddad et al. [1968] have determined the oscillator strengths of some of these lines, but their measurements are limited to the wavelength interval 1060 A to 1130 A. The region between 800 A and 1000 A has been studied photographically quite extensively at high resolution, and the reader is referred to papers by Namioka [1964a, b] for a discussion of the band positions and references to previous papers. The bands observed between 740 A and 840 A are known to predissociate [Comes and Wellern, 1968] and preionize [Cook and Metzger, 1964b; Chupka and Berkowitz, 1968] into the underlying continua. However, theoretical calculations indicate that the rotational lines will be quite narrow, with halfwidths of the order of 1 cm⁻¹ [Nielsen and Berry, 1968].

The total absorption cross section of molecular hydrogen has been measured in the wavelength interval 200 A to 840 A by Cook and Metzger [1964b]; Comes and Wellern [1968]; Wainfan et al. [1955]; Bunch et al. [1958]; and Samson and Cairns [1965]. Of these measurements, those of Cook and Metzger and of Comes and Wellern used a continuum light source. Figure 32 displays the results of these groups between 200 and 700 A. The results from the paper of Wainfan et al. are not shown, since they fall outside the range of this figure.

The narrow width of the rotational lines between 740 A and 840 A means that the absorption cross sections of Cook and Metzger and those of Comes and Wellern will be bandwidth-dependent in this spectral range. The underlying dissociation continuum is of considerable interest, since the dissociation process leaves one of the hydrogen atoms in the $2s$ or $2p$ state, leading to the emission of Lyman α (1216 A) [Beyer and Welge, 1967; Comes and Wellern, 1968]. Comes and Wellern, who have also investigated the production of Lyman α by absorption in the band structure between 800 A and 840 A, indicate an efficiency for production of about 1. In their paper, Cook and Metzger have connected the minima between these bands and ascribed the shape to the underlying continuum. However, recent measurements by R. D. Hudson and V. L. Carter (personal communication, 1970) between 800 and 840 A at a bandwidth of 0.04 A have shown that the underlying continuum as drawn by Cook and Metzger is not correct, and that the shape obtained at high resolution agrees well with recent theoretical calculations of Dalgarno and Allison [1969]. These latter results also cast doubt on the validity of the shape of the ionization continuum depicted by Cook and Metzger.

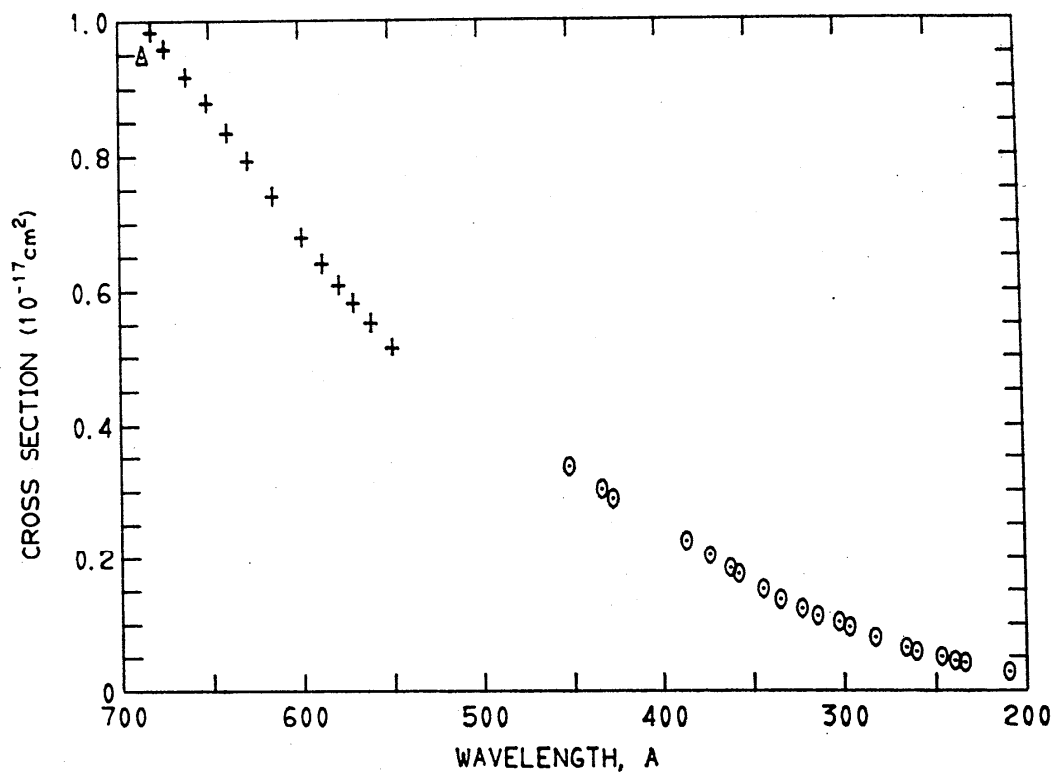The photoionization yield for molecular hydrogen has been measured by

Fig. 32. Comparison of measured total absorption cross section data for H_2 between 200 and 700 A; +, *Metzger and Cook* [1964b]; circled dot, *Samson and Cairns* [1965]; triangle dot, *Bunch et al.* [1958].
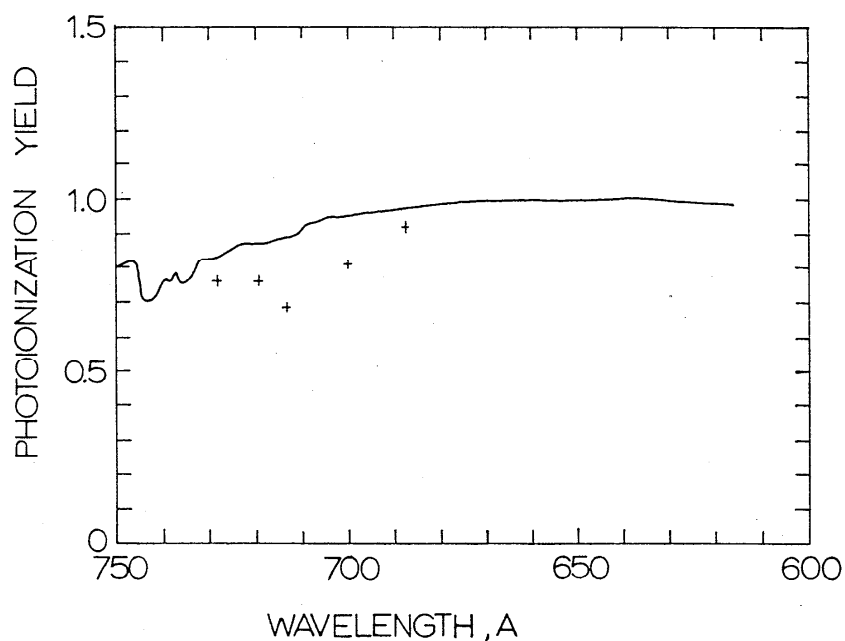

Fig. 33. Comparison of measured photoionization yield data for H_2 between 600 and 750 A; solid line, *Metzger and Cook* [1964b]; +, *Wainfan et al.* [1955].

Cook et al. and Wainfan et al., and the results obtained by these two groups between 600 A and 750 A are displayed in Figure 33. The yield appears to be 1.0 for wavelengths shorter than 700 A, and it fluctuates for wavelengths longer than 700 A. In the vicinity of the bands the yield will be strongly bandwidth-dependent, and *Chupka and Berkowitz* [1968] have shown that the individual rotational lines have varying probabilities for preionization. It is recommended that for wavelengths less than 700 A the ionization cross section be made numerically equal to the total absorption cross section.

Photoionization efficiency measurements have been made with mass spectrometers by *Comes* [1967] and by *Dibeler, Reese, and Krauss* [1965]. The former were obtained at an instrumental resolution of 0.4 A, the latter at 2 A. These sets of data are in qualitative agreement with the results obtained by Cook and Metzger.

E. Carbon Monoxide, CO

The absorption spectrum of carbon monoxide between 200 A and 3000 A consists of a smooth continuum from 200 A to 630 A and strong bands from 630 A to 3000 A, some of which overlie possible continua. The ionization limit is at 885 A.

The wavelength interval between 1060 A and 2100 A has been investigated by two groups: *Watanabe et al.* [1953c], who investigated the region between 1060 and 1650 A, and *Thompson et al.* [1963], who investigated the region between 1850 and 2100 A. Both groups employed photoelectric techniques at a resolution of the order of 1 A. The high-resolution photographic studies of *Tanaka et al.* [1957] and of *Read* [1934] have found strong, sharp bands in this spectral region. It is not surprising, therefore, that both Watanabe et al. and Thompson et al. report that their measured absorption cross sections were strongly pressure-dependent, i.e., strongly bandwidth-dependent. Watanabe et al. indicate a continuum between 1250 and 1650 A, but the photographic data of *Tanaka et al.* [1957] show no such dissociation continuum, even at the highest pressures used by the latter authors. Thus, it is likely that this apparent continuum can be ascribed to insufficient resolution. The bands observed in this spectral region have been assigned to several systems, and these are discussed in detail by *Tanaka et al.* [1957]. The recommendation is that the absorption data obtained between 1170 and 3000 A be treated as qualitative. There is an obvious need for higher-resolution studies to be made in this particular spectral region.

The spectral region between 885 and 1000 A has been investigated with a continuum light source by *Huffman et al.* [1964b] and by *Cook et al.* [1965], and with a line emission source by *Cairns and Samson* [1965]. The spectrum of carbon monoxide in this spectral region consists of many strong bands, some of which have been arranged by *Takamine et al.* [1943] into two Rydberg series, but many of which remain to be classified. All groups report 'apparent pressure effects' between 885 and 1000 A. Huffman et al. indicate in their tables where this effect occurs (mainly at the peaks); Cook et al. give values in their tables that were obtained by extrapolating the measured cross sections to zero

pressure; whereas Samson and Cairns give their measured cross section at three pressure values. Figure 34 compares the cross sections obtained by these three groups between 900 and 980 A; the data of Huffman et al. and Cook et al. have been displaced for the sake of clarity. One thing immediately apparent is the random discrepancy between the two sets of data obtained with the use of a continuum light source. It would also appear that the data of Huffman et al. were obtained with the smaller bandwidth. The three points shown at each
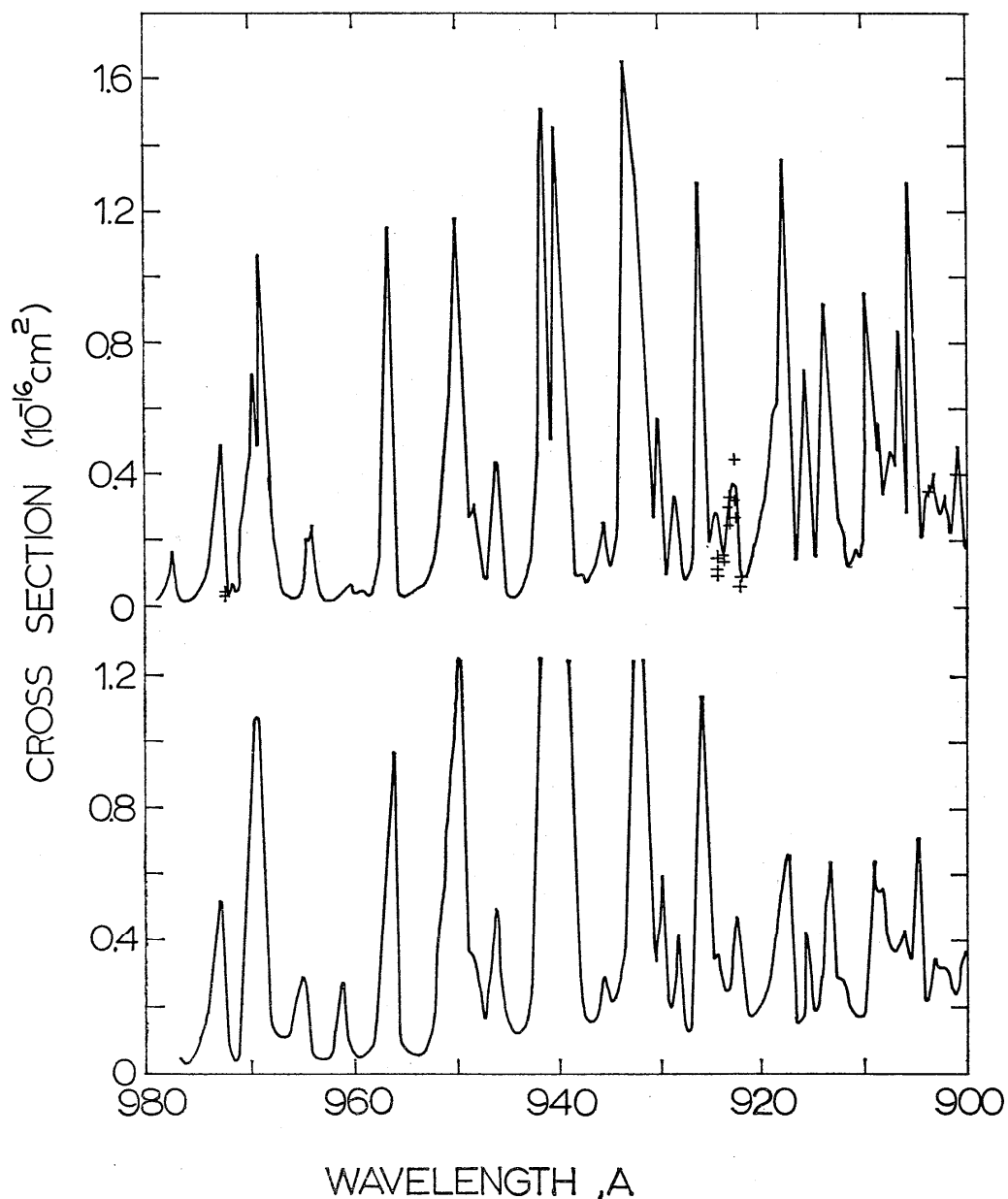
Fig. 34. Comparison of measured total absorption cross section data for CO between 900 and 980 A; upper curve, *Huffman et al.* [1964b]; bottom curve, *Cook et al.* [1965]; +, *Cairns and Samson* [1965].

wavelength for Cairns and Samson represent the 'pressure effect.' As the published cross sections between 885 and 1000 A are obviously strongly bandwidth-dependent, they should be treated as qualitative. Both Huffman et al. and Cook et al. report the existence of an absorption continuum that begins at 960 A and becomes stronger toward shorter wavelengths. However, since this continuum seems to get stronger as the band structure becomes more crowded, it is likely that this continuum is due purely to band overlap; and there seems no reason to ascribe a continuum to this particular spectral region.

Between 885 A and 750 A (the latter wavelength corresponding to the second ionization limit of the molecule) the absorption bands appear to be weaker when compared with those at wavelengths above 885 A. Both *Cook et al.* [1965] and *Huffman et al.* [1964b] report that the peak absorption cross sections of the bands in this region exhibit no pressure effects. The illustration that was used in section V from the data of Huffman et al. indicates the number of possible band shapes and corrected absorption cross sections that are possible under these conditions. Both groups see the Rydberg bands leading up to the $a^2\Pi$ state of CO^+ (750 A) and report that the higher vibrational states in the Rydberg series appear to be stronger. Cook et al. believe that this is due to the large difference in internuclear separation between the $a^2\Pi$ state of CO^+ and the

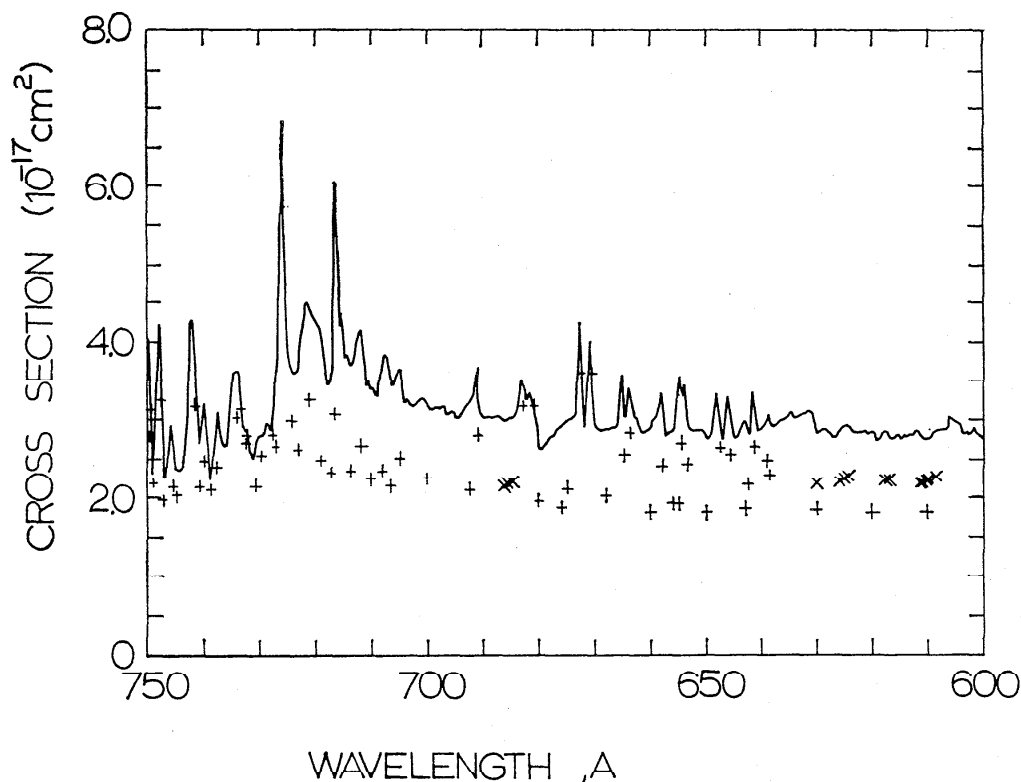Fig. 35. Comparison of measured total absorption cross section data for CO between 600 and 750 A; solid line, *Huffman et al.* [1964b]; +, *Cook et al.* [1965]; ×, *Cairns and Samson* [1965].

ground state of CO. However, as indicated before, this could also be explained by the broadening of the lines in these bands as the series approaches the second ionization limit. It seems, therefore, that until cross sections are obtained at higher resolution in this spectral region, one can make no simple comparison of the relative strengths of the Rydberg bands. It is felt that, at present, the data of either Cook et al. or Huffman et al. should be used between 750 A and 885 A except where values obtained by Cairns and Samson are available; however, the reader is cautioned that the published cross sections are subject to bandwidth dependence.

Figure 35 compares the absorption cross sections obtained by the three groups cited above between 600 A and 750 A. In this wavelength interval, Cook et al. and Huffman et al. report finding weak absorption bands that are identified with the Rydberg bands first seen by *Tanaka* [1942]. It will be noted that there is a decided discrepancy between the three sets of results. Both Cook et al. and Huffman et al. report fluorescent emission from CO when the wavelength of the incident light is shorter than 760 A. Huffman et al., who used a sodium-salicylate-coated photomultiplier and a short cell, applied a correction to their measured transmitted intensity at these wavelengths, whereas Cook et al., who used a platinum photodetector, report that such a correction was not needed. The published cross sections of Huffman et al. show a distinct jump at 730 A, analogous to a similar jump seen in molecular nitrogen by this group at 660 A. As was
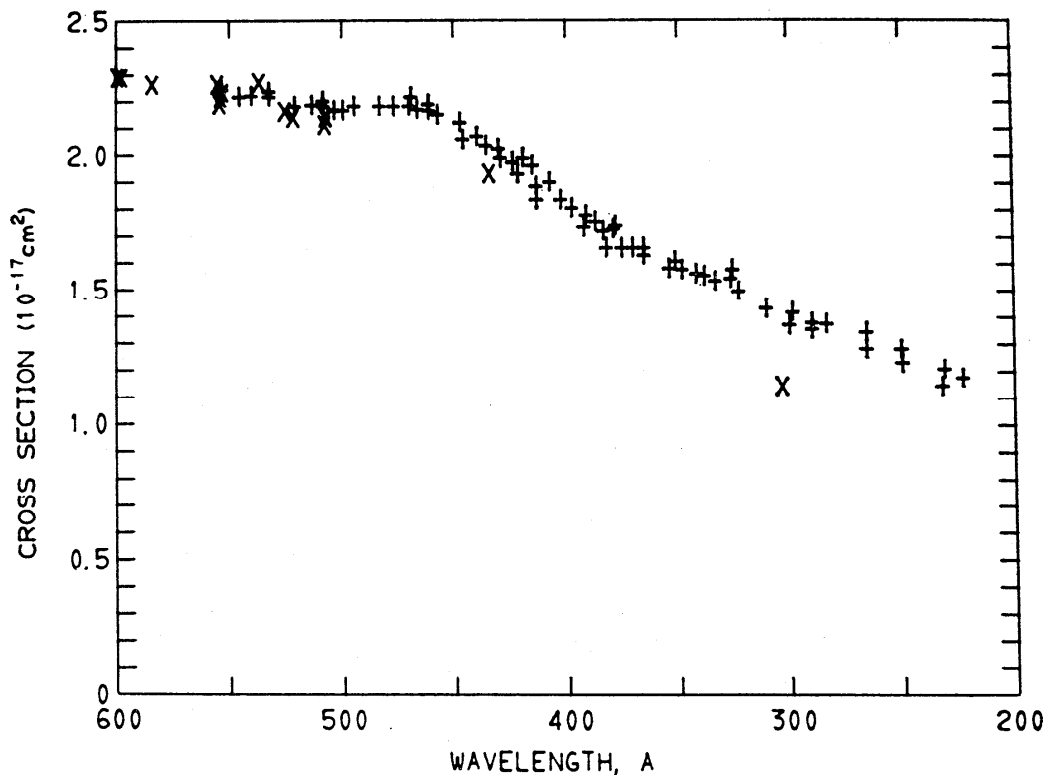

Fig. 36. Comparison of measured total absorption cross section data for CO between 200 and 600 A; ×, *Cairns and Samson* [1965]; +, *Cairns and Samson* [1966].

discussed in section VI-B, this jump in N_2 could be artificial, resulting from an over-correction for fluorescence, and the jump in CO at 730 A may be subject to the same error. The results of Cook et al. and of Cairns and Samson agree just within their quoted errors.

The absorption cross section for carbon monoxide between 200 A and 600 A has been investigated by *Cairns and Samson* [1965, 1966], who used the double-ion-chamber technique; the results are presented in Figure 36. The authors estimate their error to be ±5% between 550 A and 340 A and ±10% at shorter wavelengths.

Photoionization yields between 100 A and 885 A have been obtained by *Cairns and Samson* [1965] and by *Cook et al.* [1965]. A comparison of the results obtained by these two groups between 600 A and 885 A is given in Figure 37. The yield would appear to be 100% between 300 A and 600 A [*Cairns and Samson*, 1965]. Cook and Metzger indicate fluctuating yields in the vicinity of the Rydberg series, which will be expected to be subject to bandwidth effects.

In summary, the absorption curve shown in Figure 36 should be applicable to both the absorption and the ionization cross sections, whereas above 600 A the photoionization curve, as published by Cook et al., should be used, with the proviso that both the absorption cross section and the ionization cross section
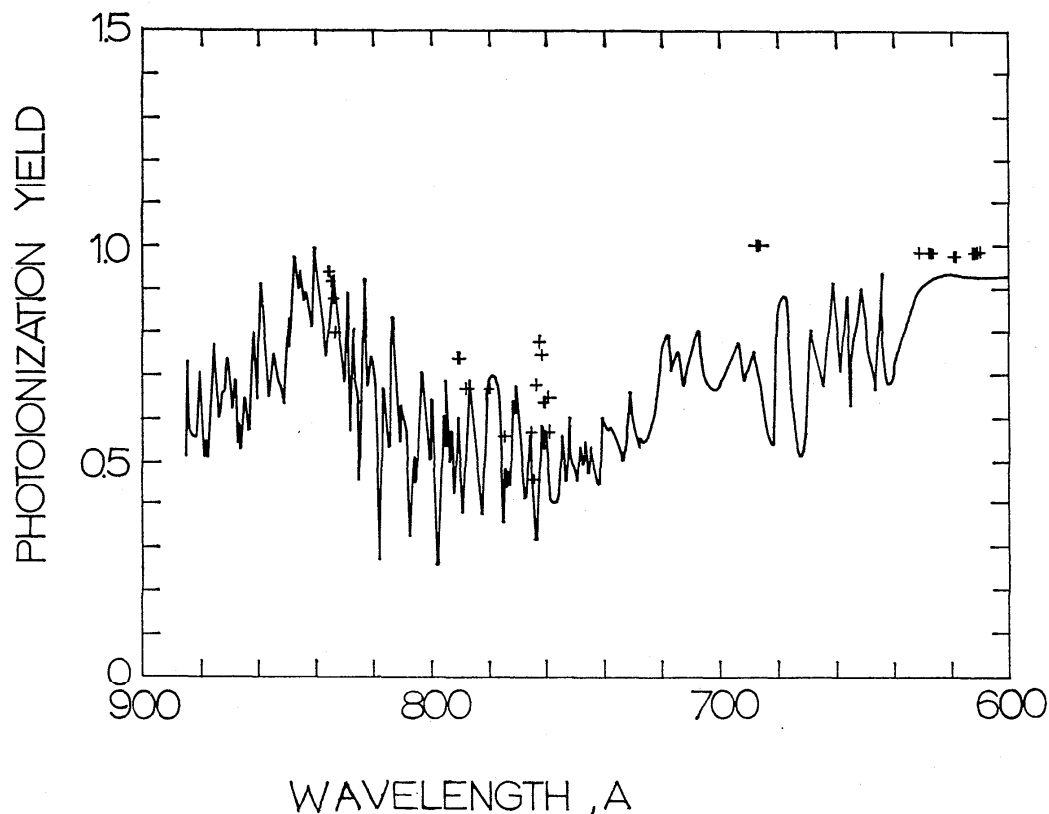

Fig. 37. Comparison of measured photoionization yield data for CO between 600 and 900 A; solid line, *Cook et al.* [1965]; +, *Cairns and Samson* [1965].

will be bandwidth-dependent. There have been no measurements by mass spectrometers of the photoionization efficiency for carbon monoxide.

F. Nitric Oxide, NO

Absorption cross sections for nitric oxide have been obtained between 580 A and 2350 A. In this wavelength interval the spectrum consists of band structure superposed on ionization and dissociation continua. The first ionization limit of nitric oxide is at 1350 A.

The total absorption cross section of nitric oxide between 1340 A and 2350 A has been investigated by *Marmo* [1953] and by *Thompson et al.* [1963]. The bands between 1350 A and 2350 A, consisting of the β, Δ, ϵ, and γ band systems, have been studied extensively by high-resolution photographic techniques (see, for example, *Lagerquist and Meischer* [1958] and *Dressler and Meischer* [1965]). These photographic spectra show sharp and well-resolved rotational structure, and both Marmo and Thompson et al. report strong 'apparent pressure effects.' Marmo considers his published cross sections to be only semiquantitative, and it is obvious that the data of both groups will be strongly bandwidth-dependent. Marmo identifies two possible continua in this wavelength interval, one between 1400 A and 1600 A, the other extending from 1390 to shorter wavelengths; but he indicates that the former continuum is probably due to band overlap. It would seem that the same argument could be applied to the latter continuum, at least down to 1350 A.

The wavelength region between 580 A and 1340 A has been studied by *Walker and Weissler* [1955c], *Watanabe* [1954], *Watanabe et al.* [1967], and *Metzger et al.* [1967]. All these papers include measurements of both the photoionization efficiency and the photoabsorption cross section. The data of Walker and Weissler are labeled 'preliminary.' The data of Watanabe et al. contain a correction to the original yield data of *Watanabe* [1954] and were obtained at much better resolution (0.2 A compared with 1.0 A); thus in this review the former paper only has been considered.

In general, the agreement between the results of Watanabe et al. and Metzger et al. is well within their quoted errors except at the peaks of some of the bands, where the smaller bandwidth of Watanabe et al. yields larger cross sections. This observation indicates that the cross sections obtained by both groups will be subject to some bandwidth dependence. The data of Watanabe et al. are given in tabular form only, and the reader is referred to the paper of Metzger et al. for figures displaying the cross-section curves.

The bands between 680 and 1340 A are observed to have varying degrees of preionization, and the yield measurements in this wavelength interval show considerable structure. In general, the yield measurements of Metzger et al. are about 25% lower than those of Watanabe et al. This is illustrated in Figure 38, which shows the yield for the wavelength interval 600 A to 700 A. Although the results probably agree within the mutual experimental errors of the two groups, the large discrepancy is disturbing. The values of the yield obtained by Watanabe et al. between 1070 A and 1350 A are about 8% lower than the yields obtained by *Watanabe* [1954]. The choice between these three sets of data is
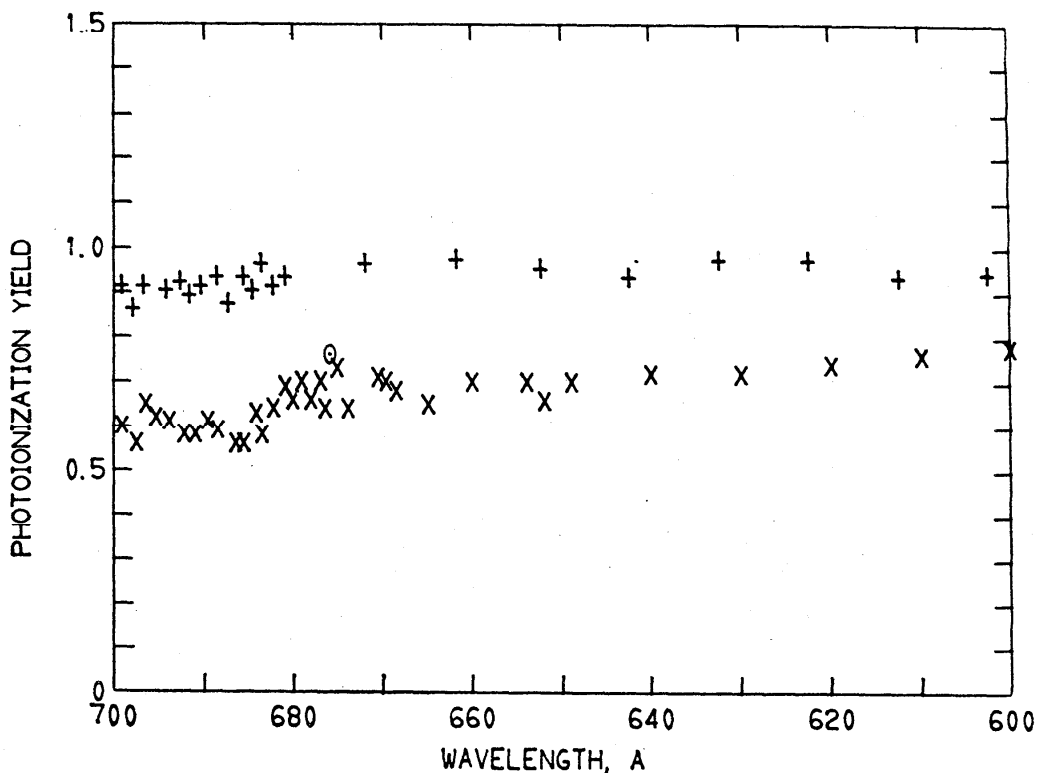
Fig. 38. Comparison of measured photoionization yield data for NO between 600 and 700 A; +, *Watanabe et al.* [1967]; ×, *Metzger et al.* [1967].

not easy; but because of the consistency of the Watanabe data and the fact that the total-absorption technique should be more accurate, these yield data are probably to be preferred.

Both Watanabe et al. and Metzger et al. indicate the presence of a dissociation continuum between 750 A and 1050 A based largely on the yield measurements. These designations should be treated with caution in view of uncertainty in the yield measurements and band overlap. *Beyer and Welge* [1964] and Metzger et al. observed fluorescence between 1100 A and 1600 A from nitric oxide irradiated with wavelengths less than 750 A and 677 A, respectively. Beyer and Welge postulate that this radiation arises as a result of dissociation (i.e., from excited atomic products), thus supporting the contention of underlying dissociation continua. However, the data of Metzger et al. can be explained by emission from the Miescher-Baer bands of NO^+ [*Baer and Meischer*, 1953; *Tanaka*, 1953] in the allowed transition $A^1\Pi \rightarrow X^1\Sigma^+$ (677 A correlates well with the $A^1\Pi$ state of NO^+). The fluorescence study of Metzger et al. was performed with the use of a continuum light source, whereas Beyer and Welge used a line emission source, with the result that Metzger et al. were able to observe the sharp onsets of fluorescence. Thus their explanation of the fluorescence is felt to carry greater weight.

The photoionization efficiency has been measured with mass spectrometric

techniques by *Weissler et al.* [1959], and by *Reese and Rosenstock* [1966]. The former results were obtained with a line emission source, the latter with continuum light sources at an instrumental resolution of 2 A. Their results are in qualitative agreement with the results of Watanabe et al.

G. Carbon Dioxide, CO_2

The absorption spectrum of carbon dioxide between 1060 A and 1800 A consists of three apparent absorption continua, overlaid by bands, which appear from photographic experiments to be diffuse in nature [*Price and Simpson*, 1939]. Between 1100 A and 900 A the spectrum consists of another apparent continuum, which again is overlaid by both sharp and diffuse bands, the intensity of both types of bands increasing toward shorter wavelengths. The ionization edge of carbon dioxide is at 986 A, and from this wavelength to 840 A the absorption is characterized by a smooth continuum. Bands begin to appear again at 840 A and continue down to 680 A, at which point a smooth continuum extends to 100 A [*Tanaka et al.*, 1960a; *Tanaka and Ogawa*, 1962].

The absorption cross section between 1200 A and 1800 A has been investigated by *Wilkinson and Johnston* [1950]; *Inn et al.* [1953]; *Thompson et al.* [1963]; and *Nakata et al.* [1965]. The data obtained by Nakata et al. are in good agreement with those of Inn et al., except at the peaks of the absorption bands and the minima between the bands. At these points the data of Nakata et al. are consistently higher for the peaks and consistently lower for the minima, as would be expected if the absorption cross sections are bandwidth-dependent. Although Nakata et al. note the discrepancy between their results and those of Inn et al., they draw no conclusions. Many authors quote the conclusion reached in the paper of Inn et al., namely that the spectrum between 1200 A and 1700 A consists of two continua, one centered at 1450 A and the other at 1325 A, both of which are overlaid by bands. As has already been discussed in the introduction to this review, this is not necessarily a valid assumption. Indeed, a comparison of the spectrum of carbon dioxide with that of sulphur dioxide in Figure 8 would indicate that it is just as likely that these continua are due to band overlap. Dissociation, however, has been observed, at pressures greater than 10 mm, at 1470 A and 1236 A, with a quantum efficiency of about 1 [*McNesby and Okabe*, 1964]. The data obtained by Wilkinson et al. are markedly different from those of both Nakata et al. and Inn et al. in that this former group observed a continuum that peaked at 1500 A and then fell off to zero at 1400 A. Both Inn et al. and Nakata et al. used cells less than 7 cm in length and pressures of up to 100 mm in their measurements. Wilkinson et al., on the other hand, used a cell of 38 cm in length and pressures up to 2.4 mm. One could speculate, therefore, that the difference between these three groups could be the pressure at which the measurements were obtained; that is, the broadening that has given rise to the apparent continua at both 1450 and 1325 A could be collisional broadening giving rise to induced predissociation.

The continuum centered at 1325 A is particularly in doubt, since the measured peaks still appear sharp and almost symmetric. High-resolution photographs taken by *Price and Simpson* [1939] would appear to confirm these doubts:

these authors report that as the pressure in their experiment was reduced to a few tenths of a millimeter, the continuous absorption below 1620 A became weak, and that between 1390 A and 1240 A a set of distinct bands appeared. No mention of an underlying continuum is made. There would appear to be a need for high-resolution absorption spectra obtained at low pressures for this particular spectral region.

Nakata et al. and Inn et al. have also measured the absorption cross section between 1000 A and 1200 A. Both groups report finding no pressure dependence of the absorption cross section, and yet bandwidth dependence is evident when the results at the peaks and at the minima are compared. The strong bands at 1150 A show this bandwidth dependence particularly, and a comparison of the measured cross sections is shown in Figure 39. It will be noted that the peak absorption cross sections obtained by Nakata et al. are almost 25% higher than those obtained by Inn et al. Both groups of authors identify a continuum at 1115 A, but in view of the marked bandwidth dependence that their measurements would indicate, this hardly seems justified. A continuum has also been ascribed to the minima absorption cross section as measured between 1100 A and 890 A. It is probable that most of this continuum can also be due to band overlap, although there is some evidence from fluorescence studies of D. L. Judge
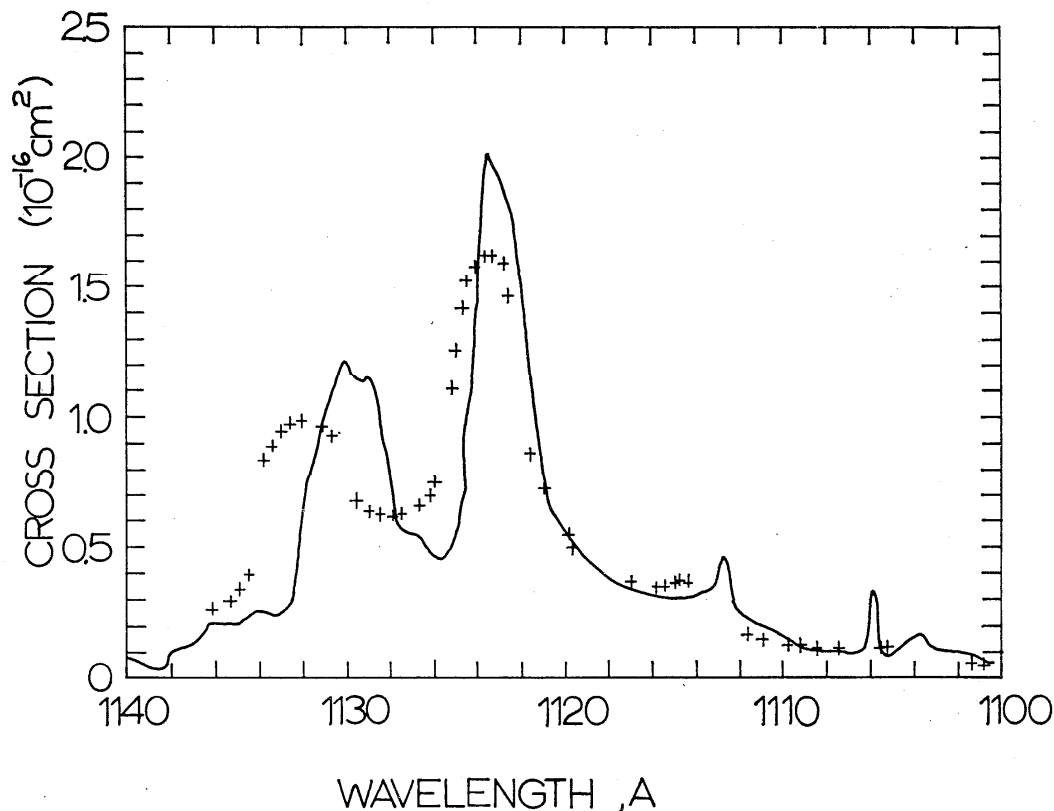

Fig. 39.   Comparison of measured total absorption cross section data for CO_2 between 1100 and 1140 A; solid line, *Nakata et al.* [1965]; +, *Inn et al.* [1953].

(personal communication, 1969) that a dissociation continuum does begin at around 1000 A, which gives rise to carbon monoxide in an excited state.

The absorption cross section between 580 A and 1000 A has been measured by *Nakata et al.* [1965], *Cook et al.* [1966], and *Cairns and Samson* [1965]. A detailed comparison of the cross-section curves of Nakata et al. and Cook et al. indicates that the instrumental bandwidth used by Cook et al. was greater than that used by Nakata et al. However, the reader will find that such discrepancies as there are cannot be explained entirely by bandwidth dependence, although this phenomenon does undoubtedly exist. Where comparison can be made, the data of Nakata et al. and those of Cairns and Samson are in reasonable agreement. For this reason, and because of their smaller bandwidth, it is recommended that the data of Nakata et al. be preferred between 900 A and 1450 A until higher-resolution results are available.

An example of the discrepancies that exist is shown in Figure 40, which compares the experimental results obtained between 800 A and 900 A, a region where there is a relatively smooth continuum. The curves appear to be displaced from one another, and the points of Cairns and Samson could support either set of data. Figure 41 compares the absorption cross sections obtained by these three groups between 600 A and 700 A. Again the three sets of data differ
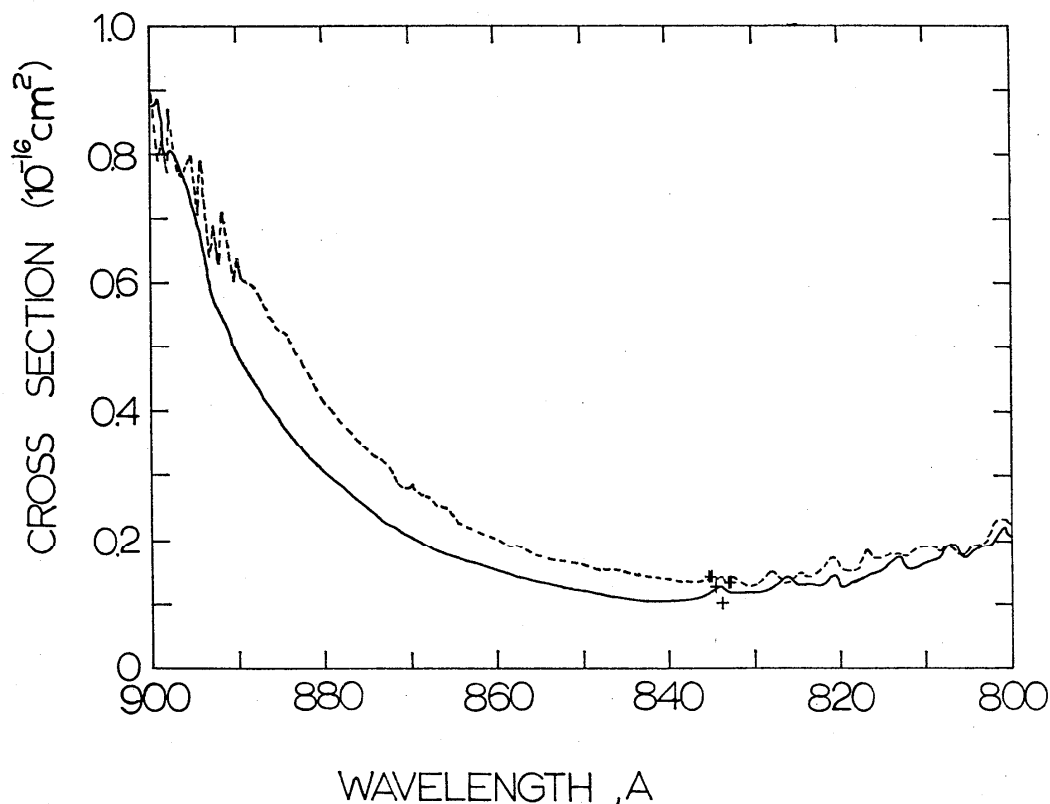

Fig. 40. Comparison of measured total absorption cross section data for CO_2 between 800 and 900 A; solid line, *Cook et al.* [1966]; dashed line, *Nakata et al.* [1965]; +, *Cairns and Samson* [1965].

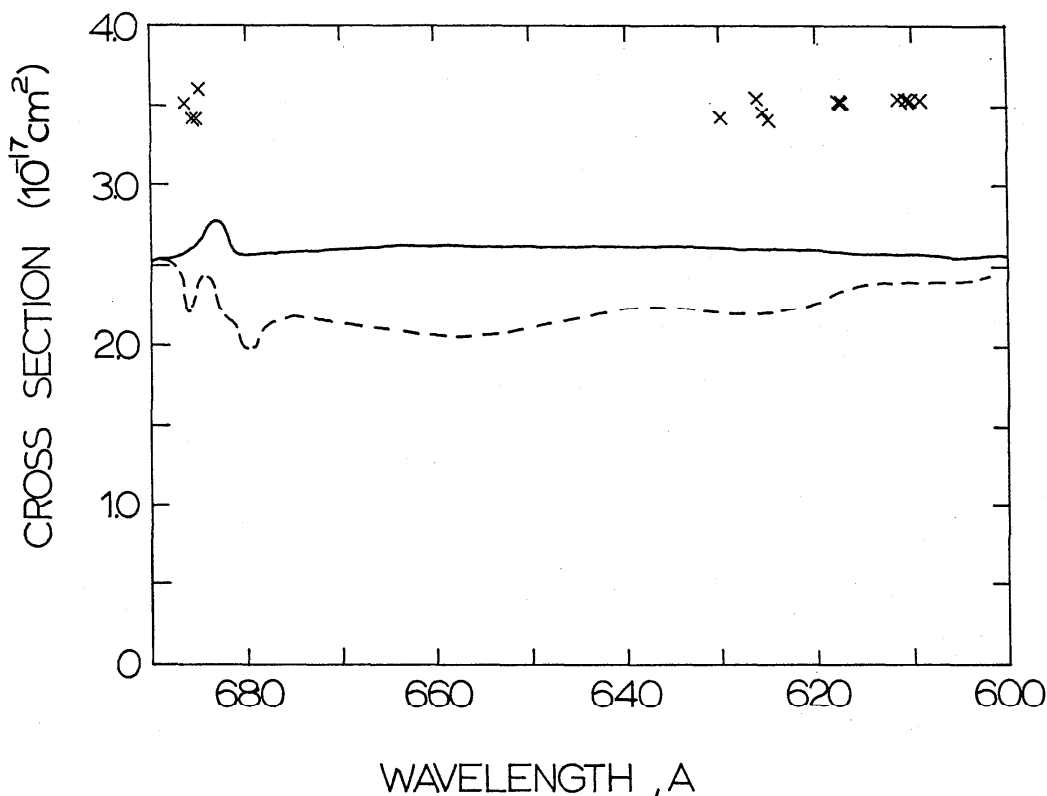Fig. 41. Comparison of measured total absorption cross section data for CO_2 between 600 and 700 A; solid line, *Cook et al.* [1966]; dashed line, *Nakata et al.* [1965]; +, *Cairns and Samson* [1965].

markedly. Cairns and Samson have re-examined the wavelength interval between 200 A and 500 A [*Cairns and Samson*, 1966] and find that the data in their former paper are consistent with their new results. The over-all picture of the absorption cross section for carbon dioxide between 600 A and 900 A is one of confusion, and this bears directly on the data to be used at wavelengths shorter than 600 A. It seems obvious that other measurements will need to be made to clarify the situation.

The photoionization yield has been measured between 200 A and 900 A by *Cairns and Samson* [1965], *Cook et al.* [1966], *Nakata et al.* [1965], and *Wainfan et al.* [1955]. The yield in the regions of band structure shows fluctuations, indicating that the probability of preionization in the bands is not 100%. This could be because the bands are also subject to predissociation, but the possibility of resonance fluorescence is not precluded. In Figures 42 and 43 results of the yield measurements between 800 A and 900 A and between 600 A and 700 A are displayed. The yield measurements of Cairns and Samson and of Nakata et al. were obtained with the total-absorption technique, whereas Cook et al. and Wainfan et al. used secondary standards to measure the absolute photon flux: Cook et al. used a platinum photodiode, while Wainfan et al. used a sodium-salicylate–coated photomultiplier. Cairns and Samson give an estimated error of ±5%, Nakata et al. ±10%, Cook et al. ±5%, and Wainfan et al. ±15%.
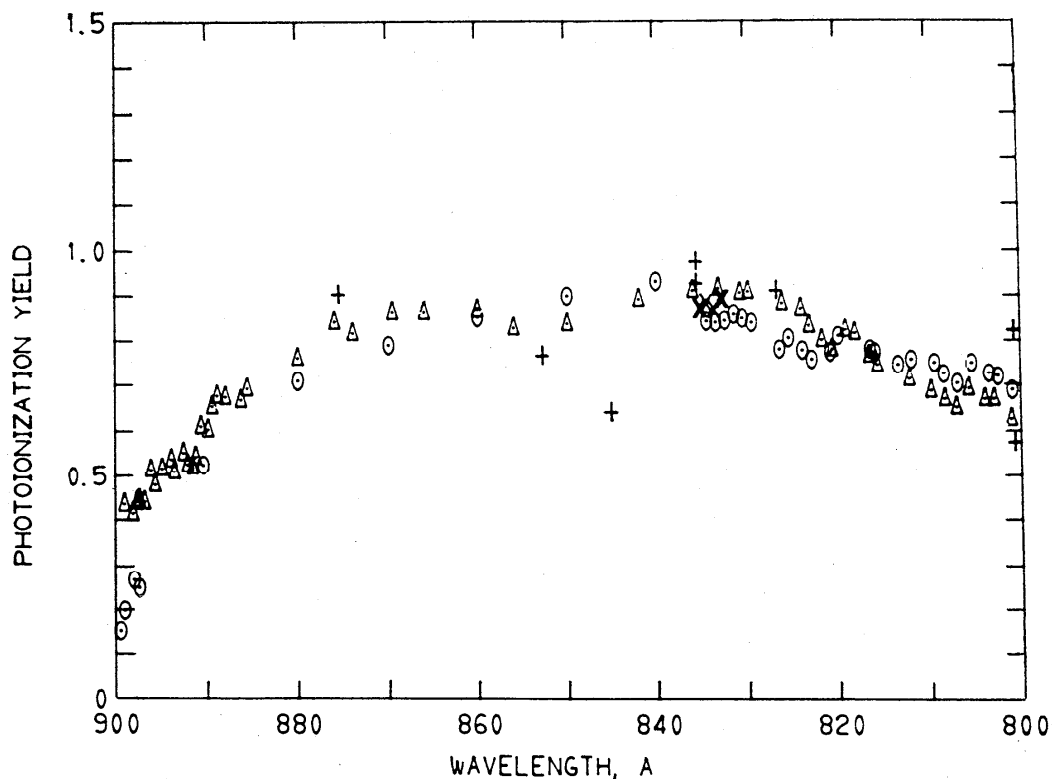
Fig. 42. Comparison of measured photoionization yield data for CO_2 between 800 and 900 A; +, *Wainfan et al.* [1955]; ×, *Cairns and Samson* [1965]; circled dot, *Cook et al.* [1966]; triangle dot, *Nakata et al.* [1965].

Within these error limits the agreement between the four sets of data is not good. The more accurate data should be those of Cairns and Samson and of Nakata et al., indicating that the yield of CO_2 between 600 A and 700 A is probably between 90 and 100%.

Relative ionization cross sections, i.e., the photoionization efficiency (PE), have been measured by *Dibeler and Walker* [1967] and *Weissler et al.* [1959]. Dibeler and Walker used poor resolution, of the order of 2 A, and thus one cannot directly compare their measurements with those of Nakata et al. or Cook et al. except in the region of continuous absorption. Between 800 A and 900 A the ionization-cross-section curves that have been obtained from both the absorption measurements and the photoionization yield measurements of Nakata et al. agree in shape best with the relative photoionization measurements of Dibeler and Walker. However, Dibeler and Walker observe the onset of dissociative ionization at 649 A, and below this wavelength any simple comparison is not possible. Thus, the PE data cannot resolve the discrepancies in the absorption-cross-section data at 600 A.

H. Ozone, O_3

Absolute absorption cross sections for ozone have been obtained between 1000 A and 3500 A. The spectrum can be conveniently divided into two regions, the first (between 1000 A and 2000 A) consisting of broad bands overlying a
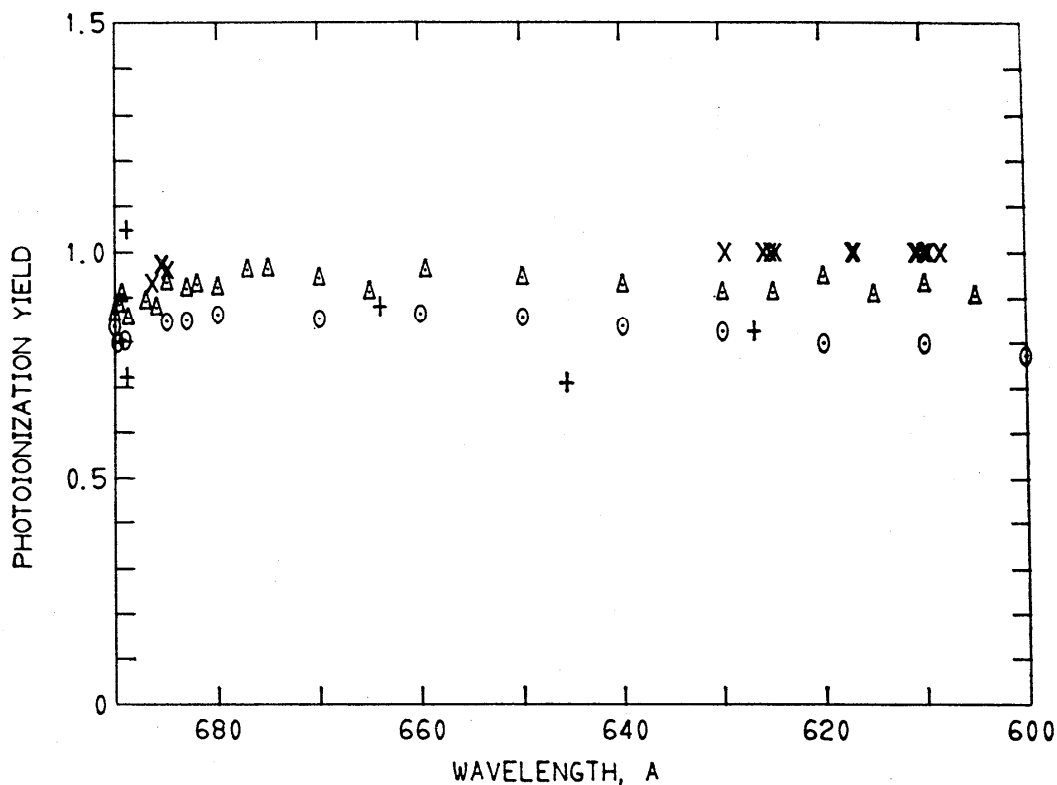
Fig. 43. Comparison of measured photoionization yield data for CO_2 between 600 and 680 A; +, *Wainfan et al.* [1955]; ×, *Cairns and Samson* [1965]; circled dot, *Cook et al.* [1966]; triangle dot, *Nakata et al.* [1965].

possible continuum [*Price and Simpson*, 1941]; the second, between 2000 A and 3500 A, consisting of the well-known Hartley bands and continuum between 2000 A and 3000 A, and the Huggins bands between 3000 A and 3500 A.

The absorption cross sections between 2000 A and 3500 A have been measured by many groups. Measurements using photoelectric techniques have been made by *Inn and Tanaka* [1953] and by *Griggs* [1968], who used a continuum light source; and by *Hearn* [1961] and *DeMore and Raper* [1964], who used a line emission source. The reader is cautioned that the cross sections obtained by these groups are not defined as in equation 1, the exponentiation being to the base 10.

In all of these experiments great care was taken to ensure that the ozone was of high purity and that the loss of ozone due to photodissociation during the experiment did not falsify the final results. In Table 6, results obtained at selected wavelengths by these groups are compared [after *Griggs*, 1968]. The agreement is within ±2%, which is indicative of the great care that was taken in these measurements and in particular in the derivation of the ozone concentration. This agreement does not preclude the possibility of a common systematic error in the measurement of the ozone concentration.

Figures 44 and 45, taken from *Griggs* [1968], compare the data obtained

TABLE 6.   Comparison of Cross Sections for Ozone between 2536 and 3022 A
[Cross Section, $Mb(10^{-18}\ cm^2)$]

Investigators	Wavelength, A			
	2536.5	2893.6	2967.3	3021.5
Inn and Tanaka [1953]	11.38	1.46	0.575	0.284
Hearn [1961]	11.45	1.47	0.596	0.286
DeMore and Raper [1964]	11.54	1.48	0.586	
Griggs [1968]	11.27	1.48	0.599	0.284

by Griggs and by *Inn and Tanaka* [1953]. The agreement between these two groups is within their quoted cross-section errors; however, there are some differences in the location of maxima and minima that are as large as 5 A, i.e., greater than the quoted wavelength errors. It is perhaps interesting to note that this molecule, for which the most consistent set of data is available, is one of the most reactive gases reviewed.

The region between 1050 A and 2000 A has been studied by only one group, *Tanaka et al.* [1953]. This group used photoelectric techniques and estimated the over-all error in their measurement to be ±10%. The relative cross section
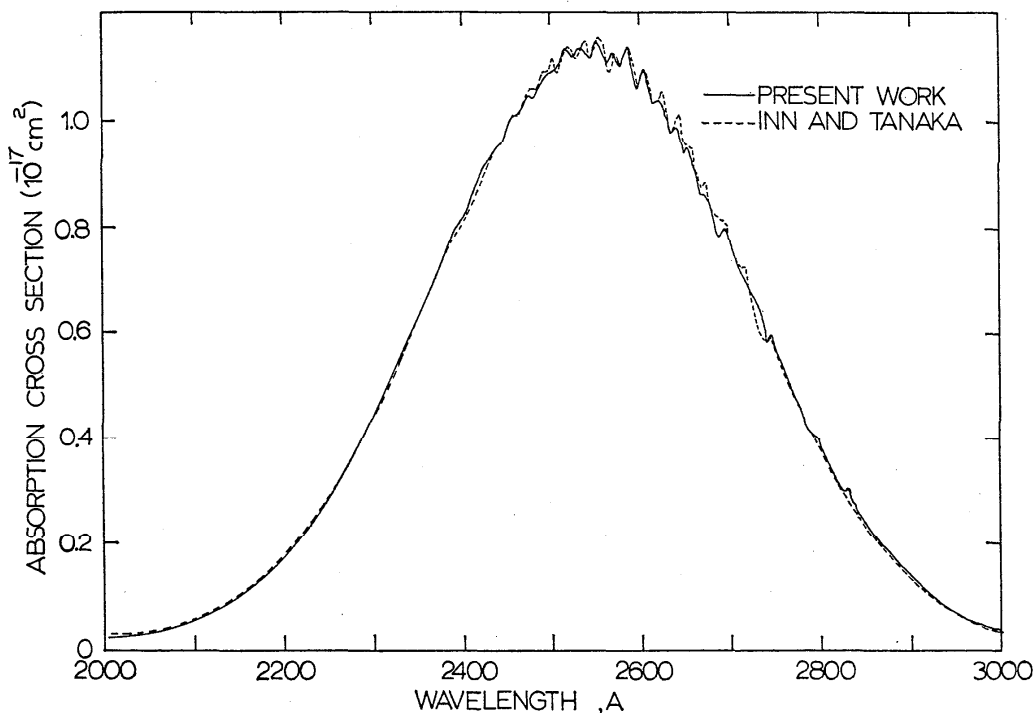
Fig. 44.   Comparison of measured total absorption cross section data for O_3 between 2000 and 3000 A (from *Griggs* [1968]); solid line, *Griggs* [1968]; dashed line, *Inn and Tanaka* [1953].
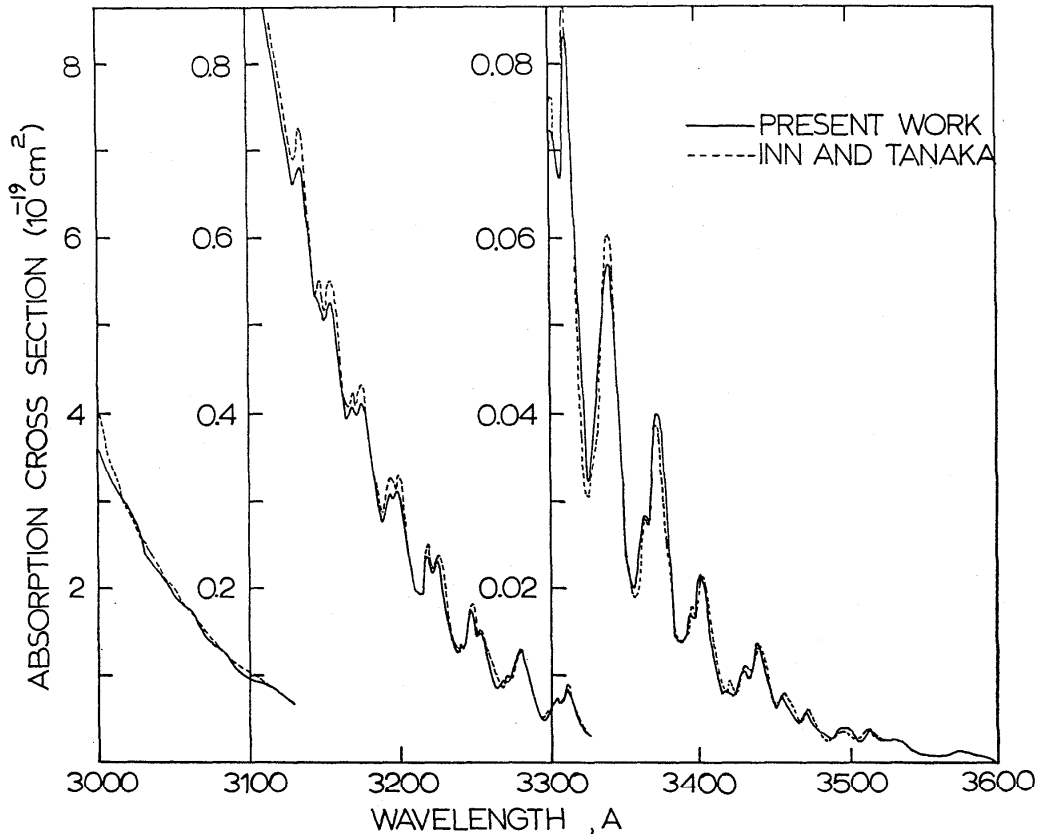
Fig. 45. Comparison of measured total absorption cross section data for O₃ between 3000 and 3600 A (from *Griggs* [1968]); solid line, *Griggs* [1968]; dashed line, *Inn and Tanaka* [1953].

below 1000 A has been measured by *Ogawa and Cook* [1958], who used photographic techniques. They assign no error to their measurements.

I. Ammonia, NH₃

The absorption spectrum of ammonia between 370 A and 2400 A consists of a continuum between 370 A and 1000 A and strong band structure between 1000 A and 2400 A. The ionization edge of ammonia is at 1220 A. Photographic spectra have been obtained for ammonia for wavelengths greater than 1000 A by *Duncan* [1936a]. The region between 1000 A and 2400 A has been investigated by *Watanabe and Sood* [1965], *Watanabe* [1954], *Thompson et al.* [1963], and *Tannenbaum et al.* [1953].

The data of *Watanabe* [1954] and of *Tannenbaum et al.* [1953] are in reasonable agreement with the cross sections of Watanabe and Sood except at the peaks and minima, where the smaller bandwidth used by Watanabe and Sood yields higher peak values and lower minimum values. Watanabe and Sood report that many of the peak absorption cross sections they measured showed an apparent pressure dependence, indicating strong bandwidth dependence.

In the same way that underlying continua have been postulated for carbon dioxide, continua have been postulated for ammonia centered at 1900 A, 1500 A, and 1350 A, respectively. The arguments in section III have indicated that such a choice would be subject to doubt, and in the case of ammonia this doubt is borne out by the measurement by *Okabe and Lenzi* [1967] of the fluorescence from ammonia when it was irradiated with ultraviolet radiation at selected wavelengths between 1080 and 2000 A. NH_2 fluorescence in the $^2A_1$ state has a theoretical threshold at 2175 A, but Okabe and Lenzi observed the onset of this radiation at 1640 A. This indicates that if there is an underlying continuum between 1640 A and 2175 A, or if the bands seen between 1640 A and 2175 A are broadened by predissociation, then the dissociation product must be NH_2 in the ground state. The NH_2 fluorescence seen by Okabe and Lenzi closely follows the band profiles from 1640 A to shorter wavelengths, indicating that these bands predissociate to a dissociation level, leaving NH_2 in the $^2A_1$ state plus atomic hydrogen in the ground state.

Between 500 A and 1000 A the absorption spectrum is continuous, and one should expect good agreement between the various experimental measurements that have been made. In Figure 46 a comparison is made between the results of *Metzger and Cook* [1964a] and those of *Watanabe and Sood* [1965]. These
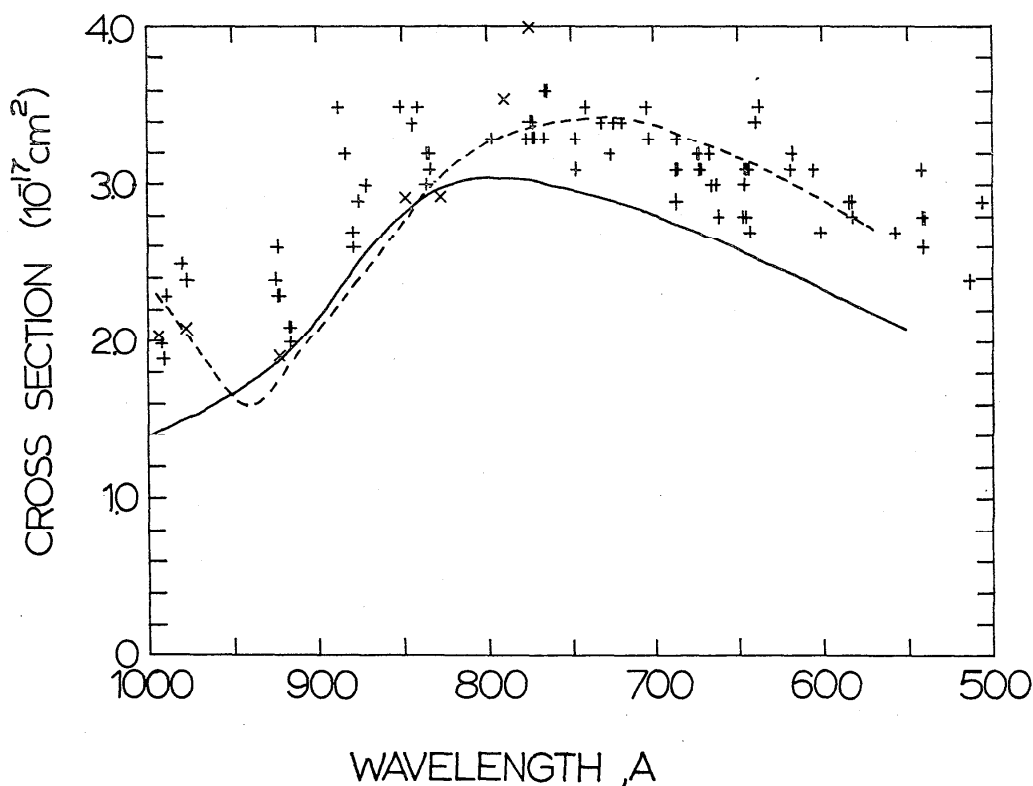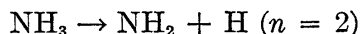

Fig. 46. Comparison of measured total absorption cross section data for NH₃ between 500 and 1000 A; solid line, *Metzger and Cook* [1964a]; dashed line, *Watanabe and Sood* [1965]; +, *Sun and Weissler* [1955]; ×, *Walker and Weissler* [1955a].

results were obtained with the helium continuum light source at instrumental bandwidths of 0.5 and 0.3 A, respectively. The results shown in Figure 46 are most disturbing, as the groups differ both in magnitude and shape as to the resultant absorption cross section curve. In the region of overlap between the data of Watanabe and those Watanabe and Sood, the cross sections of the latter group are about 10% higher than those of the former. *Sun and Weisseler* [1955] and *Walker and Weissler* [1955a] have also measured the total absorption cross section in this wavelength region, using a line emission light source. Their results are shown in Figure 46 as points. These authors estimate an average error of ±10%, but for some lines the error is greater. Their data show some scatter, but in general would tend to favor the results of Watanabe and Sood.

The photoionization yield for ammonia has been measured between 600 A and 1000 A by *Metzger and Cook* [1964a], *Watanabe* [1954], *Watanabe and Sood* [1965], and *Walker and Weissler* [1955a]. The data of Watanabe were obtained by means of the total-absorption technique, with nitric oxide as the standard. The yield for nitric oxide assumed by Watanabe has since been lowered by 8% [see *Watanabe et al.*, 1967]; thus the yield measurements for ammonia quoted by Watanabe should be lowered by this same amount. (Watanabe and Sood also used the total-absorption technique, but with xenon as the standard.) Metzger and Cook, as well as Walker and Weissler, used secondary standards: the former used a platinum photodiode, and the latter used a sodium-salicylate–coated photomultiplier; and both quote an error of ±10%. Watanabe and Sood do not give one. A comparison of the results for these groups between 600 A and 1000 A is shown in Figure 47.

The shape of the yield curve obtained by Metzger and Cook differs in shape and magnitude from that of Walker and Weissler and that of Watanabe and Sood. Again this discrepancy is hard to account for, unless the yield of the platinum photodiode used by Cook and Metzger changed as a result of being immersed in the ammonia vapor. Photoionization efficiency (PE) measurements have been made in ammonia by *Dibeler et al.* [1966], and the shape of this curve versus wavelength between 1250 and 800 A can be compared with the photoionization-cross-section curves of Metzger and Cook and those of Watanabe and Sood. Such a comparison favors most strongly the yield measurements of Watanabe and Sood. The lower limit of 800 A to the comparison is set by the observation by Dibeler et al. of the onset of dissociative ionization at this wavelength.

Watanabe and Sood identify a dissociation continuum between 700 A and 950 A. From the measurements of *Beyer and Welge* [1967], this continuum can be ascribed to the process

$$NH_3 \rightarrow NH_2 + H \ (n = 2)$$

giving rise to the emission of Lyman-α radiation.

J. Hydrogen Sulfide, H_2S

Only one paper giving the absorption and photoionization cross sections of hydrogen sulfide has been published [*Watanabe and Jursa*, 1964], and this
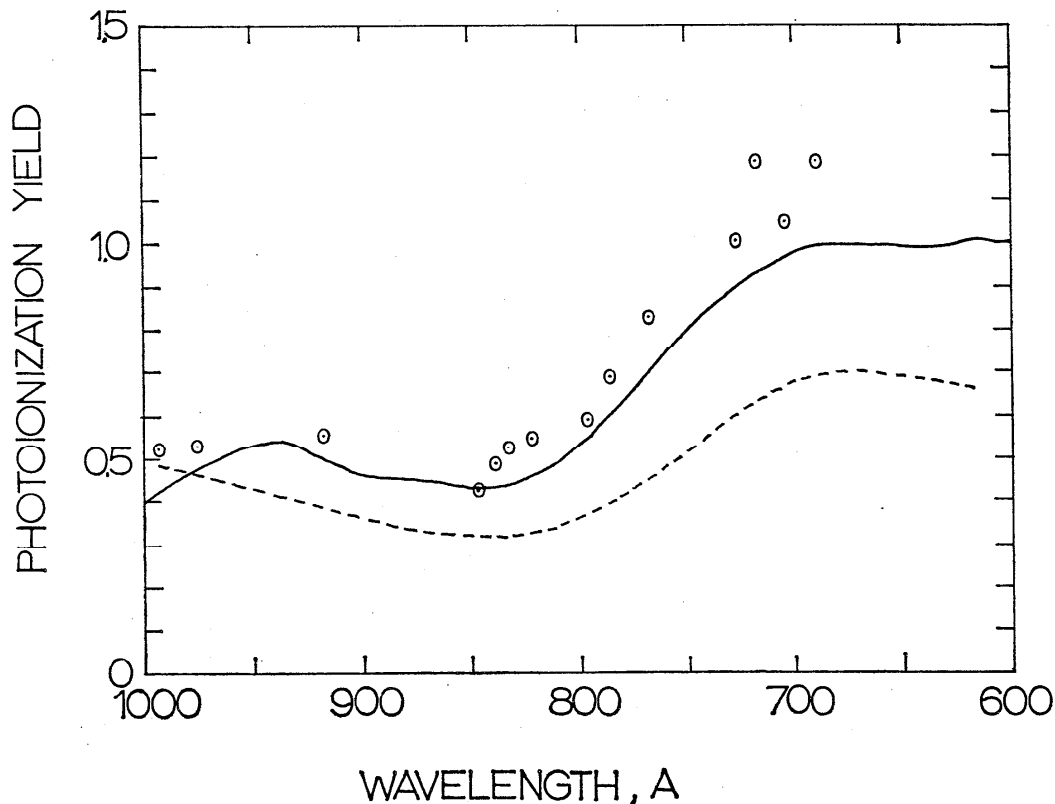
Fig. 47. Comparison of measured photoionization yield data for NH₃ between 600 and 1000 A; solid line, *Watanabe and Sood* [1965]; dashed line, *Metzger and Cook* [1964a]; circled dot, *Walker and Weissler* [1955a].

covers the wavelength range 1060 A to 2100 A. These measurements were made by photoelectric techniques, with an instrumental bandwidth of 0.85 A. The hydrogen sulfide gas was purified by repeated fractional distillation in a vacuum system, and the purity was checked by the use of spectrometric analysis. The total impurity was less than 0.05%. The pressure was measured with a consolidated micromanometer and an alphatron gage that had been calibrated against a McLeod gage. The photoionization yields of hydrogen sulfide were determined by comparison of ion currents of hydrogen sulfide and nitric oxide obtained under the same conditions and then by using the known yield of nitric oxide that had previously been obtained by *Watanabe* [1954]. In the more recent paper by *Watanabe et al.* [1967], the ionization yield for NO has been lowered by 8% from that obtained by *Watanabe* [1954]; presumably these measured yields for hydrogen sulfide should also be lowered by 8%.

In the interval between 1600 A and 2100 A the spectrum consists of a broad continuum with almost no discrete structure, and the authors quote an experimental error of about 10%. The continuum apparently extends beyond 2100 A, and it peaks at about 1960 A. It has been attributed to predissociation [*Mulliken*, 1935].

The absorption spectrum between 1200 A and 1600 A has been investigated

photographically by *Price* [1936] and by *Bloch et al.* [1936]. Price arranged most of the prominent bands into four Rydberg series, converging to the first ionization potential at about 1185 A. Price reports that the observed bands between 1200 A and 1600 A are discrete, strong, and well separated. He observed that the bands at shorter wavelengths became weaker and closer together, eventually merging into continuous absorption around 1190 A. It is not surprising, therefore, that Watanabe and Jursa report considerable amounts of pressure dependence for the peak absorption cross sections, which they ascribe to incomplete resolution. The data published for the peaks are the values obtained at the lowest pressures used in their measurements, and they will probably be strongly bandwidth-dependent. Experimental errors, other than at the peaks, are quoted as from 10% to 20%. In view of the findings of Price, the existence of an underlying continuum has not been proven at this time.

K.   Nitrous Oxide, N_2O

The absorption spectrum of nitrous oxide between 600 A and 1000 A consists of a series of Rydberg bands superimposed on underlying ionization and dissociation continua. Between 1080 A and 1200 A these bands become diffuse, and at 1200 A an intense, sharp continuum, which has a maximum at 1285 A,
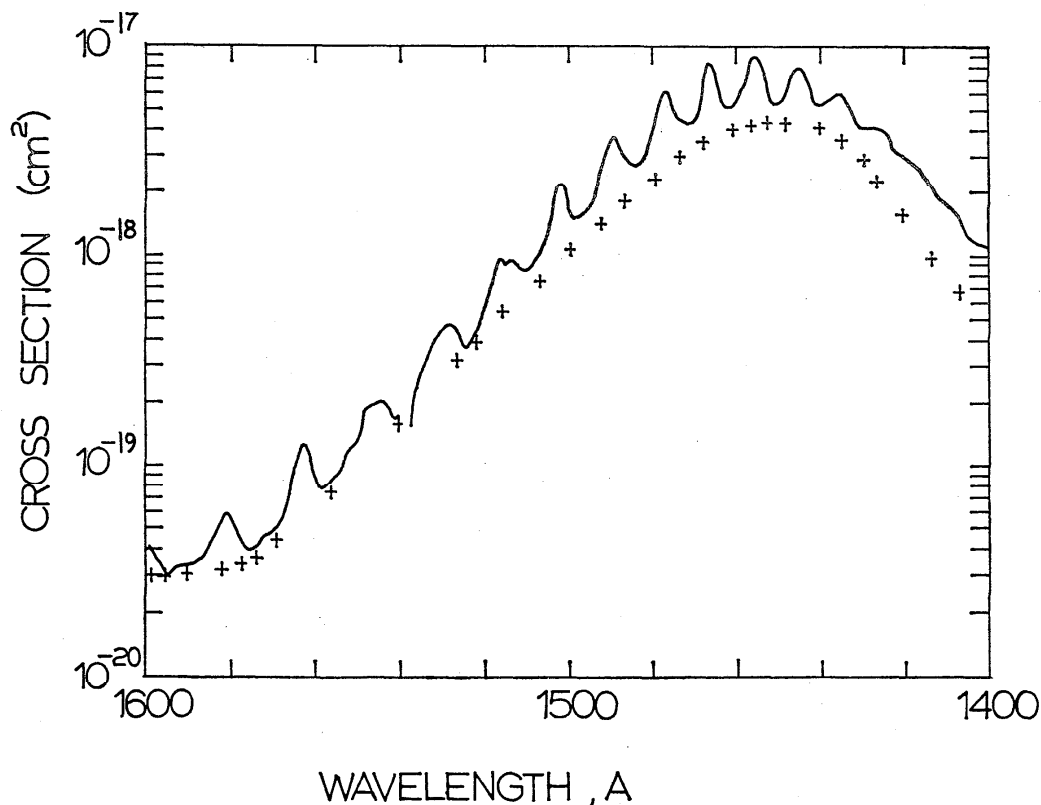

Fig. 48. Comparison of measured total absorption cross section data for N_2O between 1400 and 1600 A; solid line, *Zelikoff et al.* [1953]; +, *Romand and Mayence* [1949].

has been observed. The photographic work of *Duncan* [1936*b*] has reported this region to be perfectly smooth, with no structure. The photoelectric measurements of *Zelikoff et al.* [1953], however, report the location of several weak diffuse bands on the long wavelength slope. Between 1380 A and 1620 A the spectrum consists of an apparent continuum on which are superimposed 20 diffuse bands. Above 1600 A the absorption spectrum is continuous, rising to a maximum at 1800 A and then dropping off quickly toward longer wavelengths.

The wavelength interval between 1080 A and 2400 A has been investigated by *Romand and Mayence* [1949], *Zelikoff et al.* [1953], and *Thompson et al.* [1963]. Figures 48 and 49 compare the absorption cross section obtained by these three groups for the wavelength intervals 1380 A to 1600 A and 1600 A to 2100 A. In general, the agreement between the three groups is well within the experimental errors that one might expect for these particular measurements. However, since none of them discuss their errors in detail, one should look upon the composite curves of Figures 48 and 49 as indicating the present state of the nitrous-oxide absorption cross section measurements.

In the region between 1080 A and 1380 A the data of Zelikoff et al. are the only cross-section data available. The reader is referred, therefore, to their paper for detailed curves. Absorption cross sections between 600 A and 1000 A have been obtained by *Cook et al.* [1968] and by *Walker and Weissler* [1955*c*].
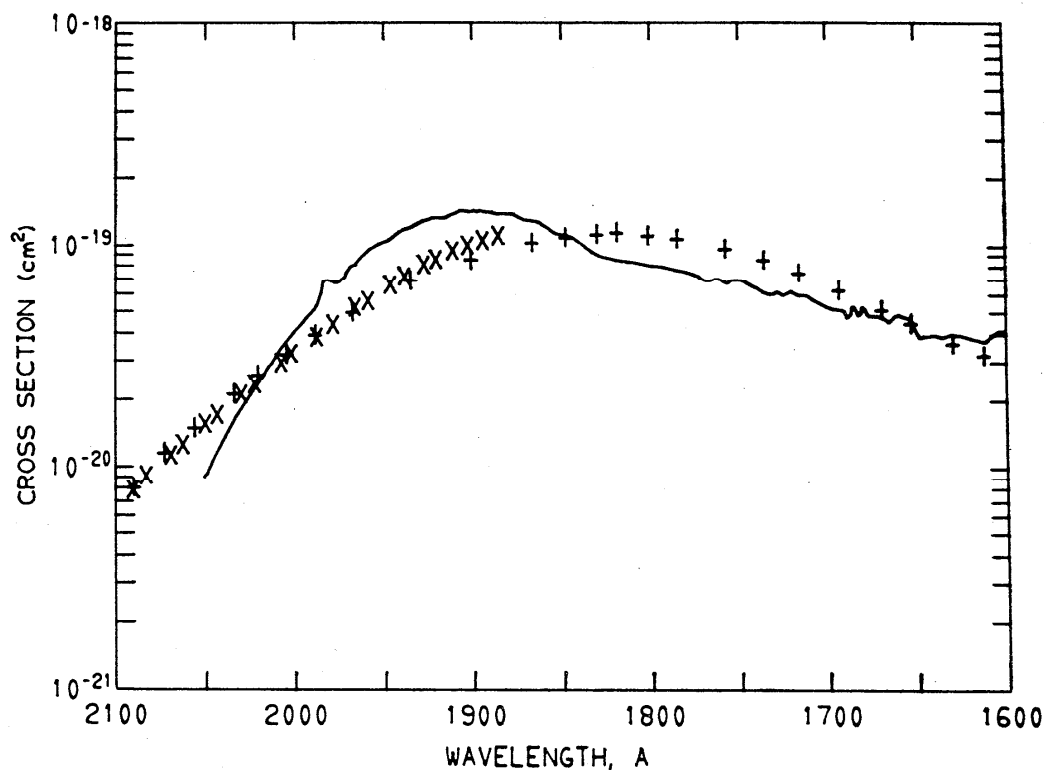

Fig. 49. Comparison of measured total absorption cross section data for N$_2$O between 1600 and 2100 A; solid line, *Zelikoff et al.* [1953]; +, *Romand and Mayence* [1949]; ×, *Thompson et al.* [1963].

Cook et al. report finding no pressure dependence at the peaks in this wavelength interval, although this still does not preclude the possibility of bandwidth dependence. Figure 50 compares the data of Cook et al. and those of Walker and Weissler. A comparison of the photoionization yield measured by these groups is given in Figure 51.

A measurement of the photoionization efficiency (PE) has been made by *Dibeler et al.* [1967] at an instrumental resolution of 2 A. These data were obtained with the helium continuum light source. The relative ionization cross sections of Dibeler et al., however, can be compared to those of Cook et al. only at wavelengths above 800 A, because at this wavelength Dibeler et al. observed the onset of dissociative ionization, the products being the molecular nitrogen ion and atomic oxygen. The agreement between the shapes is not good.

Cook et al. distinguish several dissociation continua in this wavelength interval, but a consideration of the bandwidth dependence of the yield data would indicate that only one, extending from 800 to 950 A, can be definitely identified. This has been shown by Cook et al., from fluorescence studies, to correspond to

$$N_2O + hv \rightarrow N_2(C^3\Pi_u) + O(3p)$$

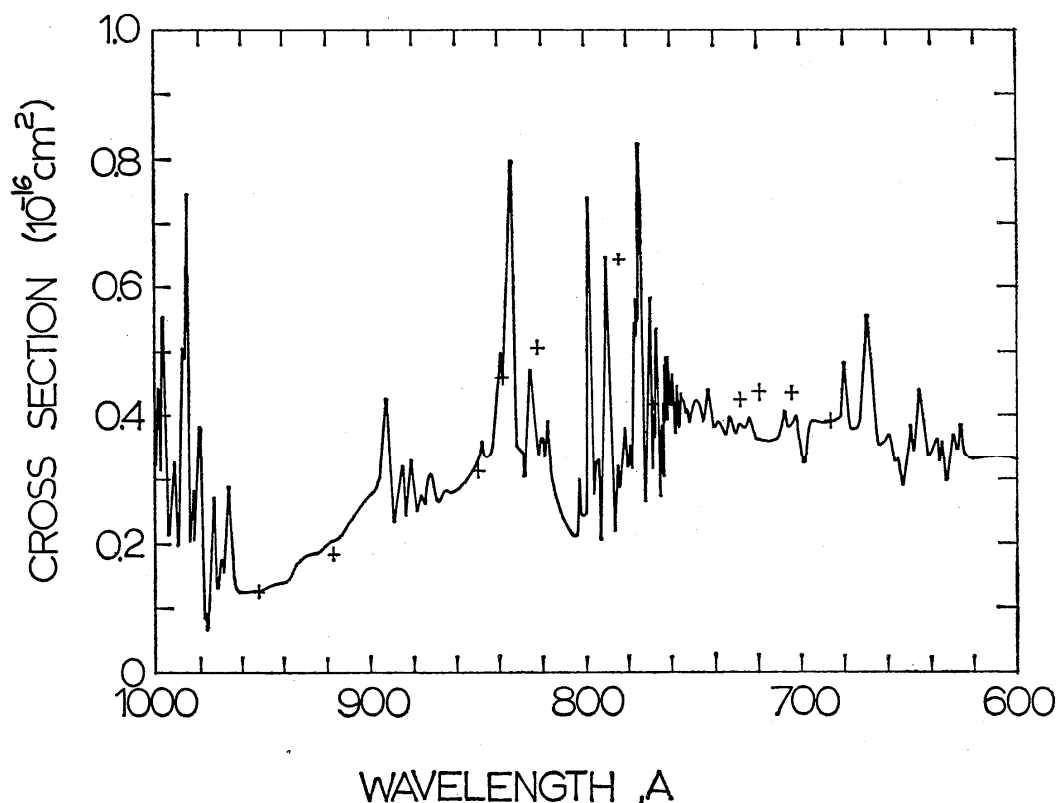Fluorescence has also been observed, with an onset at 756 A, by Cook et al. and

Fig. 50. Comparison of measured total absorption cross section data for N_2O, between 600 and 1000 A; solid line, *Cook et al.* [1968]; +, *Walker and Weissler* [1955c].
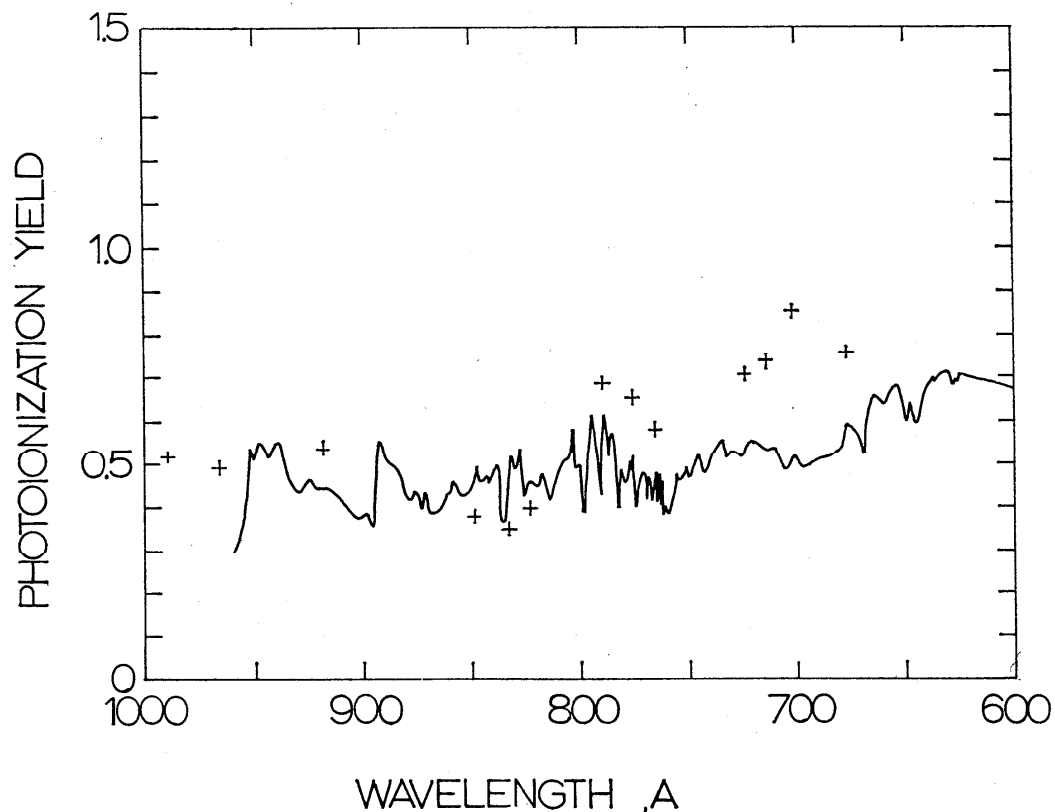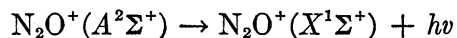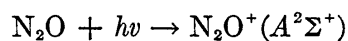
Fig. 51. Comparison of measured photoionization yield data for N_2O between 600 and 1000 A; solid line, *Cook et al.* [1968]; +, *Walker and Weissler* [1955c].

by *Judge et al.* [1963], corresponding to

$$N_2O + hv \rightarrow N_2O^+(A^2\Sigma^+)$$

$$N_2O^+(A^2\Sigma^+) \rightarrow N_2O^+(X^1\Sigma^+) + hv$$

L. Nitrogen Dioxide, NO_2

The absorption spectrum of nitrogen dioxide between 600 A and 3000 A has been obtained photographically by *Price and Simpson* [1941], by *Mori* [1954, 1955], and by *Tanaka et al.* [1960b]. Absolute photoabsorption-cross-section measurements, however, have been limited to wavelengths above 1080 A and were obtained by two groups: *Nakayama et al.* [1959] and *Hall and Blacet* [1952].

Nitrogen dioxide gas has the property that the dimer can be present even at room temperature. As a consequence, it is necessary to consider the presence of N_2O_4 as well as NO_2 in the gas sample. The absorption cross sections can be obtained by solving the equation

$$\ln A_0/A = N_1\sigma_1 + N_2\sigma_2 \tag{12}$$

where subscripts 1 and 2 refer to the monomer and dimer, respectively. Both

groups obtained the ratios of the partial pressures of N_2O_4 to NO_2 from the formula determined by *Verhoek and Daniels* [1931]. Nakayama et al. assign an error of between 10% and 20% for their values below 1800 A, but higher errors at longer wavelengths. Hall and Blacet discuss the cause of errors in their measurements but do not give numbers.

These two sets of data overlap over a very limited wavelength range, between 2400 A and 2700 A, but in this region of overlap the agreement is within ±5%. Nakayama et al. observe that in general the absorption cross sections do not show an apparent pressure dependence, but that in the regions between 1850 A and 2400 A some slight pressure effects were observed. However, this was probably due to concentrations of N_2O_4 in their absorption cell. The region between 1300 A and 1600 A is characterized by many bands that appear to be comparatively sharp. These bands have been analyzed by Price and Simpson and by Mori. Nakayama et al. postulate strong continua underlying these bands, but for reasons explained in the introduction to this review, their presence is not necessarily definite. Recent fluorescence studies by *Lenzi and Okabe* [1968] have shown that dissociation of nitrogen dioxide does not give rise to electronically excited nitric oxide above 1400 A, and then only weakly down to 1180 A, indicat-
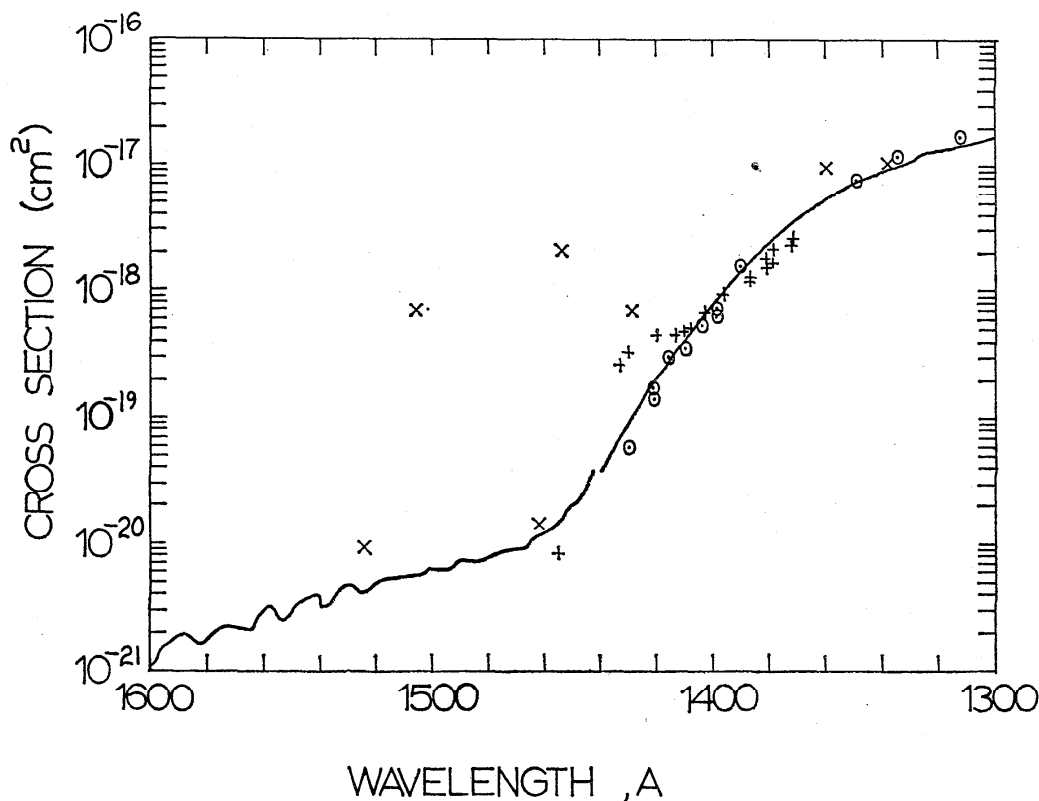

Fig. 52. Comparison of measured total absorption cross section data for CH_4 between 1300 and 1600 A; solid line, *Watanabe, Zelikoff, and Inn* [1953]; +, *Ditchburn* [1955]; ×, *Sun and Weissler* [1955]; circled dot, *Laufer and McNesby* [1955].

ing that any apparent continua above 1400 A are probably due to predissocia-
tion broadening of the bands.

Photoionization yield measurements between the ionization edge at 1288 A
and 1080 A have been made by Nakayama et al. The yield data were obtained
by means of the total absorption technique; the standard gas used was nitric
oxide. The yields for nitric oxide were obtained from the paper of *Watanabe*
[1954]. The reader is cautioned that these nitric oxide data have since been
revised by *Watanabe et al.* [1967]. The estimated error for the yield measure-
ments by Nakayama et al. is about 20%; however, allowance had to be made
for an amount of nitric oxide that was present in their NO_2 sample. The amount
of nitric oxide was determined by working at wavelengths between 1290 A and
1340 A, using the photoionization coefficient that had already been determined
by *Watanabe et al.* [1953b]. Once the amount of impurity was known, a cor-
rection was applied to the NO_2 data for the region between 1200 A and 1290 A.
In some cases, the correction was about 50% of the total ion current, and the
authors indicate that the error in the absolute value of the photoionization yield
can be expected to be large.

For wavelengths less than 1000 A, the only data available are those obtained
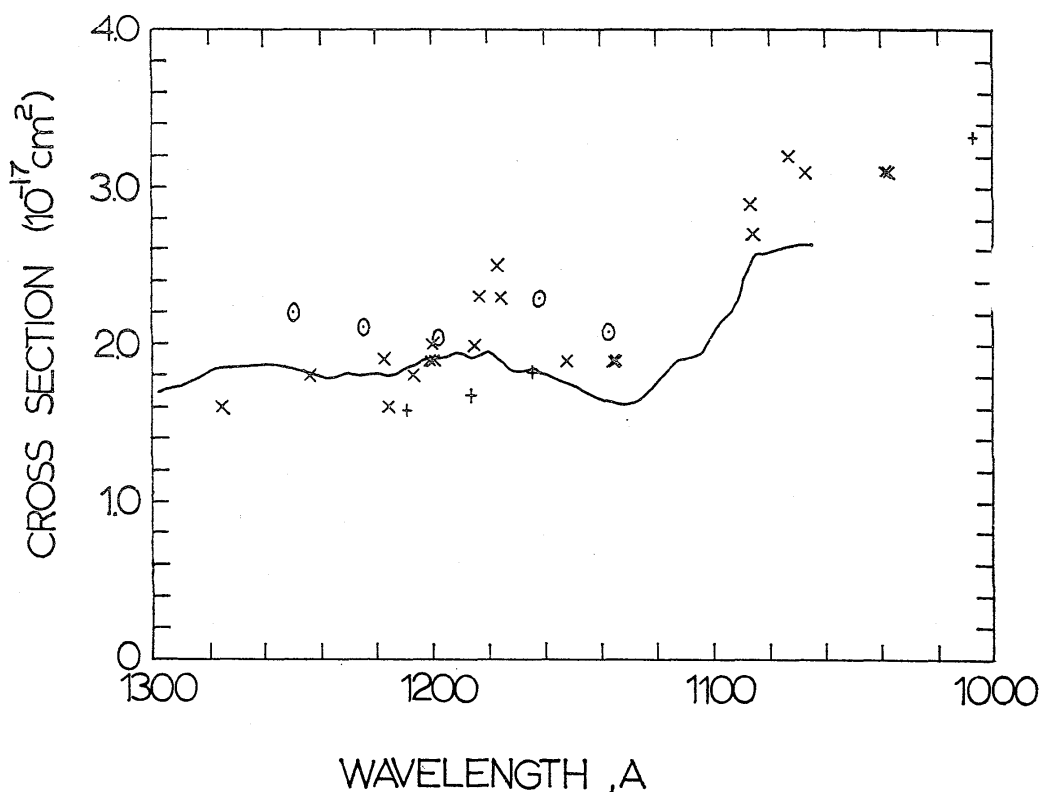for the photoionization efficiency (PE) with mass spectrometers. Three sets of

Fig. 53. Comparison of measured total absorption cross section data for CH_4 between 1000
and 1300 A; solid line, *Watanabe et al.* [1953c]; +, *Wilkinson and Johnston* [1950]; ×,
Ditchburn [1955]; circled dot, *Laufer and McNesby* [1965].

data have been obtained: *Dibeler et al.* [1967], *Weissler et al.* [1959], and *Frost et al.* [1962]. Dibeler et al. used the helium continuum light source in their experiments at an instrumental resolution of 2 A. The other two groups used line emission sources. Dibeler et al. and Weissler et al. observed NO_2^+ ions, NO^+, O^+, and N^+ ions; and they display the onsets in their papers. In general, where such a comparison can be made, the agreement between these groups is good. It is difficult to make these relative values absolute, since dissociative ionization gives rise to energetic ions, and this can change the collection efficiency of the mass spectrometer for these ions.

M. Methane, CH₄

The absorption cross section of methane in the ultraviolet is essentially continuous from the limits of measurement at 100 A to 1600 A. Beyond 1850 A, the absorption cross section has fallen to less than 10^{-23} cm² [*Thompson et al.*, 1963].

The absorption cross section of methane between 1000 A and 1600 A has been measured by *Wilkinson and Johnston* [1950], *Ditchburn* [1955], *Sun and Weissler* [1955], *Laufer and McNesby* [1965], and *Watanabe et al.* [1953c]. The latter results are contained in a technical report from the Air Force Cambridge Research Center. The results of these five groups are compared in Figures 52 and 53. The agreement between the data of Laufer and McNesby and
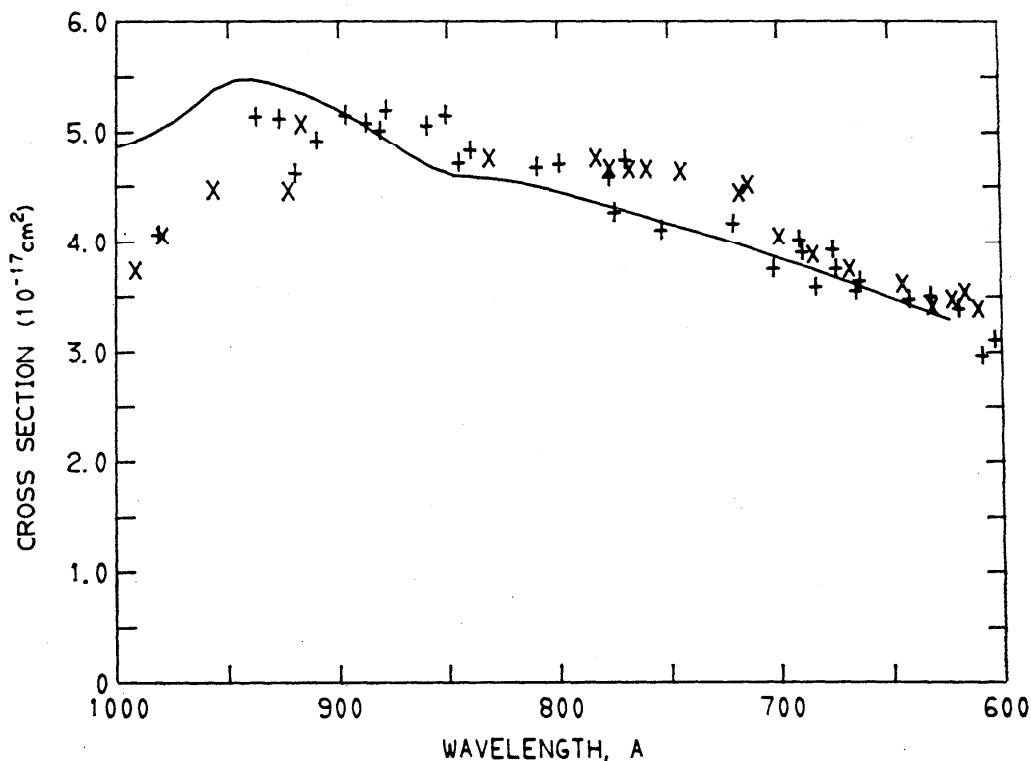
Fig. 54. Comparison of measured total absorption cross section data for CH₄ between 600 and 1000 A; solid line, *Metzger and Cook* [1964a]; +, *Ditchburn* [1955]; ×, *Rustgi* [1964].

Watanabe et al. is extremely good in the region of overlap of these two measurements, agreeing within ±3%. The data of Ditchburn, of Sun and Weissler, and of Wilkinson and Johnston show much more scatter, although the general shape agrees with that of Watanabe et al.

In the interval between 600 A and 1000 A, photoabsorption cross sections have been measured by *Metzger and Cook* [1964a], *Rustgi* [1964], *Schoen* [1962], and *Wainfan et al.* [1955], in addition to the measurements already discussed by *Ditchburn* [1955] and *Sun and Weissler* [1955]. All of these additional measurements used photoelectric techniques. Since the absorption cross section would appear to be continuous in this spectral region, the bandwidths that were used should not be important, and this should be one region where the cross sections can be compared most favorably. *Metzger and Cook* [1964a], *Rustgi* [1964], and *Sun and Weissler* [1955] do not give an estimate of the accuracy of their photoabsorption cross sections. *Wainfan et al.* [1955] give an error for each emission line that they used; the average error would appear to be of the order of ±10%.

Figure 54 compares results for the absorption cross section of methane between 600 A and 1000 A as obtained by *Metzger and Cook* [1964a], *Ditchburn* [1955], and *Rustgi* [1964]. As can be seen, the over-all agreement between the sets of data is within ±20%. The region between 20 A and 600 A has been measured by *Ditchburn* [1955], *Rustgi* [1964], and *Lukirskii et al.* [1964], and the

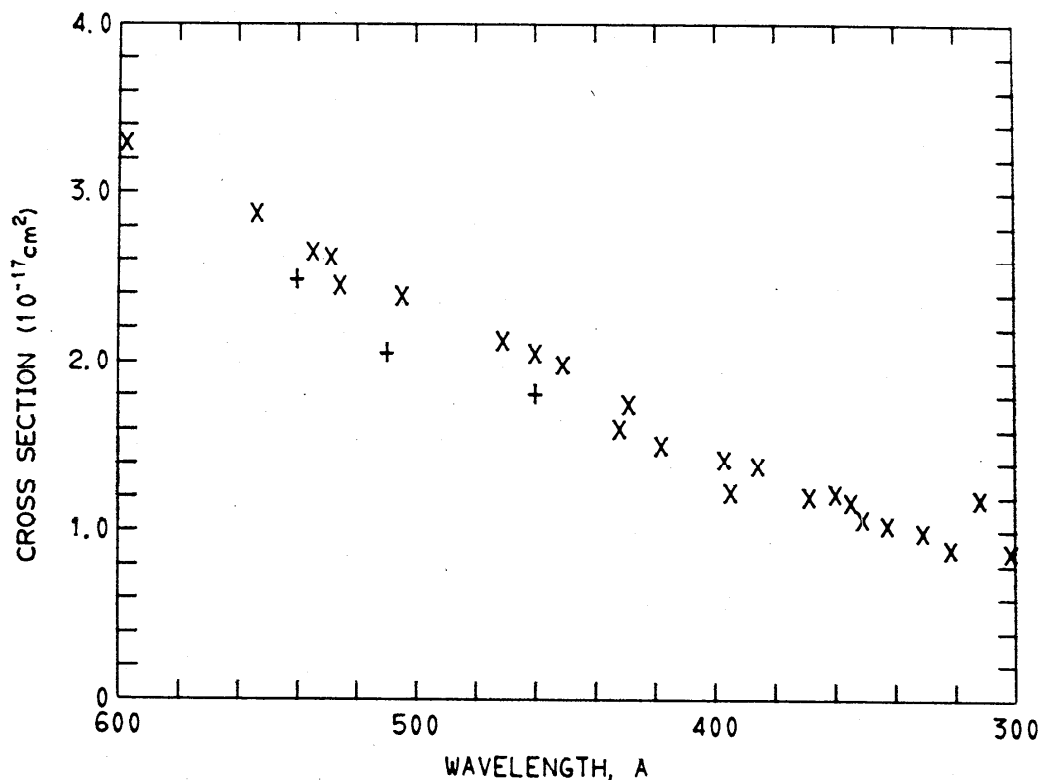Fig. 55. Comparison of measured total absorption cross section data for CH₄ between 300 and 600 A; ×, *Rustgi* [1964]; +, *Ditchburn* [1955].

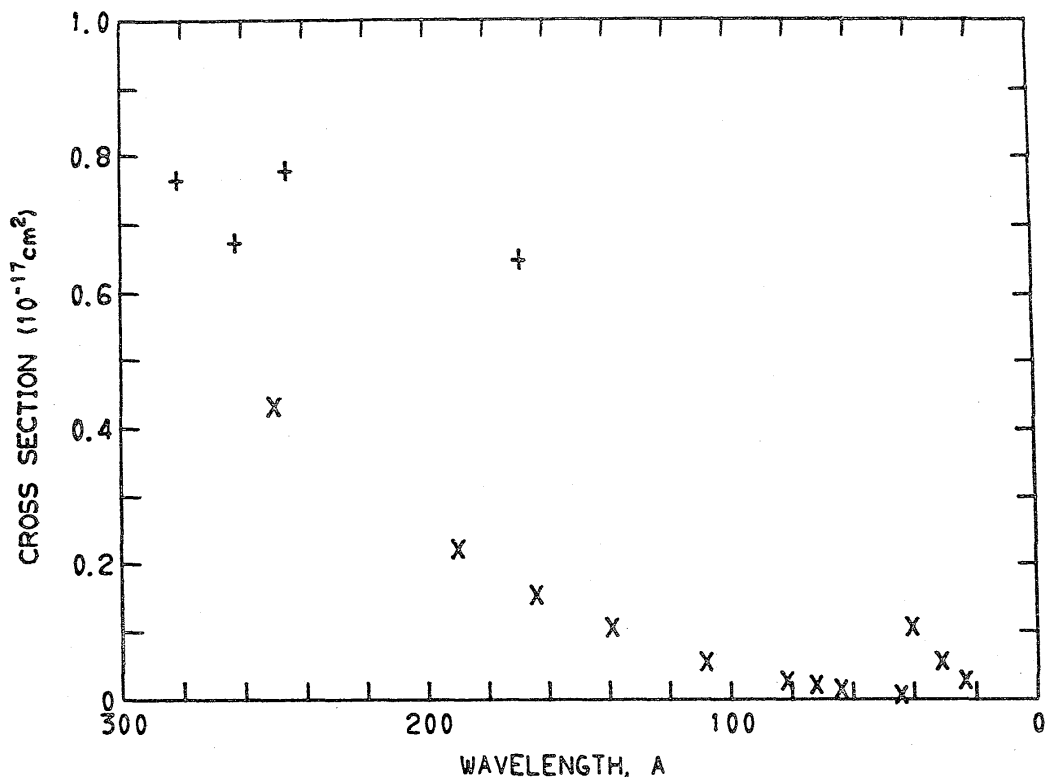Fig. 56. Comparison of measured total absorption section data for CH₄, between 20 and 300
A; +, *Rustgi* [1964]; ×, *Lukirskii et al.* [1964].

results obtained by these groups are displayed in Figures 55 and 56. It is recommended that a smooth curve be drawn through these points to obtain an approximation to the photoabsorption cross section curve.

The photoionization yield for methane has been measured between 600 A and 980 A by *Wainfan et al.* [1955] and by *Metzger and Cook* [1964a], and a comparison of their results in this spectral range is shown in Figure 57. The data of Metzger and Cook were obtained with the helium continuum light source, whereas those of Wainfan et al. were obtained with a line emission source. Both groups measured the absolute photon flux with secondary standards; Metzger and Cook used a platinum photodiode, and Wainfan et al. used a sodium-salicylate–coated photomultiplier. Metzger and Cook and Wainfan et al. both estimate the error in their yield measurements to be ±10%. The data of Metzger and Cook rise to a maxima of 80% at 800 A and then fall off to shorter wavelengths, whereas the data of Wainfan et al. rise to a value of 120% at 800 A and from then remain reasonably constant at 100%. It seems likely from a comparison of these two sets of data that the photoionization yield lies between 80% and 100% at 800 A and remains at this level to shorter wavelengths. Metzger and Cook also observed fluorescence from methane between 1000 A and 800 A, the fluorescent yield falling to zero at 780 A. Thus, either the dissociation continuum that gives rise to this fluorescence is replaced by another continuum at

780 A, which then extends to shorter wavelengths; or the photoionization yield becomes 100% at 780 A. The latter explanation seems more likely.

The photoionization efficiency has been measured by *Dibeler, Krause, Reese, and Harllee* [1965] and by *Chupka* [1968] through the use of mass spectrometers. The onset of ionization has been determined to be 980 A, and at this wavelength the CH_4^+ ion is the only one formed. At about 880 A, CH_3^+ is formed, and at 820 A CH_2^+ is formed. Both of these latter ions must be produced in some dissociative ionization process. The data of Chupka were obtained at better resolution than those of Dibeler et al. (1.6 A compared to 2 A), and there appears to be considerably more scatter on the data of Dibeler et al. than on the data of Chupka. In general, however, the shapes of the relative photoionization curves for the particular ions that these two groups obtained are in reasonable agreement within the experimental errors that one might expect. No comparisons can usefully be made between the relative values and the absolute values of Metzger and Cook or of Wainfan et al.

N.   Carbon Disulfide, CS_2

Absolute photoabsorption and photoionization cross sections for carbon disulfide have been limited to the wavelength region 600 A to 1000 A. This
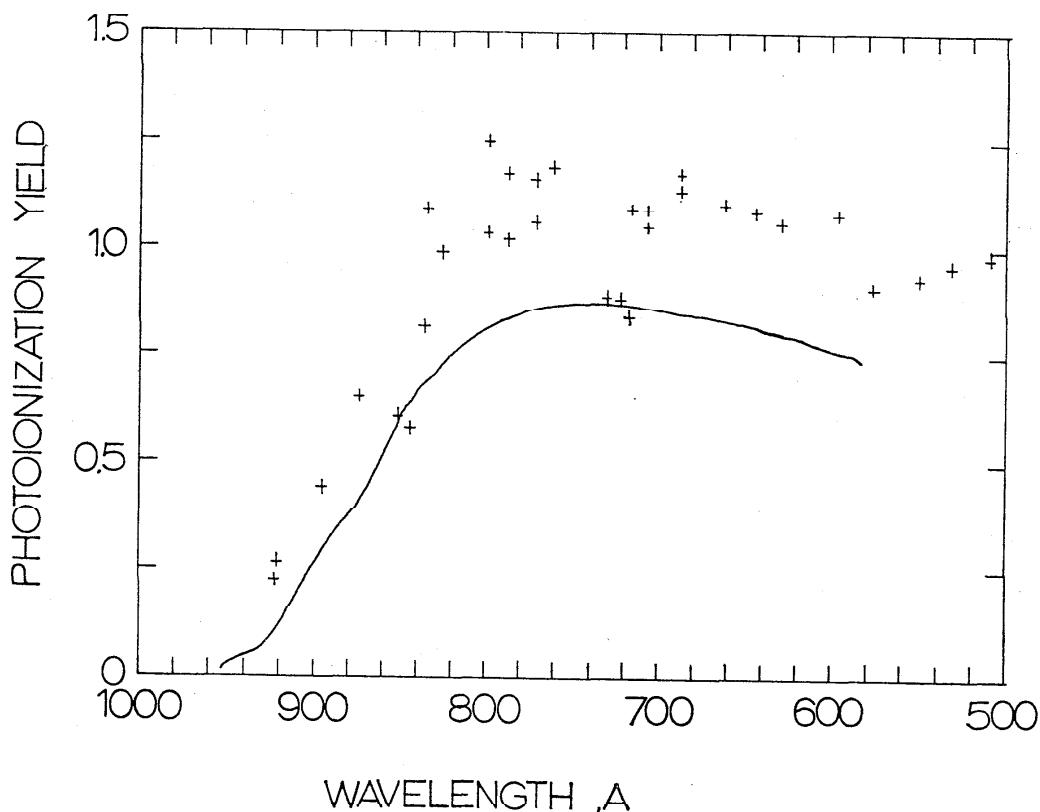

Fig. 57.   Comparison of measured photoionization yield data for CH_4 between 500 and 1000 A; solid line, *Metzger and Cook* [1964a]; +, *Wainfan et al.* [1955].

region has been investigated photographically by *Price and Simpson* [1938] and
by *Tanaka et al.* [1960*b*]. These two groups observed a large number of bands
between 750 A and 1000 A, most of which have been identified by Tanaka et al.
as Rydberg series leading to excited states of the ion, the ionization limits being
at 860 A and 760 A. The ionization potential would appear to be at 10.06 ev or
1232.5 A, and these Rydberg series appear to lie on a well-defined ionization
continuum.

Absolute photoabsorption cross sections and photoelectric yields have been
measured by *Cook and Ogawa* [1969*b*]. Figure 58 shows a plot of the photoioniza-
tion yield versus wavelength between 600 A and 1000 A. The yield would appear
to have a value of about 80% between 600 A and 800 A, although a considera-
tion of the errors in this measurement does not preclude the possibility that the
photoionization yield is 100% in this spectral region. The structure in the yield
between 700 A and 1000 A indicates that although the bands preionize to some
extent, predissociation must also be taking place, or, of course, excitation to
some upper state of the CS_2 molecule. Although the yield at the peak of
the Rydberg band will be bandwidth-dependent, there is nevertheless some
preionization, as is indicated by the ion current curve shown by the authors.

Photoionization efficiency (PE) measurements using mass spectrometers
have been obtained for carbon disulfide at an instrumental resolution of 2 A
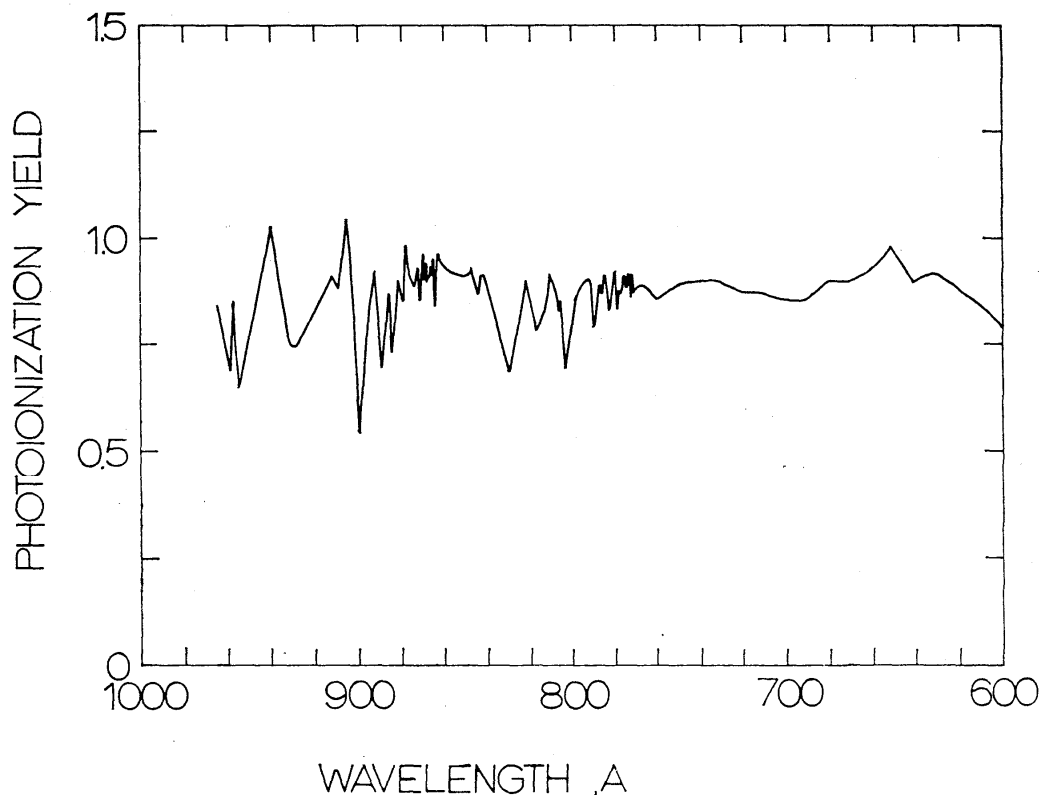

Fig. 58. Photoionization yield data for CS_2 between 600 and 1000 A, of *Cook and Ogawa*
[1969*b*].

by *Dibeler and Walker* [1967]. Apart from systematic errors, the authors estimate that the uncertainty of the photoionization efficiency is of the order of 1%, which is ascribed principally to the uncertainty of measuring the photon intensities. Unfortunately, there is no simple way in which the systematic error may be estimated for this work. These authors observe the formation of CS_2^+ ions, S_2^+, CS^+, S^+, and C^+ ions. Photoionization efficiency curves are shown for CS_2^+, CS^+, and S^+. The latter two curves will be subject to a large systematic error, since the ions are formed by dissociative ionization and therefore will have a finite amount of kinetic energy. There does not seem to be good agreement between the relative ionization cross sections of Dibeler and Walker and the absolute cross sections of Cook and Ogawa. Although some of this discrepancy can be ascribed to the effects of dissociative ionization, it does appear that the discrepancy is outside the errors one might ascribe to such a phenomenon.

Finally, the reader is cautioned when using the absolute data of Cook and Ogawa that the absorption cross sections given in the vicinity of the Rydberg bands could be subject to bandwidth dependence.

O. Sulfur Dioxide, SO_2

Absolute photoabsorption cross sections for sulfur dioxide have been limited to the wavelength range 1050 A to 3400 A. In this spectral region sulfur dioxide shows a complex absorption cross section, consisting of many band systems overlying apparent continua. The bands have been classified by *Duchesne and Rosen* [1947] and by *Metropolis* [1941]. Cross sections have been obtained by *Golomb et al.* [1962], who studied the region between 1050 A and 1850 A, by *Warneck et al.* [1964], who studied the spectral region between 1850 and 3150 A, and by *Thompson et al.* [1963], who studied the region between 1850 and 3400 A. All three groups employed photoelectric techniques, placing the absorption cell at the exit slit of the monochromator. Thompson et al. do not give their instrumental bandwidth, but both Golomb et al. and Warneck et al. quote an instrumental bandwidth of the order of 1 A. All three groups employed the hydrogen-molecular discharge tube as their light source. Both Warneck et al. and Golomb et al. determined the purity of their gas samples by mass spectrometric techniques. They determined the impurity to be less than 1% and to consist mainly of molecular nitrogen or carbon monoxide, neither of which should have interferred with the results of their absorption measurements.

Between 1060 A and 1350 A, Golomb et al. observed diffuse bands approaching the first ionization potential at about 1000 A. The bands in this region had been previously investigated by *Price and Simpson* [1938]. The absorption coefficients that were measured were independent of the pressure for some wavelengths; however, at the maxima of the bands, variations of up to 10% were observed for an eightfold increase in the pressure. Thus, one must expect the published results to be bandwidth-dependent. Between 1350 A and 1850 A, Golomb et al. observed that the band maxima showed considerable pressure dependence. The authors note that the figures they give reflect arbitrary straight-line connections of the measured points and do not necessarily represent the true shape of the absorption peaks. The authors quote an uncertainty for the absorp-

tion coefficient of about 10% where structure is displayed and less in the structureless portions. However, in view of the fact that these absorption curves must be bandwidth-dependent, this error seems a little small.

Between 1850 A and 3400 A a comparison can be made between the absorption cross sections obtained by these three groups. In general, the agreement is good, indicating that the three measurements were probably obtained with the same spectral bandwidth. The reader is cautioned that the results for sulfur dioxide over most of the wavelength intervals discussed in this review will be bandwidth-dependent.

P. Carbonyl Sulfide, COS

Absolute absorption cross sections for carbonyl sulfide have been obtained between 600 A and 1700 A. This spectral region has been studied photographically by *Price and Simpson* [1939] and by *Tanaka et al.* [1960b]. These authors identified fourteen progressions between 700 A and 1400 A, but they were unable to establish a definite Rydberg series converging to the first ionization potential at 1109.5 A. Tanaka et al. found four Rydberg series converging to a higher ionization potential at 773 A.

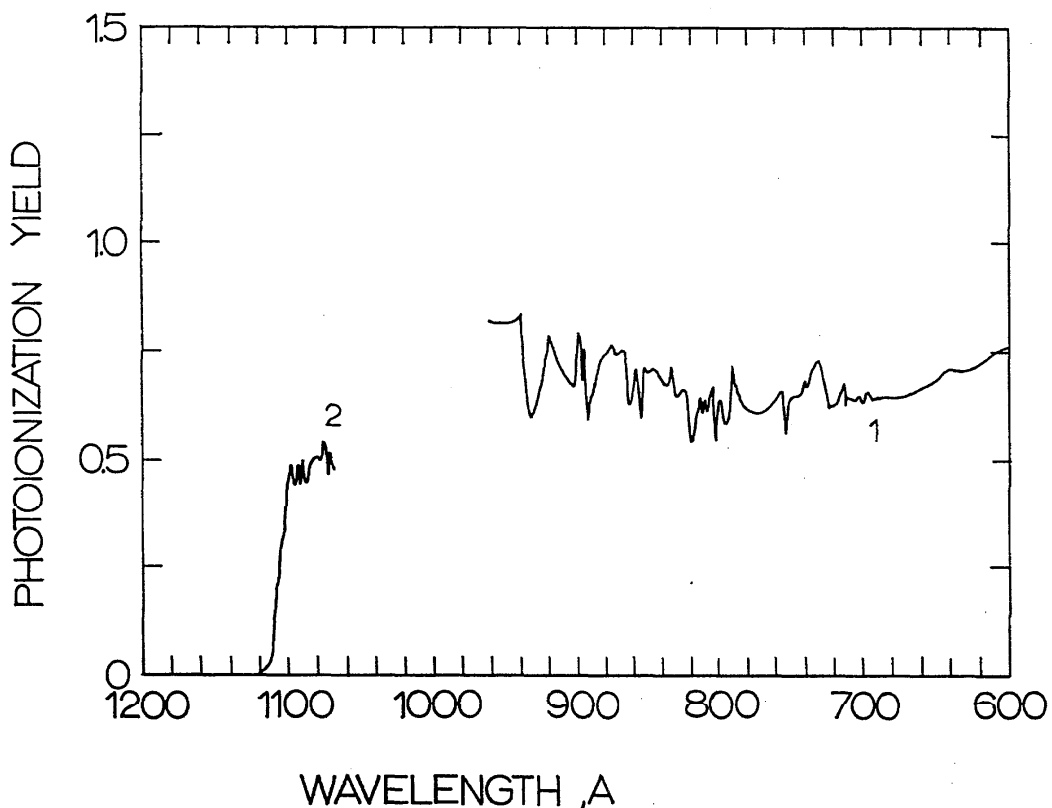Between 1070 A and 1700 A the only measurement of the total absorption

Fig. 59. Measured photoionization yield data for COS, between 600 and 1200 A; curve 1, *Cook and Ogawa* [1969a]; curve 2, *Matsunaga and Watanabe* [1967].

cross section available is that of *Matsunaga and Watanabe* [1967]. In the region between 1410 A and 1700 A these authors found strong bands whose peak values showed some apparent pressure effects, indicating that the shape of these bands will be strongly bandwidth-dependent. For this reason, it is not felt that the presence of underlying continua can be inferred at this time. Between 1100 A and 1410 A, the bands appear much sharper, and the authors report various degrees of pressure dependence. They regard their quoted values for the peaks to be semiquantitative only. The authors report that the cross sections between the bands were independent of pressure and suggest the presence of one or more dissociation continua. In view of the strong bandwidth dependence of the peaks, the authors' statement should be treated with caution. There appears to be no real evidence for underlying continua.

Only one measurement of the absolute photoabsorption cross section between 600 A and 1000 A is available, that of *Cook and Ogawa* [1969a]. Between 1000 A and 770 A, Cook and Ogawa observed the four series of Rydberg bands seen by Tanaka et al. Since the bands appear to be superposed on an ionization continuum and were seen in the ionization measurements, the authors concluded that the bands are all preionized. Between 770 A and 600 A there is a relatively
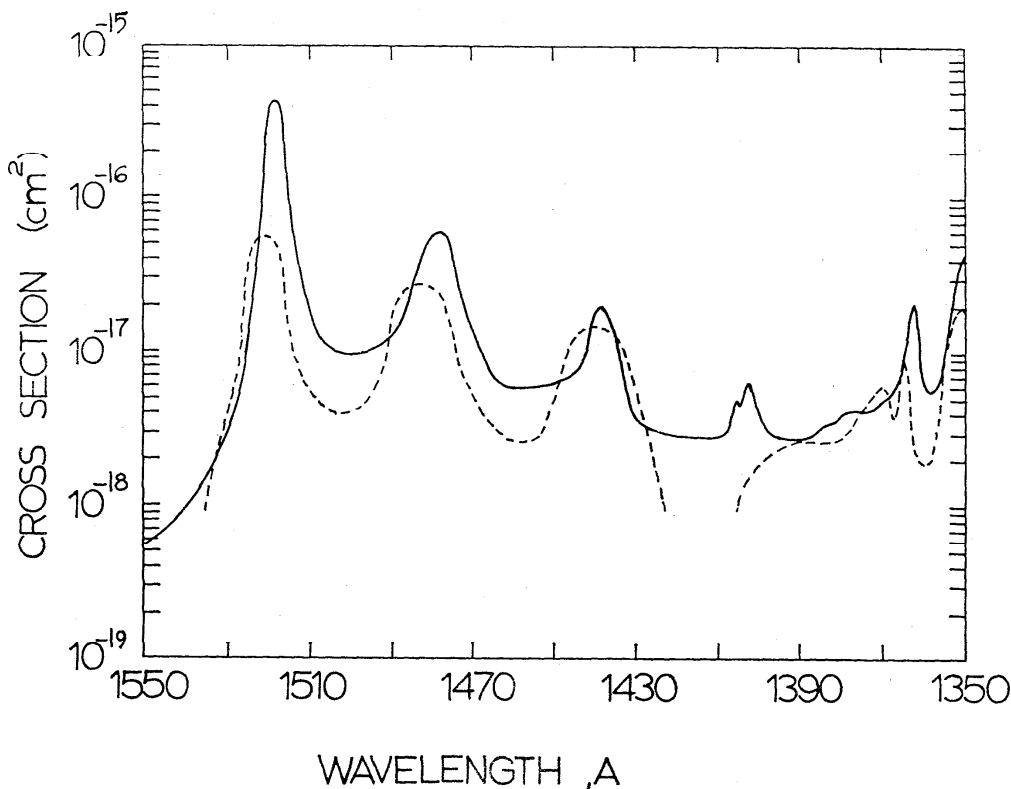

Fig. 60. Comparison of measured total absorption cross section data for C_2H_2 between 1350 and 1550 A; solid line, *Nakayama and Watanabe* [1964]; dashed line, *Moe and Duncan* [1952].
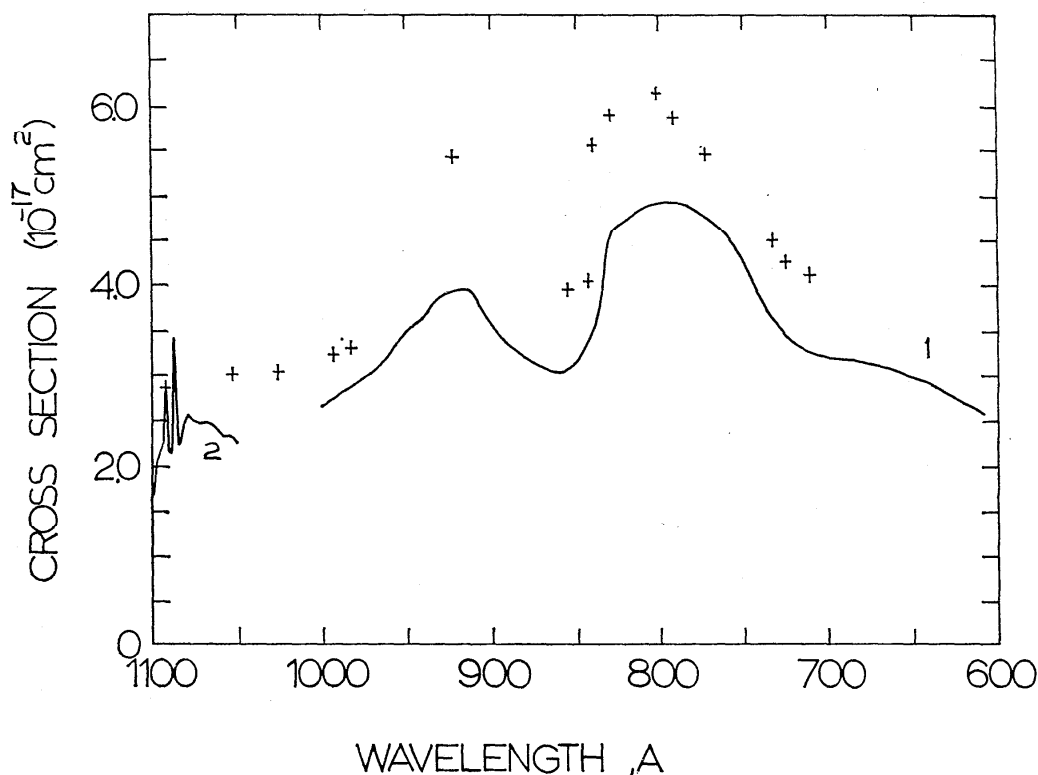
Fig. 61. Comparison of measured total absorption cross section data for C_2H_2 between 600 and 1100 A; curve 1, *Metzger and Cook* [1964]; curve 2, *Nakayama and Watanabe* [1964]; +, *Walker and Weissler* [1955b].

smooth continuum with some 'apparent emission' lines. The ionization yield was not observed to be larger than 75%, but it is likely that a probable error of at least ±25% must be applied to this measurement. Thus, the authors' conclusion that a steady dissociation continuum is apparent in this wavelength interval is open to some doubt. The photoionization yield of Matsunaga et al. and Cook and Ogawa between 600 A and 1200 A is given in Figure 59.

The photoionization efficiency obtained with mass spectrometric techniques has been measured by *Dibeler and Walker* [1967] at an instrumental bandwidth of 2 A. There is essential agreement between these relative data and photo-ionization cross sections of Cook and Ogawa in the over-all shape of the cross-section curve.

Q. Acetylene, C_2H_2

Absolute absorption cross sections for acetylene have been obtained between 600 A and 2000 A. The absorption spectrum between 600 A and 1000 A consists of ionization or dissociation continua with no overlying band structure. Between 1000 A and 1600 A the spectrum consists of band structure, which *Price* [1935] and *Wilkinson* [1958] have interpreted as members of two Rydberg series with their vibrational companion and two non-Rydberg-type bands. The spectral

region between 1550 A and 2000 A has been studied photographically by *Herzberg* [1931], *Wilkinson* [1958], and *Price and Walsh* [1945]. However, the complex spectrum of diffuse bands observed has not as yet been analyzed.

The absorption cross sections of acetylene between 1000 A and 1600 A have been investigated by *Nakayama and Watanabe* [1964] and by *Moe and Duncan* [1952]. At wavelengths less than 1350 A, Nakayama and Watanabe report that the peak values showed an apparent pressure effect that indicates strong bandwidth dependence for the measured line shapes. Although this effect is not mentioned specifically by Moe and Duncan, they are concerned in their paper about the bandwidth dependence of their results. A comparison of the results of these two groups shows, however, that there are large discrepancies not only in these regions of sharp bands but also where the bands are most diffuse, that is, between 1350 A and 1550 A. A comparison of the results in this region is given in Figure 60. Similar differences between the data of these two groups are also seen in a comparison of their cross-section measurements between 1100 A and 1350 A. The agreement at 1080 A where the spectrum is continuous is just within the mutual experimental errors. The results of Nakayama and Watanabe agree best, however, with isolated measurements using a line emission source obtained by *Walker and Weissler* [1955b].
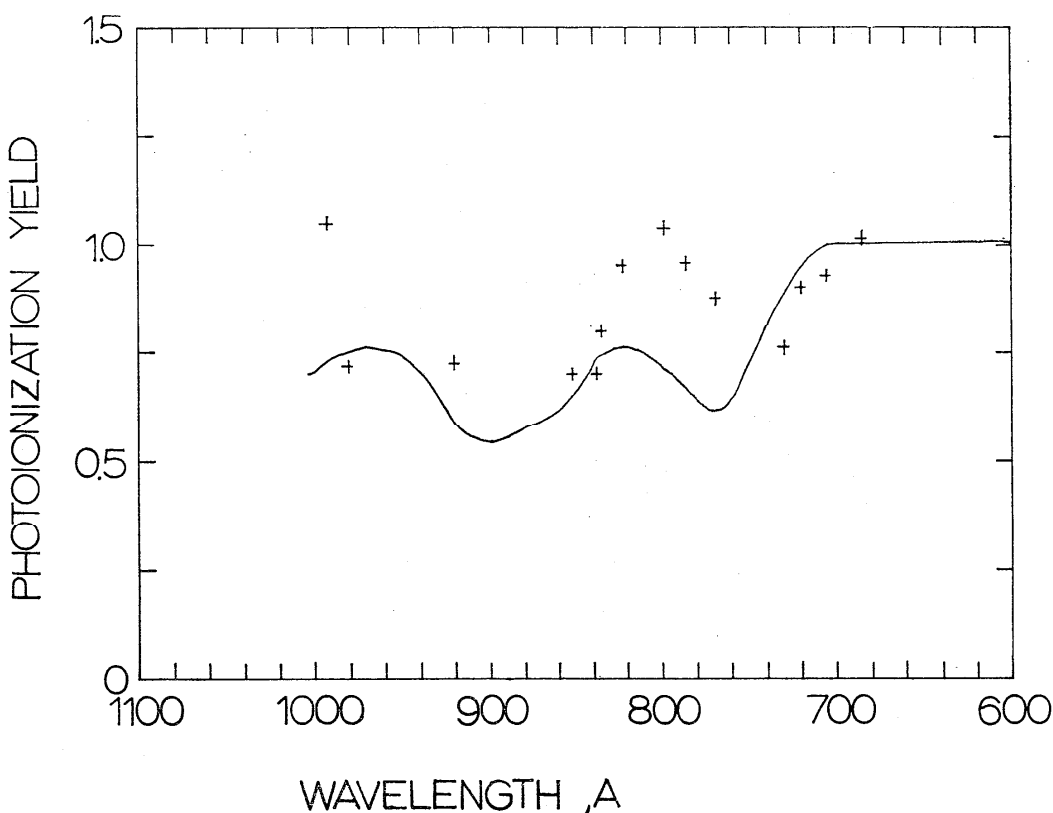

Fig. 62. Comparison of measured photoionization yield data for C_2H_2 between 600 and 1000 A; solid line, *Metzger and Cook* [1964a]; +, *Walker and Weissler* [1955b].
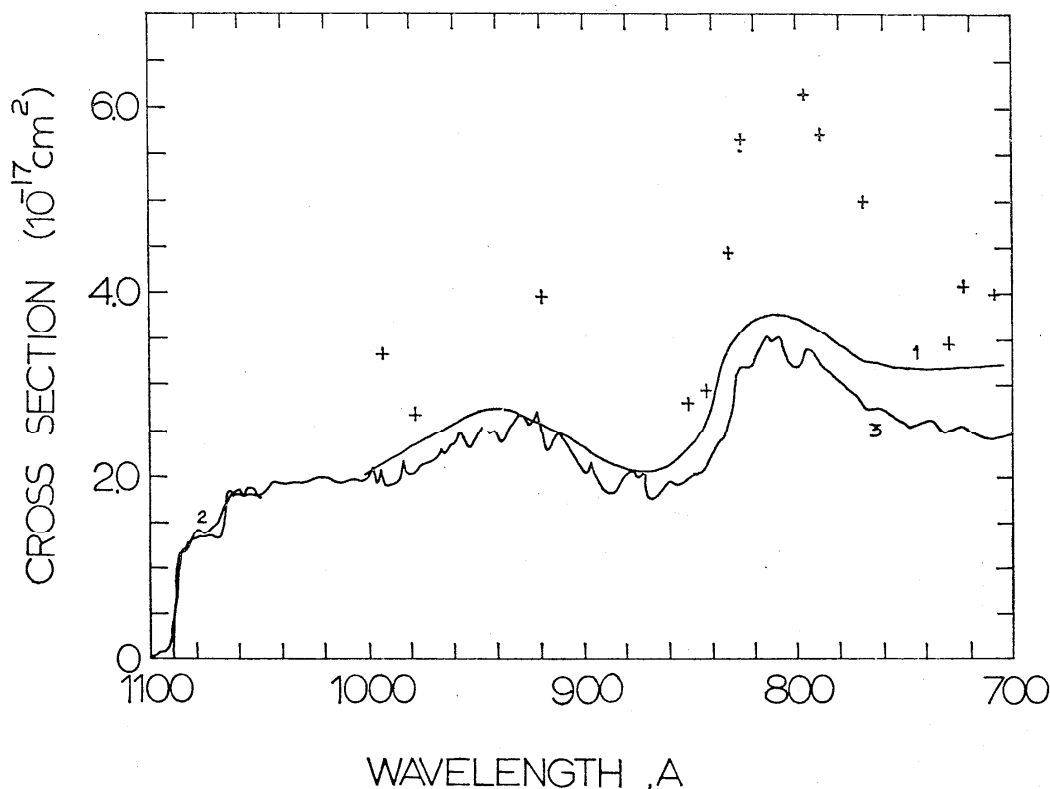
Fig. 63. Comparison of ionization cross section data for C_2H_2 between 700 and 1100 A; curve 1, normalized data of *Botter et al.* [1966a]; curve 2, *Nakayama and Watanabe* [1964]; curve 3, *Metzger and Cook* [1964a]; +, *Walker and Weissler* [1955b].

The total absorption cross sections and photoionization yields have been measured between 600 A and 1100 A by *Metzger and Cook* [1964a] and *Walker and Weissler* [1955b]. In Figure 61 a comparison is shown between the photo-absorption cross sections obtained by these two groups between 600 A and 1100 A. The data obtained by Nakayama for the short range between 1016 A and 1100 A are also shown. The agreement at 1100 A is not particularly good. In Figure 62 the yield data between 600 A and 1100 A are compared. It will be noticed that the agreement is reasonable at 700 A but gets worse at longer wavelengths.

The photoionization efficiency, as measured by *Botter et al.* [1966a] at an instrumental resolution of 2 A was obtained by use of both the helium and the argon continuum light source. Photodetectors of tungsten, gold, and aluminum that were standardized from photoionization efficiency curves obtained for the inert gases were used. For this region the relative ionization cross sections should be good. In Figure 63 the normalized data of this group are shown with values of the photoionization cross section obtained by Metzger and Cook, the data being normalized at 1000 A. The curve extends to 750 A only, since at this point dissociative ionization takes place. The agreement between the two curves

is reasonable, although the data of Botter et al. indicate some structure at the broad maxima at 925 A and 800 A.

R. Ethylene, C_2H_4

The absorption cross section for ethylene has been investigated between 600 A and 2000 A. In the spectral region between 600 A and 1181 A, the ionization potential, the spectrum consists of dissociation and/or ionization continua. Between 1040 A and 2000 A band structure has been observed, and photographic measurements have been made by *Scheibe and Greineisen* [1934], *Price* [1935], *Price and Tutte* [1940], and *Wilkinson and Mulliken* [1955].

The absorption cross sections in the vicinity of the bands have been investigated by *Zelikoff and Watanabe* [1953] and by *Wilkinson and Johnston* [1950]. *Wilkinson and Mulliken* [1955] have stated that the data of Zelikoff and Watanabe are to be preferred over the earlier work of Wilkinson and Johnston; thus only the data of the former group have been considered in this review. Zelikoff and Watanabe found no pressure dependence for the measured cross sections over the entire wavelength region between 1040 and 2000 A; however,
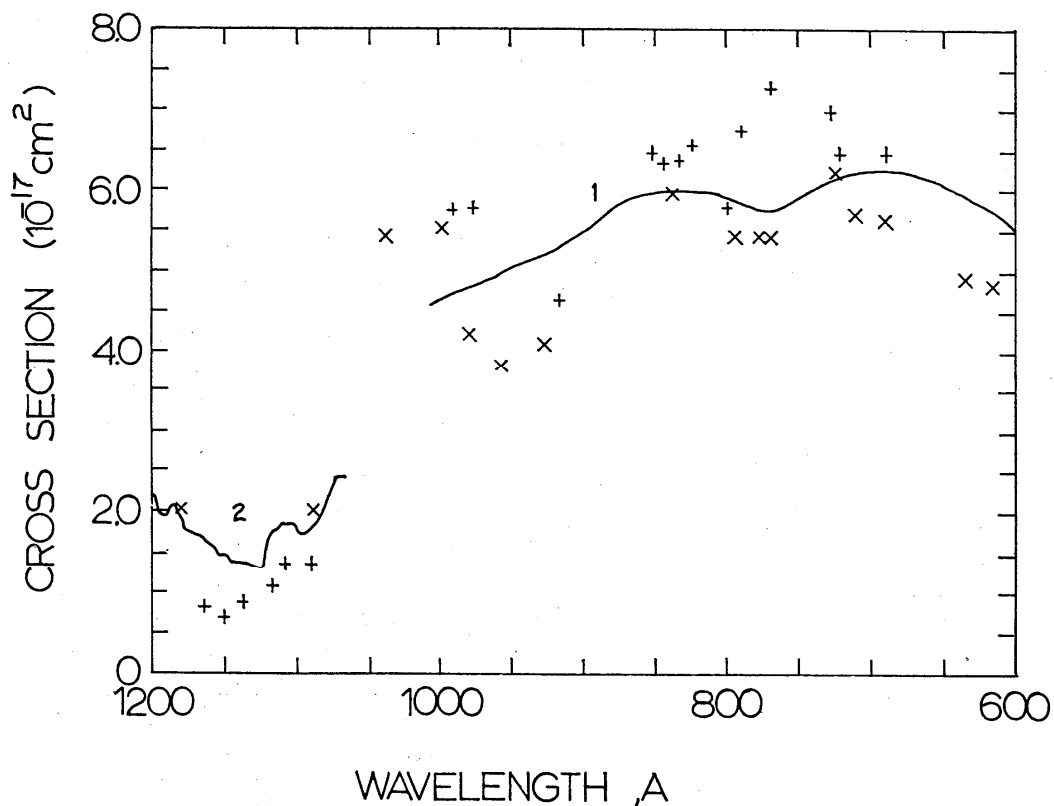

Fig. 64. Comparison of measured total absorption cross section data for C_2H_4 between 600 and 1200 A; curve 1, *Metzger and Cook* [1964a]; curve 2, *Zelikoff and Watanabe* [1953]; +, *Walker and Weissler* [1955b]; ×, *Schoen* [1962].
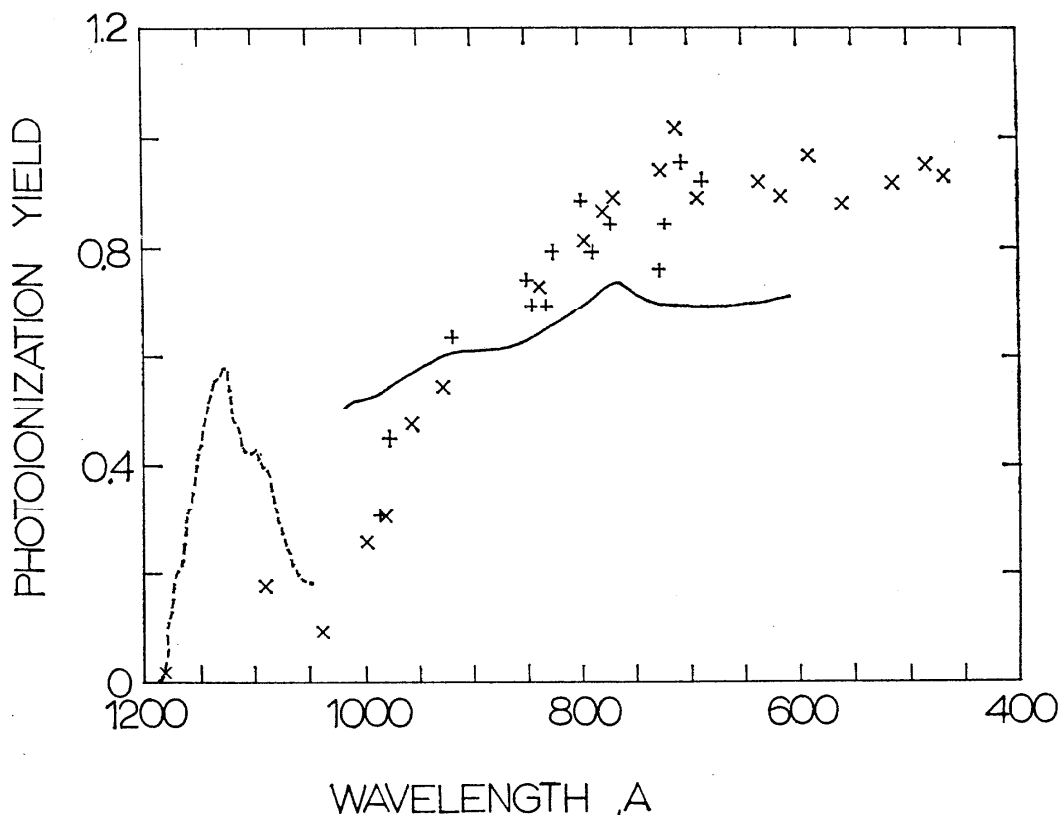
Fig. 65. Comparison of measured photoionization yield data for C_2H_4 between 400 and 1200
A; solid line, *Metzger and Cook* [1964a]; dashed line, *Person and Nicole* [1968]; +, *Walker
and Weissler* [1955b]; ×, *Schoen* [1962].

in view of the band structure observed, the cross sections and line shapes are
likely to be bandwidth-dependent. The authors discuss the appearance of con-
tinua between 1090 A and 1360 A, but these comments should be treated with
some caution in light of previous discussions in this review. Recent measure-
ments by *Person and Nicole* [1968], over the limited wavelength range 1050 A
to 1192 A, are in good agreement with those of Zelikoff and Watanabe.

Absorption cross sections between 600 A and 1000 A have been measured
by *Walker and Weissler* [1955b], by *Schoen* [1962], and by *Metzger and Cook*
[1964a]. A comparison of the results of these three groups and those of Zelikoff
and Watanabe between 600 A and 1200 A is given in Figure 64. Within the
apparent scatter in the data that were obtained using the line emission light
sources, these sets of data would appear to agree, although it is obvious that the
experimental errors must be larger than the authors have quoted.

These three groups and Person and Nicole also measured the photoionization
yield, and their results are compared in Figure 65. All groups used a secondary
standard to determine the absolute photon flux. Metzger and Cook used a
platinum photodiode; both Schoen and Walker and Weissler used a sodium-
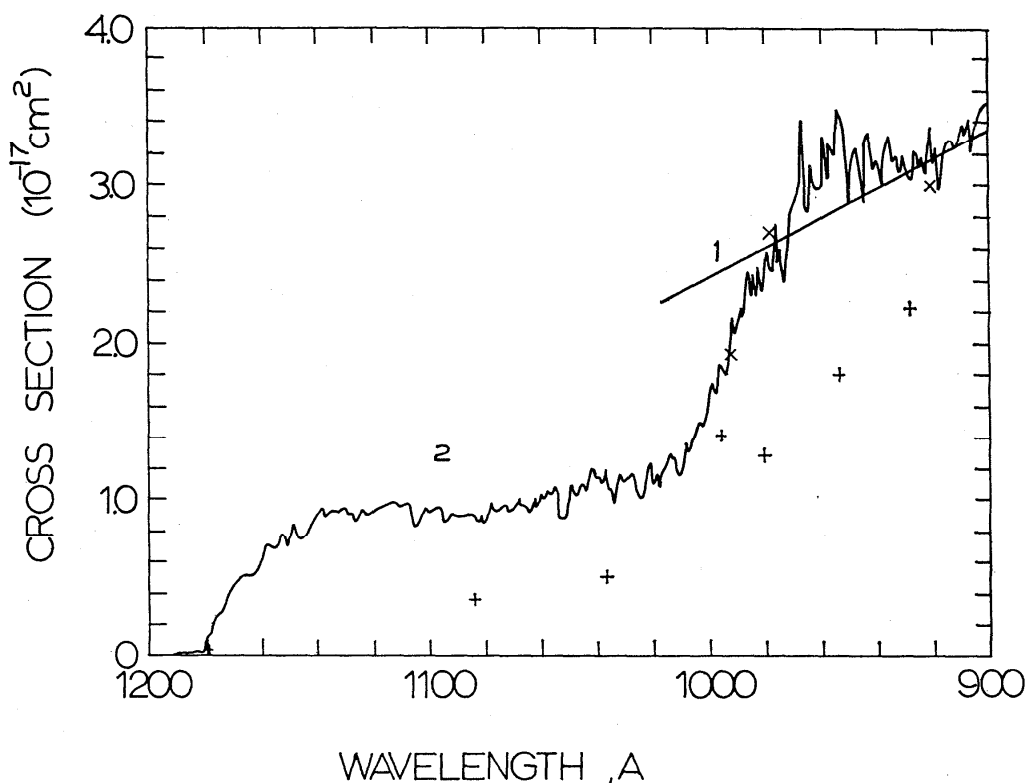salicylate-coated photomultiplier; and Person and Nicole used a nitric oxide

Fig. 66. Comparison of photoionization cross section data for C_2H_4 between 900 and 1200 A; curve 1, *Metzger and Cook* [1964a]; curve 2, normalized data of *Botter et al.* [1966b]; ✕, *Walker and Weissler* [1955b]; +, *Schoen* [1962].

ionization chamber. Metzger and Cook assign a reliability of ±10%, to their data, Walker and Weissler ±10%, Schoen ±5%, and Person and Nicole ±10%. The data of Walker and Weissler and of Schoen would seem to be consistent, although the data of Walker and Weissler have more scatter and differ from those of Metzger and Cook, not only in magnitude, but also in shape, especially near 1000 A. The data of Person and Nicole (1050–1181 A) agree in shape with those of Schoen, but have a higher magnitude.

The photoionization efficiency (PE) has been measured by *Botter et al.* [1966b] by the use of mass spectrometric techniques at an instrumental resolution of 2 A. Unfortunately, one can only compare these data with the ionization cross sections of the groups discussed above at wavelengths longer than 950 A, since Botter et al. see the onset of dissociative ionization at this wavelength. Such a comparison is shown in Figure 66, where the relative ionization cross sections of Botter have been normalized at 900 A to a value of 3.5 × 10⁻¹⁷ cm².

S. Ethane, C_2H_6

The absorption cross section of ethane has been investigated between 600 and 1200 A, over which spectral range the cross section has been observed to be essentially continuous. Photoabsorption cross sections have been measured by
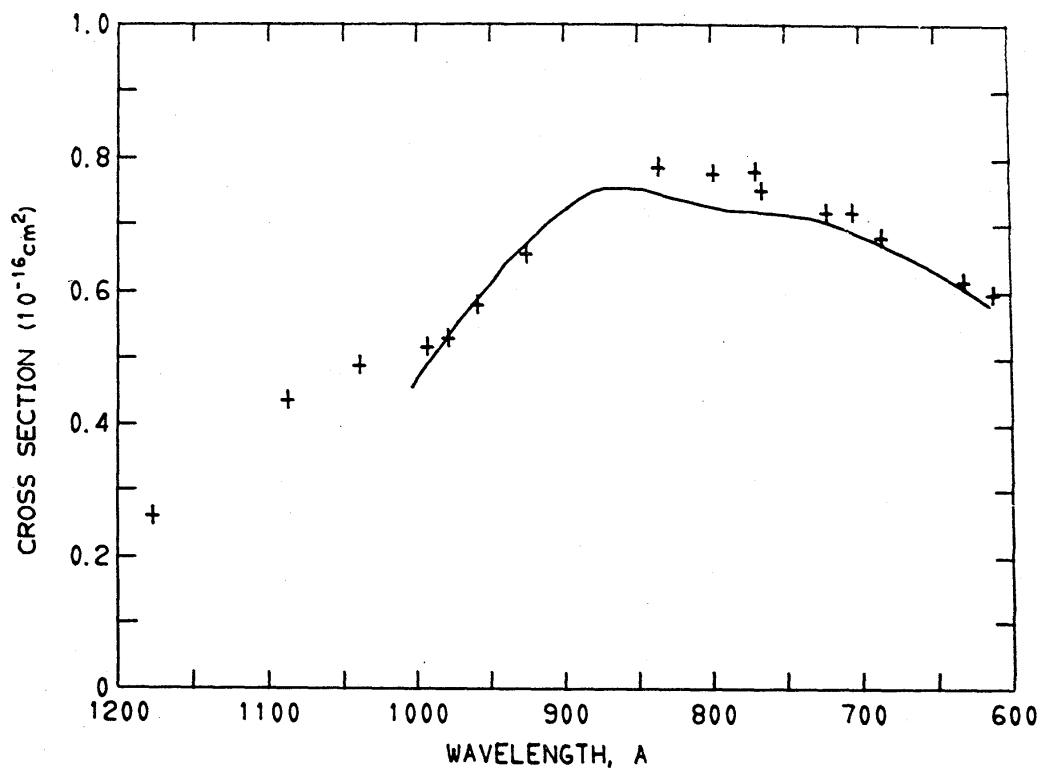
Fig. 67. Comparison of measured total absorption cross section data for C_2H_6 between 600 and 1200 A; solid line, *Metzger and Cook* [1964a]; +, *Schoen* [1962].
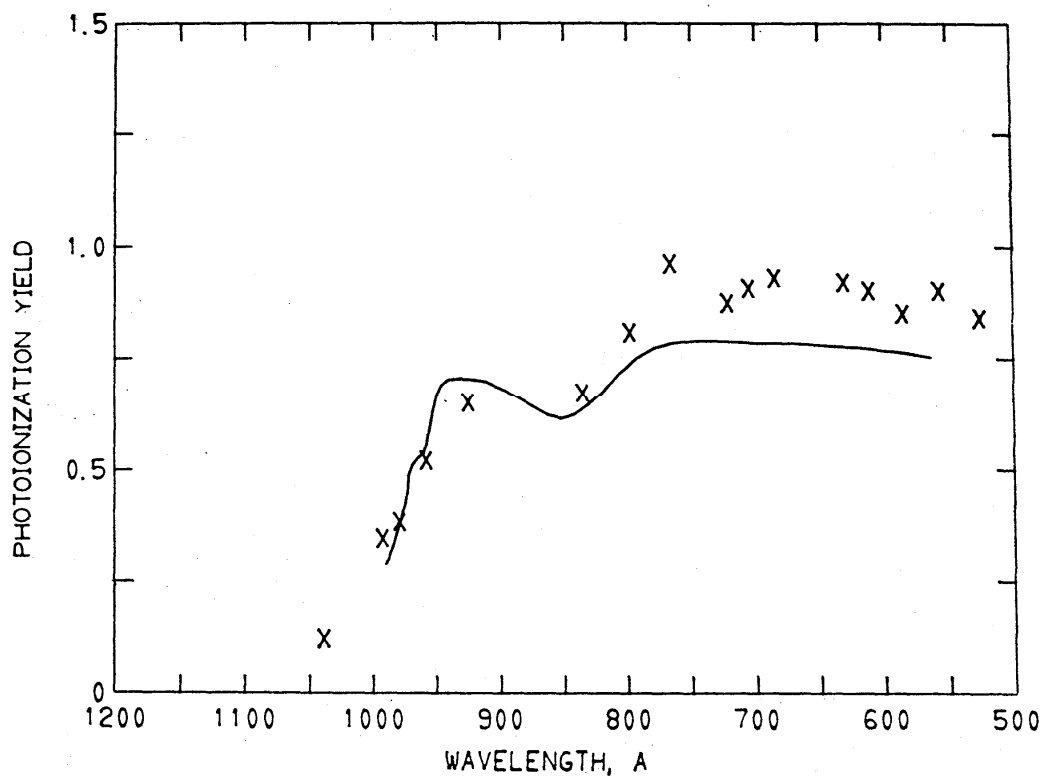

Fig. 68. Comparison of measured photoionization yield data for C_2H_6 between 500 and 1050 A; solid line, *Metzger and Cook* [1964a]; ×, *Schoen* [1962].

Schoen [1962] and by *Metzger and Cook* [1964a]. Figure 67 shows a comparison of the results obtained for the absorption cross section by these two groups. There would appear to be essential agreement on the over-all shapes and cross sections for ethane. A comparison of the photoionization yield obtained by these two groups is shown in Figure 68. Again, there is good agreement between these groups except at shorter wavelengths, where the data of Schoen indicate 100% yield, whereas those of Metzger and Cook indicate 80% yield.

The photoionization efficiency of ethane with mass spectrometric techniques has been measured by *Chupka and Berkowitz* [1967]. This work was performed at an instrumental band of 1.66 A, the photon flux being detected with a sodium-salicylate–coated photomultiplier. This detector had previously been calibrated and shown to have a sensitivity independent of wavelength in the region covered, namely between 890 and 1000 A. The over-all shapes obtained by Schoen, by Metzger and Cook, and by Chupka and Berkowitz cannot be compared easily in this spectral range, since dissociative ionization was observed to begin at 1000 A.

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