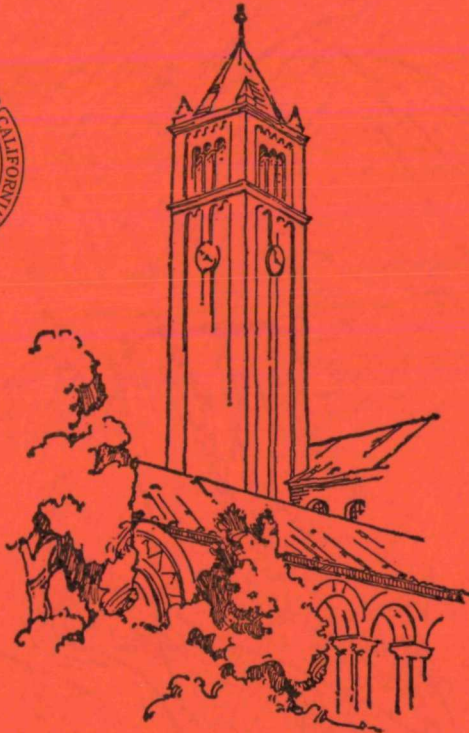
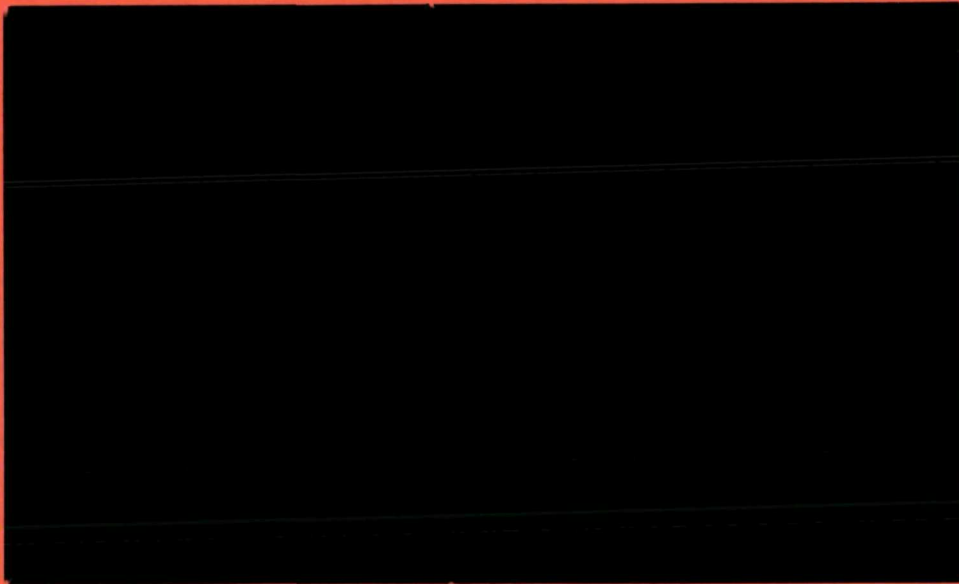


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DEPARTMENT OF PHYSICS
University of Southern California
Los Angeles, California 90007

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FOR THE PERIOD ENDING OCTOBER 31, 1971

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Darrell L. Judge
Principal Investigator
University of Southern California
Los Angeles, California 90007

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INTRODUCTORY COMMENTS

The present report summarizes the progress from the initial funding period, February 25, 1970 through October 31, 1971. Reporting periods have been combined both because of the nature of the work and because the initial funding, February 25, 1970, was six months late.

One phase of the work has been the long term evaluation of channeltrons while the second phase has been a study of photon/gas interactions with emphasis on photodissociation processes. In the channeltron evaluation the primary concern is with the effects which occur on a time scale of the order of years. The research effort on photon/gas interactions required that a new laboratory be set up and the first six-month period was occupied with such an endeavor.

A brief report on our progress during the first funding period is contained in the letter proposal to Dr. Robert Fellows dated March 26, 1971 requesting continuation of our NASA grant.

ELECTRONIC TRANSITION MOMENTS FOR THE
A $\rightarrow$ X, B $\rightarrow$ X, AND B $\rightarrow$ A TRANSITIONS IN CO $^+$
AND THE A $\leftarrow$ X AND B $\leftarrow$ X MOMENTS FOR THE CO $\rightarrow$ CO $^+$ SYSTEMS;
ABSOLUTE CROSS SECTIONS FOR THE ABSORPTION PROCESSES *

D. L. Judge and L. C. Lee
Department of Physics
University of Southern California
Los Angeles, California 90007

ABSTRACT

The A $\rightarrow$ X, B $\rightarrow$ X and B $\rightarrow$ A bands of CO $^+$ have been excited using monochromatic photons and the band intensities measured. Using such data the variation of the electronic transition moments for these above emission bands as well as for the absorption bands, CO(X $^1\Sigma^+$, $v'' = 0$) $\rightarrow$ CO $^+$ (A $^2\Pi_i$, $v' = 0-8$) and CO $^+$ (B $^2\Sigma^+$, $v' = 0, 1$), have been determined. Further, the specific cross sections for the absorption processes have been determined by measuring the total emission intensity in the band system through which the upper state decays. The band intensity measurements and the derived results are presented in the ensuing discussion.

* This research was supported by NASA Contract # NGR 05-018-138.

I. INTRODUCTION

In the present work photon excitation was used to excite ground state CO molecules into various levels of the ion and the resulting emission intensity was measured. This is in contrast with earlier work by Robinson and Nicholls¹ who studied the comet-tail band intensities using 60-100 eV electrons to obtain the excited ions. Both experimental results have been interpreted according to a method proposed by Fraser² to establish the variation of the electronic transition moments. The specific cross section measurements have not been previously obtained.

The measured intensity $I_{v',v''}$ of the (v',v'') band of a system may be written as

$$I_{v',v''} = KN_{v'} R_e^2(\bar{r}_{v',v''}) q_{v',v''} / \lambda_{v',v''}^4$$

where K is a constant, $N_{v'}$ is the population of molecules in the level v' of the upper electronic state of the system of interest, $R_e(\bar{r}_{v',v''})$ is the electronic transition moment, and $\bar{r}_{v',v''}$, $q_{v',v''}$, and $\lambda_{v',v''}$ are the r -centroid, Franck-Condon factor, and wavelength of the (v',v'') band, respectively.

The Franck-Condon factors and the r -centroids for the band systems of CO^+ have been computed by Nicholls³ using Morse potentials and by Jain and Sahni⁴ using Rydberg-Klein-Rees (RKR) potential energy curves. We have adopted the latter data for our analysis of the emission band transition moments. The precise wavelengths, $\lambda_{v',v''}$, for the transitions of interest have been collected and published by Krupenie⁵. Thus, with the intensity measurements we can plot $N_{v'} R_e^2(\bar{r}_{v',v''}) = I_{v',v''} \lambda_{v',v''}^4 / K q_{v',v''}$ against $\bar{r}_{v',v''}$. Such a plot consists of a number of segments, one for each

v'' progression ($v' = \text{constant}$). Normalizing the data ($N_{v'}, R_e^2$) for each segment as in Robinson and Nicholls¹ work, i.e., making the area under the overlapped segments equal, permits the relative number of molecules in the upper state to be determined and a plot of $R_e(\bar{r}_{v',v''})$ for the emission bands can then be given.

The absorption intensity from the neutral ground state to the ionization state of interest is given by

$$I_{v',0}^{\text{abs}} = K' R_e^2(\bar{r}_{v',0}) q_{v',0} / \lambda_{v',0} = K'' N_{v'} / \lambda_{v',0}$$

Thus, $R_e(\bar{r}_{v',0}) = K'' (N_{v'} / q_{v',0})^{\frac{1}{2}}$ and the relative variation of the electronic transition moment can be displayed by plotting the relative values of $(N_{v'} / q_{v',0})^{\frac{1}{2}}$ against $\bar{r}_{v',0}$. The Franck-Condon factors $q_{v',0}$ for transitions from the neutral ground state ($X^1\Sigma^+, v'' = 0$) to the ionization states $B^2\Sigma^+$ and $A^2\Pi_i$ have been computed by both Wachs⁶ and Halmann and Laulicht⁷ using Morse potentials. The calculations of Wachs are used although no differences appear in their results.

II. EXPERIMENTAL

The apparatus employed in the fluorescence investigations is shown in Fig. 1. Here, the vacuum ultraviolet light⁸ was obtained from a condensed spark discharge through a boron nitride capillary containing either air, nitrogen, or argon at a pressure of about 20×10^{-3} Torr. The source was operated at 40 pulses/sec with a pulse duration of approximately 5 μsec . The emission lines of interest were isolated by a one-meter normal incidence monochromator (McPherson 225). The selected

quantum efficiency ¹⁰. The region between 1800 and 2700Å could be observed directly with the 9558QB phototube which has a constant quantum efficiency in this range. The experimental errors arise from fluctuation of the light source intensity, optical calibration, and noise of the electronic equipment. The resulting experimental error is less than 15%.

III. EXPERIMENTAL RESULTS

A. The Fluorescence Spectrum

A typical fluorescence spectrum resulting from 555Å (22.4 eV) photon impact on CO is shown in Fig. 2. The bandhead data given by Krupenie ⁵ have been used to identify this spectrum which is characteristic of all spectra resulting from incident photons with sufficient energy (20.2 eV) to excite CO molecules up to the $v' = 2$ level of the $\text{CO}^+(\text{B } ^2\Sigma^+)$ state. For lower incident energies only successively lower states of excitation are possible as it illustrated in Figs. 3 and 4. Fig. 3 shows the B→X spectrum of CO^+ for various incident energies while Fig. 4 shows the A→X and B→A spectra, again for various incident energies. The features which appear at 3914, 4390, and 4610Å are spurious, and correspond to the 0-0 transition of $\text{N}_2^+(\text{B} \rightarrow \text{X})$ and the second order transitions of the 0-0 and 0-1 bands of B→X of CO^+ , respectively. These have been deleted from the data on R_e and $N_{v'}$. The band intensities used throughout have been determined by measuring the area under the curve associated with each band.

The results obtained in the analysis of the various band systems are presented in the following sections.

B. $A \ ^2\Pi_i \rightarrow X \ ^2\Sigma^+$ Bands

The plot of $N_{v'} R_e^2(\bar{r}_{v',v''})$ vs. $\bar{r}_{v',v''}$, the r-centroid, for the $A \ ^2\Pi_i \rightarrow X \ ^2\Sigma^+$ transition excited by photons of 686Å is shown in Fig. 5, where it may be noted that the $N_{v'} R_e^2(\bar{r}_{v',v''})$ segments for each v'' -progression are constant within 10%. The constancy of $R_e(\bar{r}_{v',v''})$ derived from different photon-excitation data is shown in Fig. 6. Here, $R_e(\bar{r}_{v',v''})$ for all $(v',0)$ bands are shown normalized. It is clear from the plot that no statistically significant deviations from constant R_e occur.

C. $B \ ^2\Sigma^+ \rightarrow X \ ^2\Sigma^+$ Bands

In Fig. 7, $N_{v'} R_e^2(\bar{r}_{v',v''})$ vs. $\bar{r}_{v',v''}$ for the $B \ ^2\Sigma^+ \rightarrow X \ ^2\Sigma^+$ transitions has been plotted for the case of photon excitation at 555Å. From the plot it is seen that $N_{v'} R_e^2(\bar{r}_{v',v''})$ is constant for each v'' progression within 10% and $R_e(\bar{r})$ is therefore constant. A plot of $R_e(\bar{r}_{v',v''})$ vs. $\bar{r}_{v',v''}$ is given for various incident photon energies in Fig. 8.

D. $B \ ^2\Sigma^+ \rightarrow A \ ^2\Pi_i$ Bands

Only the (0-0) and (0-1) bands were observed for the $B \ ^2\Sigma^+ \rightarrow A \ ^2\Pi_i$ transitions when CO was excited by photons which had an energy higher than 19.7 eV, the energy required to reach the second vibrational level. Since only two data points exist for the measurement of $R_e(\bar{r})$ it has not been plotted but it is constant as found for the other emission systems.

E. $CO(X \ ^1\Sigma^+, v'' = 0) \rightarrow CO^+(A \ ^2\Pi_i, v' = 0-8)$ Bands

The dependence of the electronic transition moment R_e^2 abs on the r-centroid is proportional to the bandstrength for the band of interest,

the proportionality constant being the appropriate Franck-Condon factor. The band strengths, $p_{v',v''}$, for the absorption transitions are proportional to $N_{v'}$, the relative values of which are obtained from the intensity ratios of the v' progressions, i.e., the normalization factors used earlier in normalizing the $R_e(\bar{r})$ for the $A \rightarrow X$ system of CO^+ . The band strength is related to the band intensity in absorption according to

$$I_{v',v''}^{\text{abs}} = K_1 R_e^2 \frac{\text{abs}}{v',v''} q \frac{\text{abs}}{v',v''} \frac{\text{abs}}{v',v''} = K_1 \frac{\text{abs}}{v',v''} p_{v',v''}.$$

And

$$I_{v',v''}^{\text{abs}} = K_2 N_{v'} \frac{\text{abs}}{v',v''}$$

Combining the results of the above two equations, the band strength is thus seen to be

$$p_{v',v''} = K_3 N_{v'},$$

as stated above.

The measured band strengths for the $CO(X^1\Sigma^+, v'' = 0) \rightarrow CO^+(A^2\Pi_i, v' = 0-8)$ system are given in Table I.

Table I
Relative Band Strengths for the
 $CO(X^1\Sigma^+, v'' = 0) \rightarrow CO^+(A^2\Pi_i, v' = 0-8)$ System

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	.47	.91	1.0	.83	.61	.39	.23	.12	.06

The variation of $R_{e_{v',v}}^{abs}$ with v' then is just

$$R_{e_{v',v}}^{abs} = \left(\frac{p_{v',v''}}{q_{v',v''}^{abs}} \right)^{\frac{1}{2}}$$

and is plotted in Fig. 9.

F. $\text{CO}(X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+(B^2\Sigma^+, v' = 0, 1)$ Bands

The band strength and the variation of the electronic transition moment for these bands have been determined in the same manner as for the $\text{CO}(X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+(A^2\Pi_i, v' = 0-8)$ bands. The relative band strengths are $p_{0,0} : p_{1,0} = 1.0 : 0.36$. R_e^{abs} vs. v' is given in Fig. 10.

G. Cross Section for the $\text{CO}(X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+(A^2\Pi_i, v'=0-8)$ and $\text{CO}(X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+(B^2\Sigma^+, v' = 0-1)$ Bands

The absolute cross sections for the above systems were determined by measuring the total population of the upper states relative to nitrogen, for which the cross section for the $\text{N}_2(X^1\Sigma_g^+, v'' = 0) \rightarrow \text{N}_2^+(B^2\Sigma^+, v' = 0)$ band are known to be $2.2 \times 10^{-18} \text{ cm}^2$. The cross sections are equal to the total population, $\sum_{v'} N_{v'}$, multiplied by a normalization constant, i.e.,

$$\sigma = K \sum_{v'} N_{v'}$$

where the normalization constant is determined through comparison with the nitrogen fluorescence measurements. Fig. 11 shows the cross sections as a function of incident photon energy. For incident photon energies beyond threshold, the cross section for the $\text{CO}(X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+(A^2\Pi_i,$

$v' = 0-8$) bands is about $9 \times 10^{-18} \text{ cm}^2$ and, for the $\text{CO}(\chi^1 \Sigma^+, v'' = 0) \rightarrow \text{CO}^+(\text{B}^2 \Sigma^+, v' = 0,1)$ bands is about $1.5 \times 10^{-18} \text{ cm}^2$. The sum of the band strengths of the $\text{CO}^+(\text{B}^2 \Sigma^+, v' = 0) \rightarrow \text{CO}^+(\text{A}^2 \Pi_i, v'' = 0,1)$ transitions is about 8% of that of the $\text{CO}^+(\text{B}^2 \Sigma^+, v' = 0,1) \rightarrow \text{CO}^+(\chi^2 \Sigma^+, v'' = 0-4)$ bands.

H. Fluorescence Pressure Dependence

In order to ensure that the emission process was only through radiation the pressure dependence of the fluorescence intensity was studied. The fact that at low pressure the fluorescence intensity is proportional to the number of photons absorbed confirms that the emission process is only through radiation. It has been noted that the fluorescence intensity from the $v' = 0$ level of $\text{CO}^+(\text{A}^2 \Pi_i)$ state continues to increase up to a pressure of about $50 \times 10^{-3} \text{ Torr}$, whereas the fluorescence intensities from most of the levels only increase up to approximately $30 \times 10^{-3} \text{ Torr}$. This intensity enhancement of the $v' = 0$ level of $\text{CO}^+(\text{A}^2 \Pi_i)$ is attributed to "dumping" of the higher vibrational levels through collisional relaxation into the lowest level of the state.

IV. CONCLUDING REMARKS

It has been shown that all of the electronic transition moments measured here are independent of the r -centroid. This result is in disagreement with the work of Robinson and Nicholls¹ who found a systematic variation of $R_e(\bar{r})$ for the comet-tail system but is in agreement with the semiempirical results of Spindler and Wentink¹² and is further confirmed by the lifetime measurements of Fink and Welge¹³ and Bennett and Dalby¹⁴. To compute R_e from the lifetime data recall that the

electronic moment is related to the lifetime of the m^{th} electronic level, $\tau_{v',v''}^{mn}$, according to

$$\frac{1}{\tau_{v',v''}^{mn}} = \alpha d_n v_{v',v''}^3 |R_e^{mn}|^2 q_{v',v''}$$

where m and n represent the initial and final electronic states, respectively. α is a constant and d_n is the degeneracy of the final state. The function, R_e vs. $\bar{r}$ for each of the vibrational levels for which the lifetime was measured is plotted in Fig. 12 where it may be noted that there is no systematic variation of $R_e(\bar{r})$, in agreement with the present work.

The electronic transition moment for the $B \rightarrow X$ bands of CO^+ can also be obtained from lifetime measurements. Lawrence¹⁵ has measured several of the band lifetimes and the dependence of R_e on $\bar{r}$ is shown in Fig. 13 using his data.

The constancy of the cross sections of both the $A \rightarrow X$ and $B \rightarrow X$ systems, for excitation energies well beyond threshold, is consistent with the photoelectron spectroscopy data given by Schoen¹⁶.

The ratio of specific cross sections for formation of the $B \ ^2\Sigma^+$ and $A \ ^2\Pi_1$ states is equal to 17% and agrees with Schoen's result. Taking Schoen's data that the $A \ ^2\Pi_1$ state contributes $60 \pm 18\%$ of the excitation of CO to the three CO^+ states, we find that the maximum total ionization cross section is 15 ± 5 Mb. This value is consistent with that of 17 Mb given by Cook et al.¹⁷, but is lower than that of 22 Mb given by Cairns et al.¹⁸. Finally, the branching ratio for the $B \rightarrow A$ to $B \rightarrow X$ system is 8% and agrees well with Lawrence¹⁵ who gives a value of 10% within a factor of 2.

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FIGURE CAPTIONS

- Fig. 1 Schematic diagram of the experimental apparatus.
- Fig. 2 Dispersed fluorescence of CO for 22.4 eV (555Å) photon excitation for the $A^2\Pi_i \rightarrow X^2\Sigma^+$, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, and $B^2\Sigma^+ \rightarrow A^2\Pi_i$ systems. The bandhead positions collected by Krupenie are indicated. The ordinate indicates the current output from an EMI9553QB photo-multiplier and the abscissa indicates the wavelength of the dispersed fluorescence.
- Fig. 3 Dispersed fluorescence of the $CO^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ system excited by photons of various wavelengths as indicated.
- Fig. 4 Dispersed fluorescence of the $CO(A^2\Pi_i \rightarrow X^2\Sigma^+)$ system excited by photons of various wavelengths as indicated.
- Fig. 5 A plot of $N_v R_e^2(\bar{r}_{v,v'})$ vs. $\bar{r}_{v,v'}$ in arbitrary units for the vibrational bands of the $CO^+(A^2\Pi_i \rightarrow X^2\Sigma^+)$ system excited by photons of wavelength 686Å. The values of $\bar{r}_{v,v'}$ were calculated by Jain and Sahni.
- Fig. 6 A plot of the relative electronic transition moment R_e vs. the r-centroid for the vibrational bands of the $CO^+(A^2\Pi_i \rightarrow X^2\Sigma^+)$ system. The data shown are for incident photons of wavelengths 555, 630, 686, 703, and 718Å.
- Fig. 7 A plot of $N_v R_e^2(\bar{r}_{v,v'})$ vs. $\bar{r}_{v,v'}$ in arbitrary units for the vibrational bands of the $CO^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ system excited by photons of wavelength 555Å.
- Fig. 8 A plot of the relative electronic transition moment R_e vs. the r-centroid for the vibrational bands of the $CO^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ system.
- Fig. 9 A plot of the relative transition moment $R_{e_{v'0}}$ vs. the vibrational level v' for the vibrational bands of the $CO(X^1\Sigma^+, v'' = 0) \rightarrow CO^+(A^2\Pi_i, v' = 0-8)$ system.
- Fig. 10 A plot of the electronic transition moment $R_{e_{v'0}}$ vs. vibrational level v' for the vibrational bands of the $CO(X^1\Sigma^+, v'' = 0) \rightarrow CO^+(B^2\Sigma^+, v' = 0,1)$ system.

Fig. 11 The cross sections of the $\text{CO} (X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+ (A^2\Pi_i, v' = 0-8)$ and $\text{CO} (X^1\Sigma^+, v'' = 0) \rightarrow \text{CO}^+ (B^2\Sigma^+, v' = 0, 1)$ systems for various incident photon energies.

Fig. 12 A plot of the relative electronic transition moment R_e vs. the r-centroid bands of the $\text{CO}^+ (A^2\Pi_i \rightarrow X^2\Sigma^+)$ system. $R_e(\bar{r}_{v',v''})$ are calculated from the lifetime data published by Fink and Welge.

Fig. 13 A plot of the relative electronic transition moment R_e vs. the r-centroid for the vibrational bands of the $\text{CO}^+ (B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ system. $R_e(\bar{r}_{v',v''})$ are calculated from the data of transition probabilities published by Lawrence.

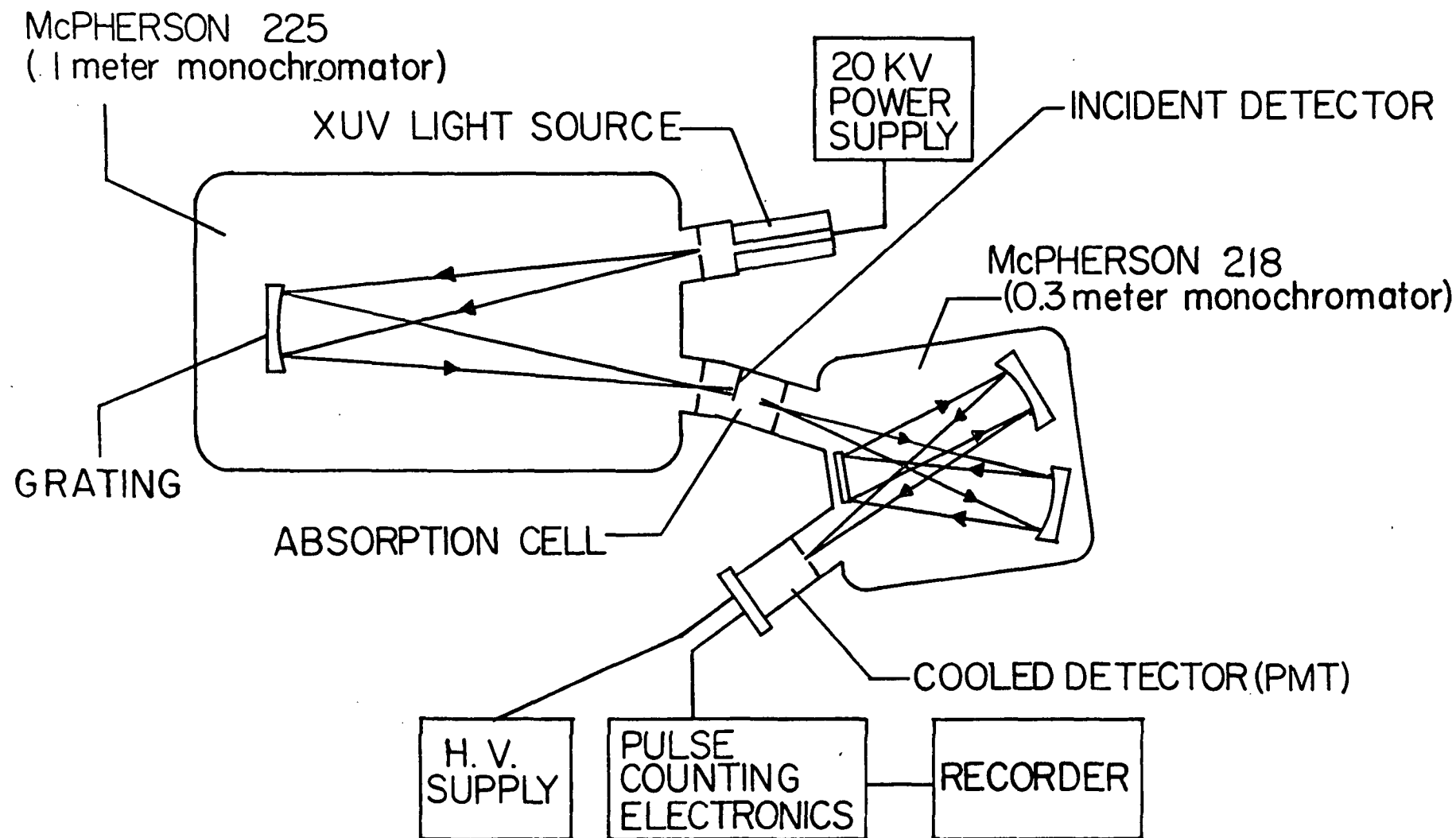


FIGURE 1. EXPERIMENTAL APPARATUS

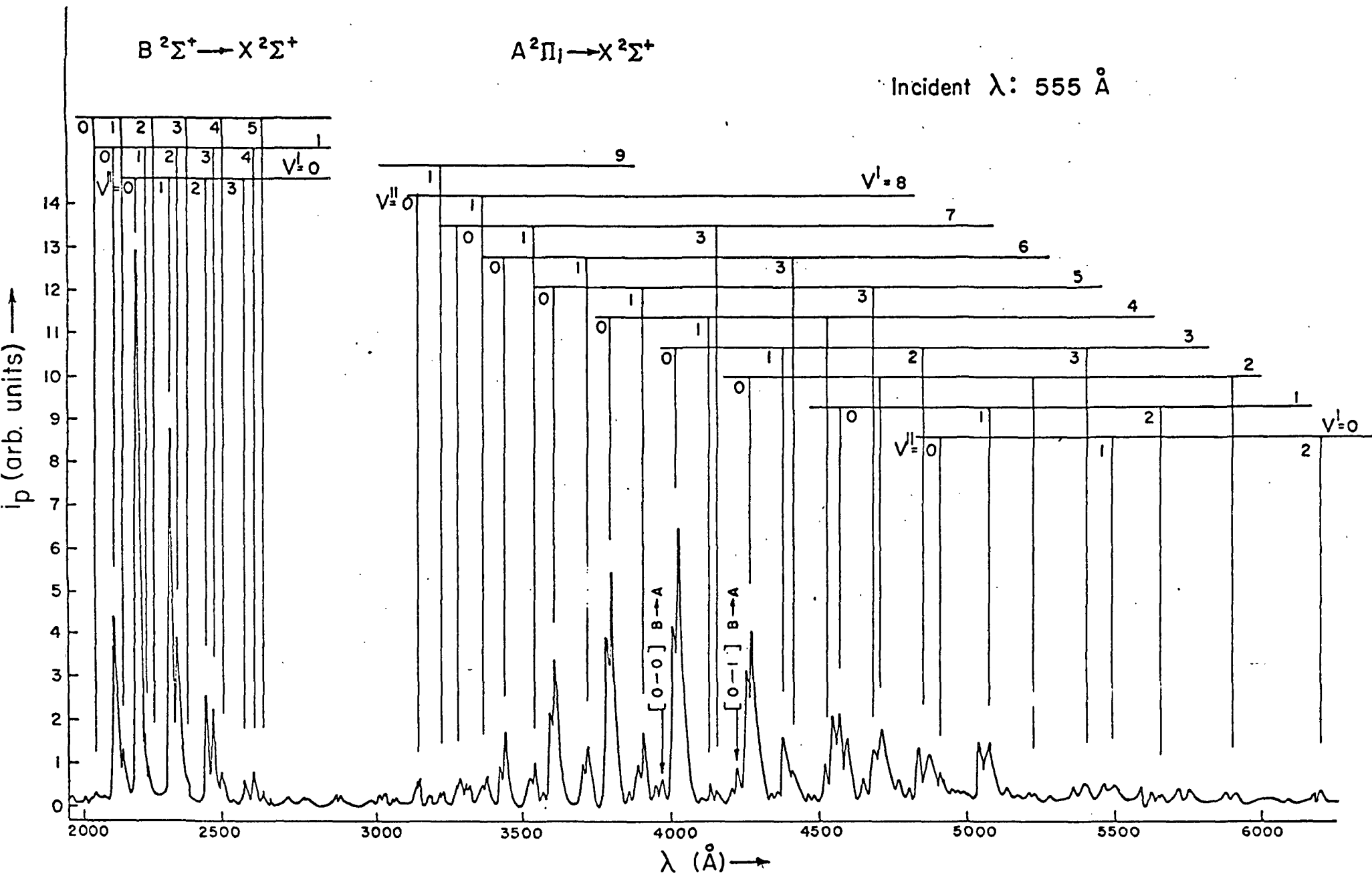


Fig. 2

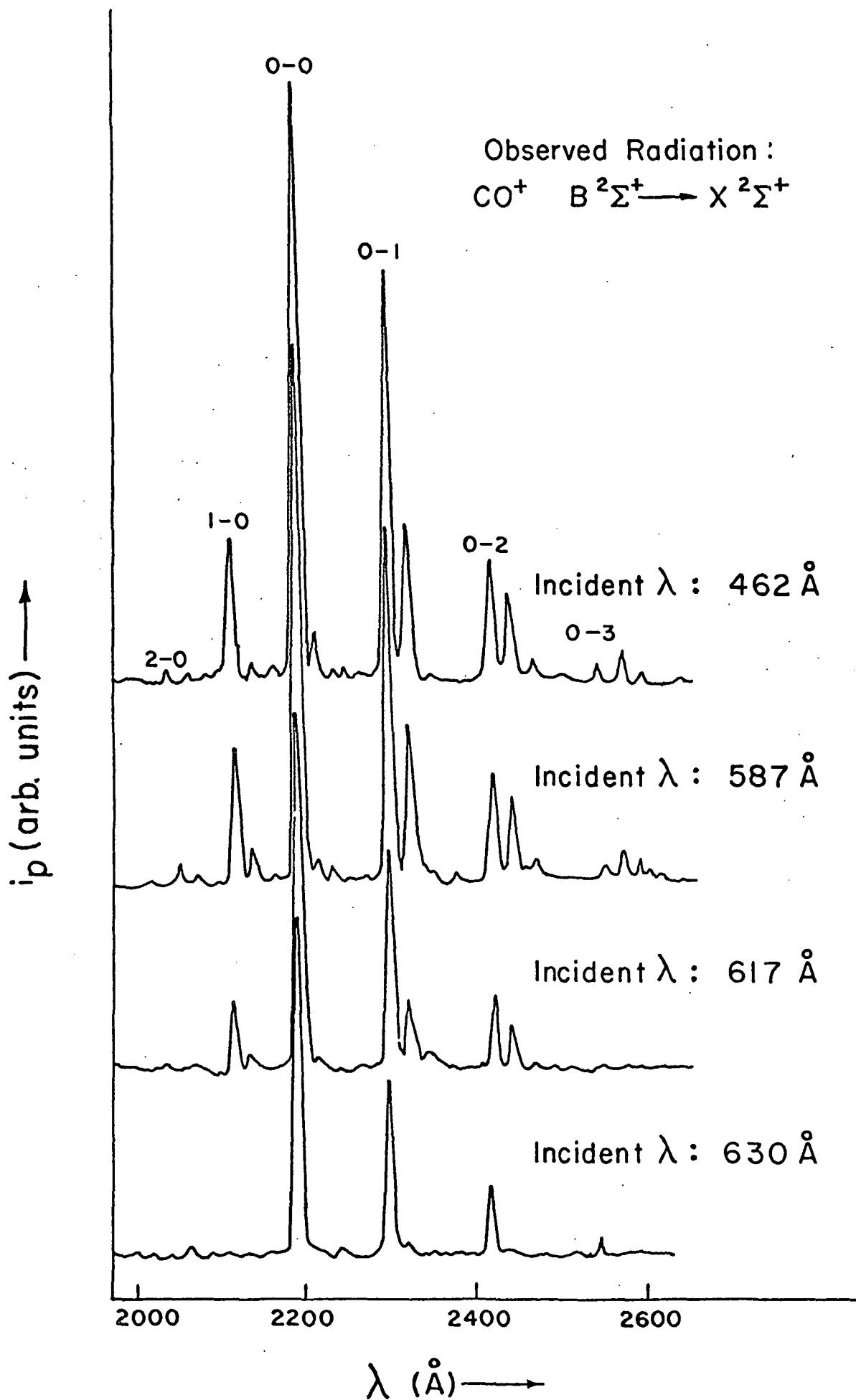


Fig. 3

i_p (arb. units) $\uparrow$

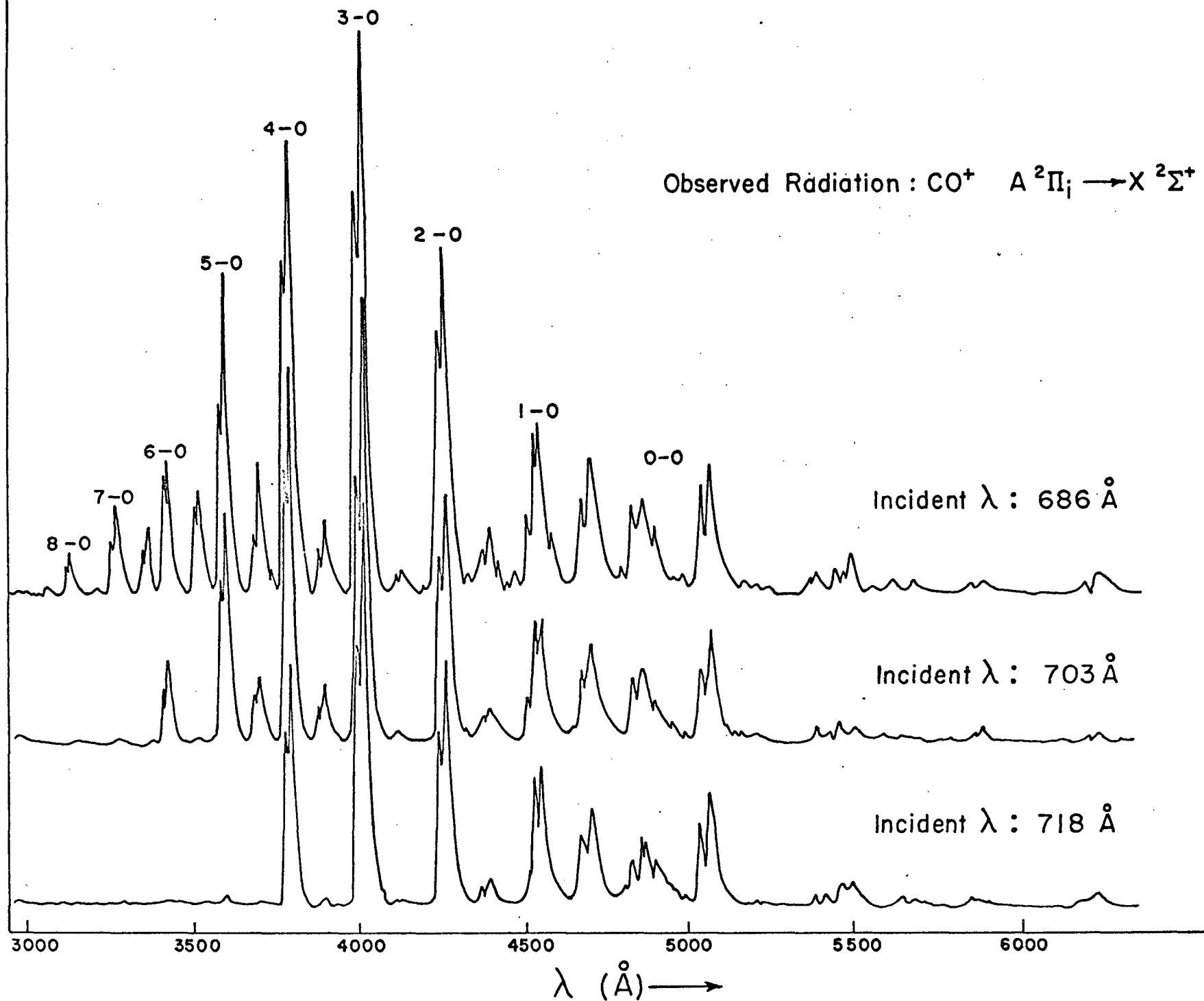


Fig. 4



Incident $\lambda: 686 \text{ \AA}$

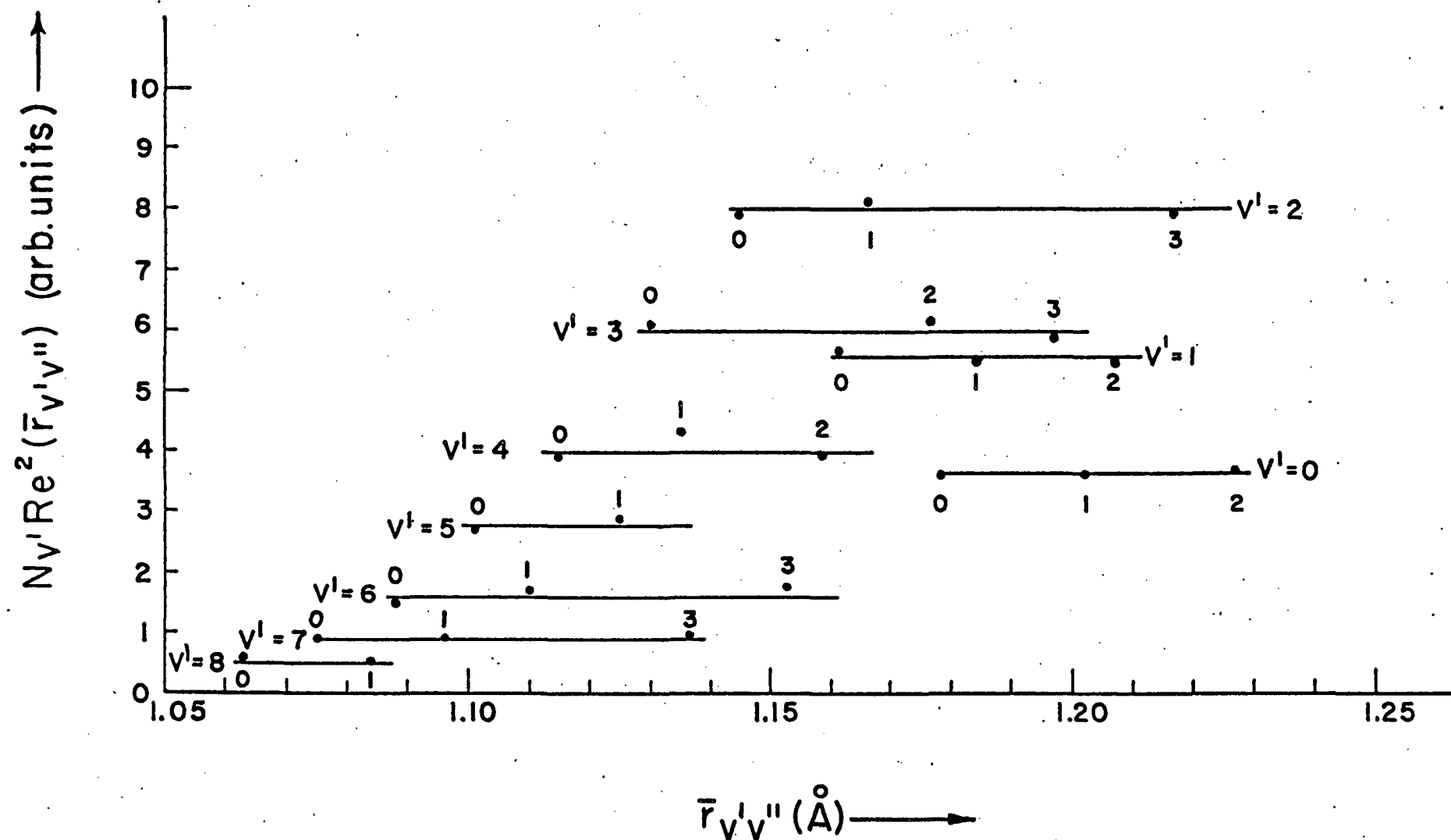
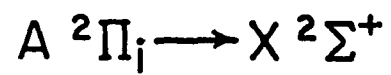


Fig. 5



$\times$ 555 Å
 $\blacktriangledown$ 630
 $\bullet$ 686
 $\blacktriangle$ 703
 $\blacksquare$ 718

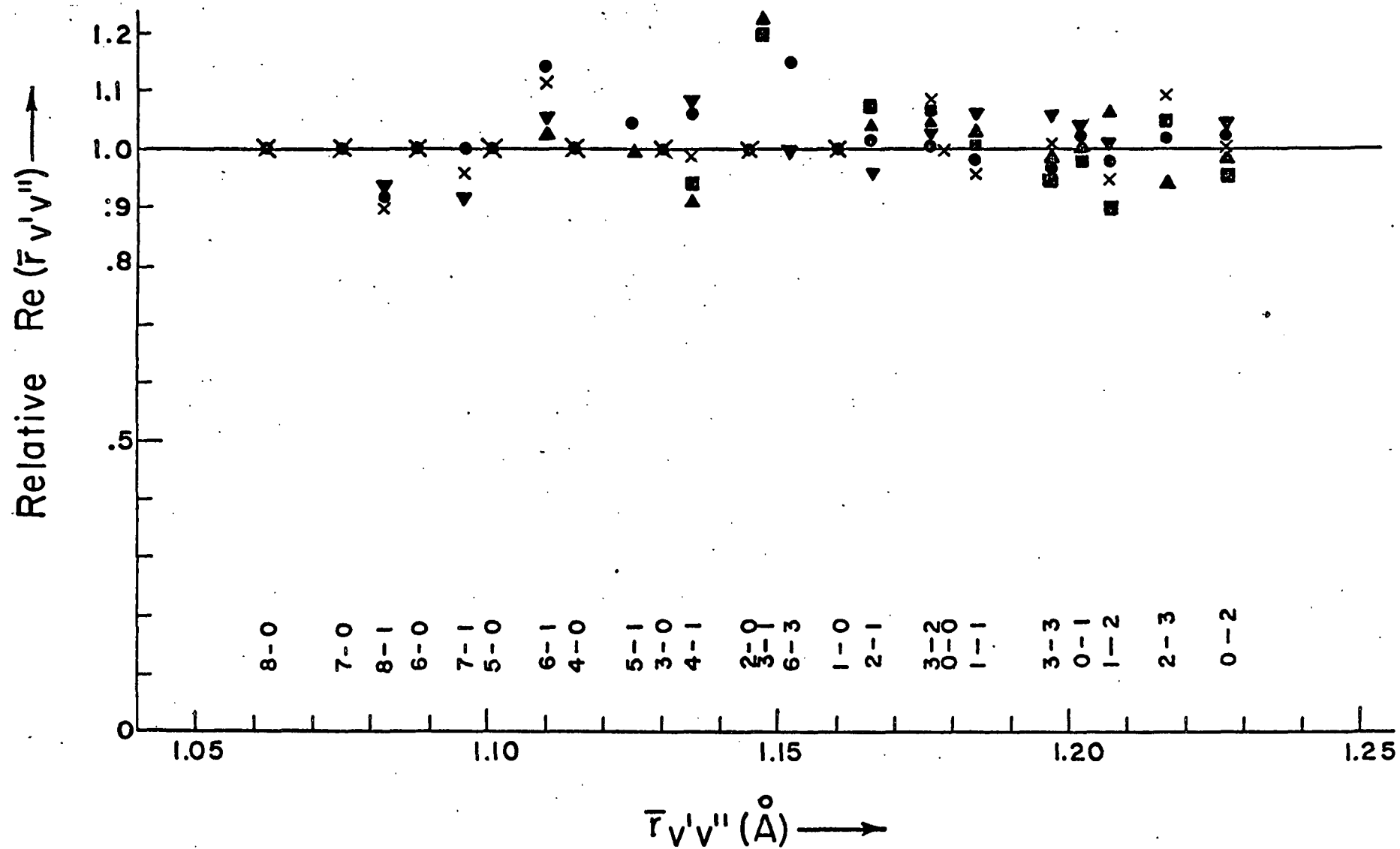
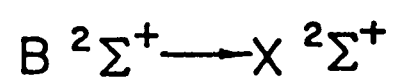


Fig. 6



Incident λ : 555 Å

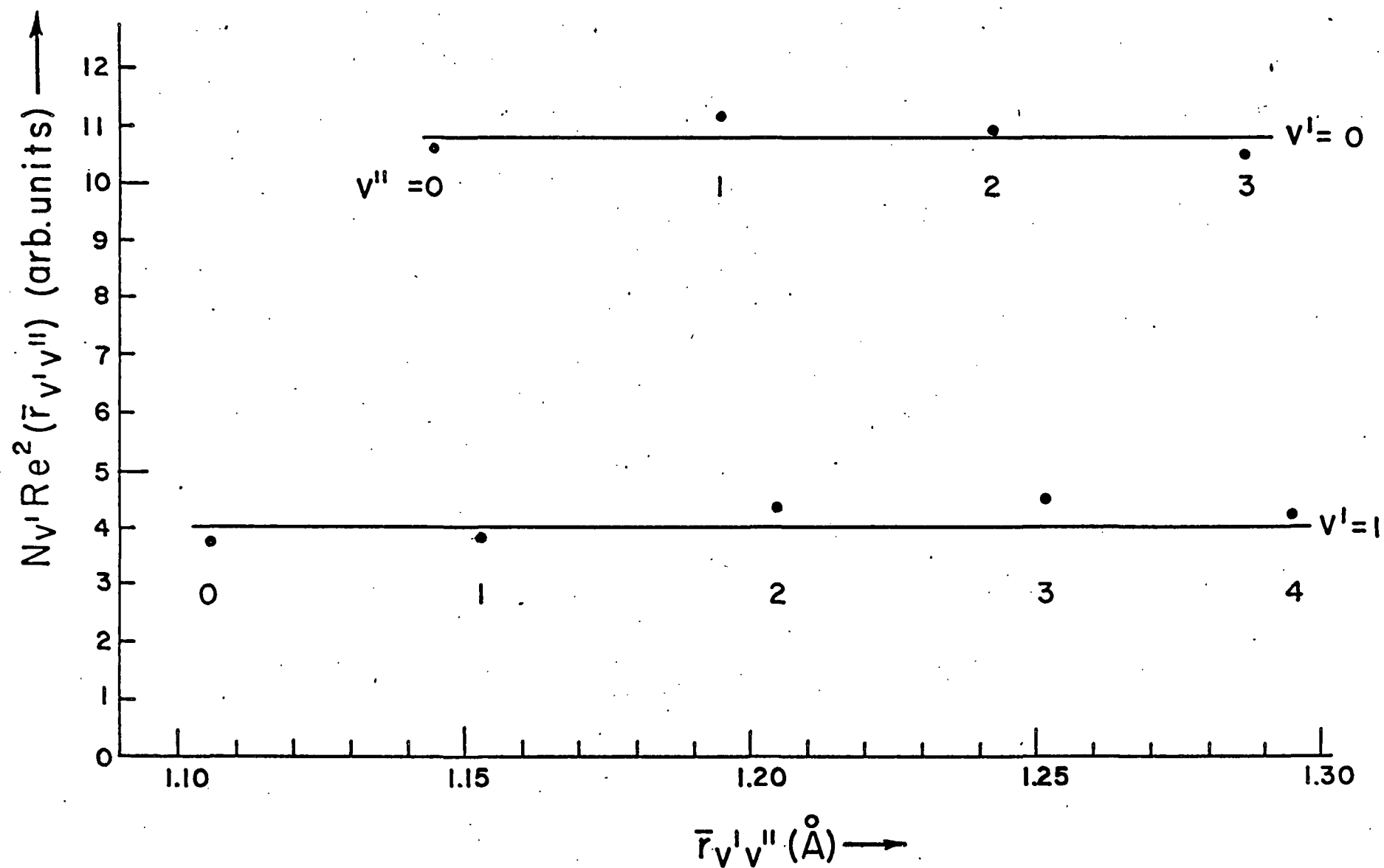


Fig. 7



x 555 Å
 ▼ 587
 • 610
 ▲ 617
 ■ 630

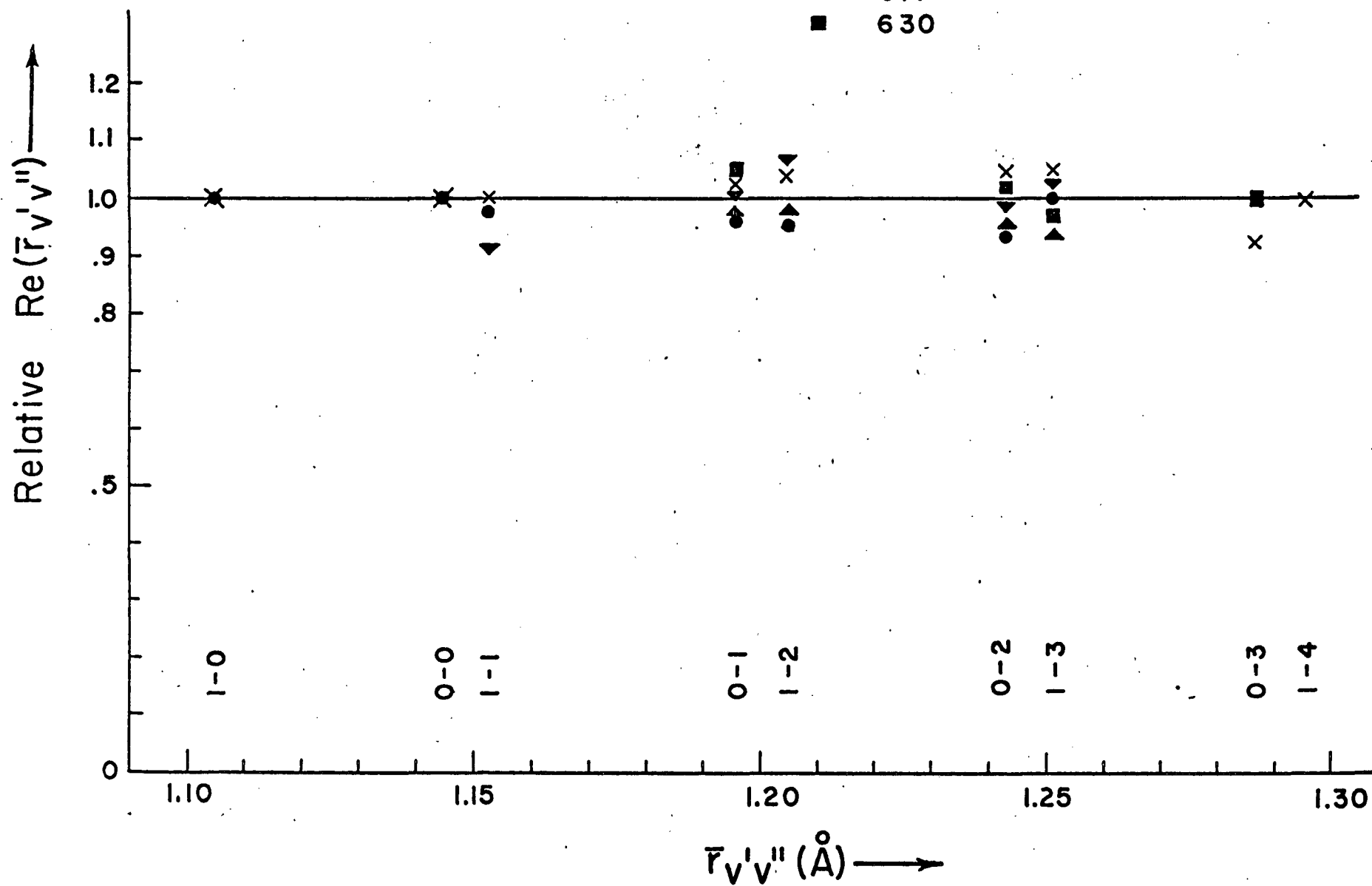


Fig. 8

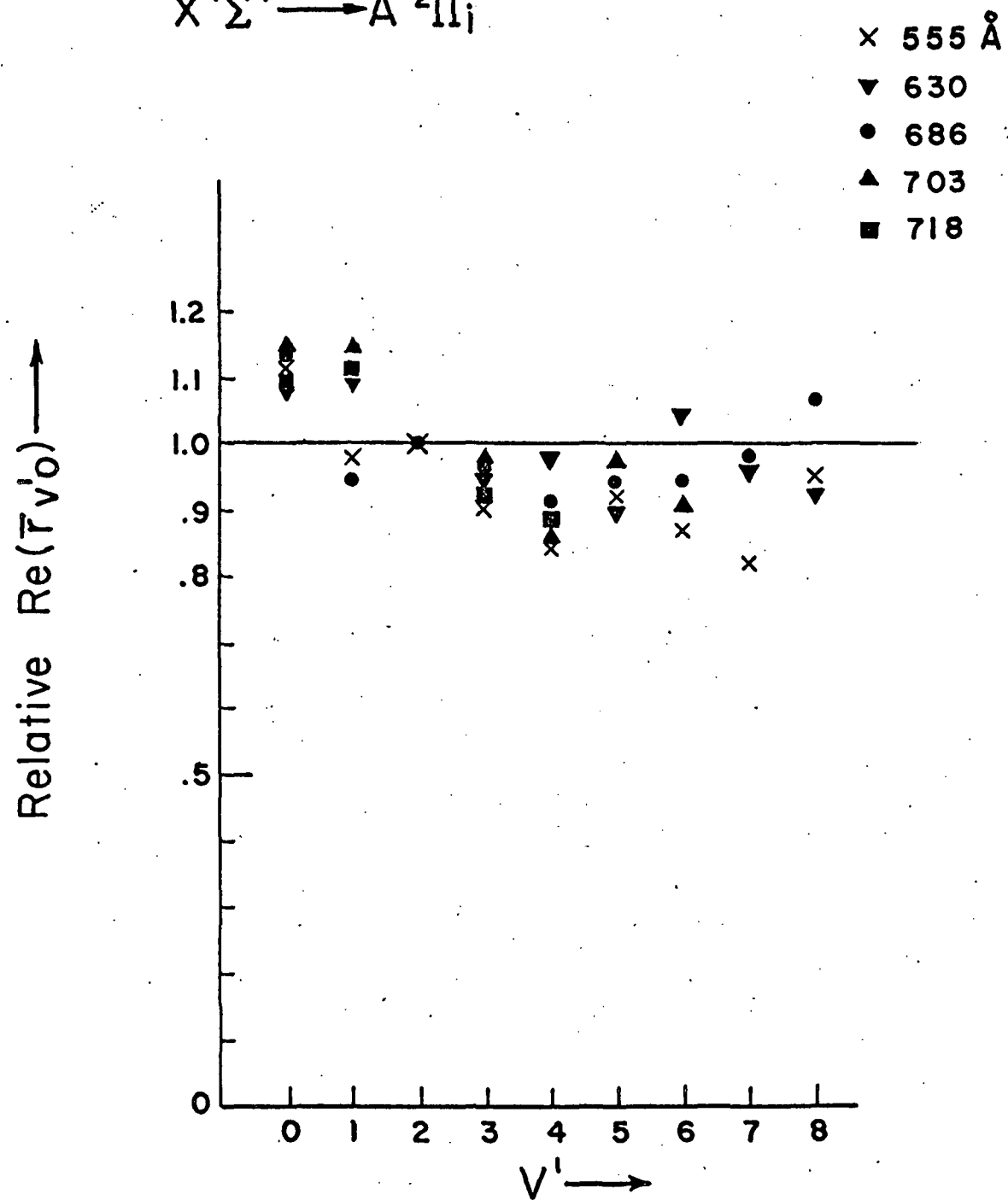
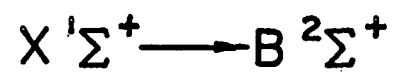


Fig. 9



- × 555 Å
- ▼ 587
- 610
- ▲ 617

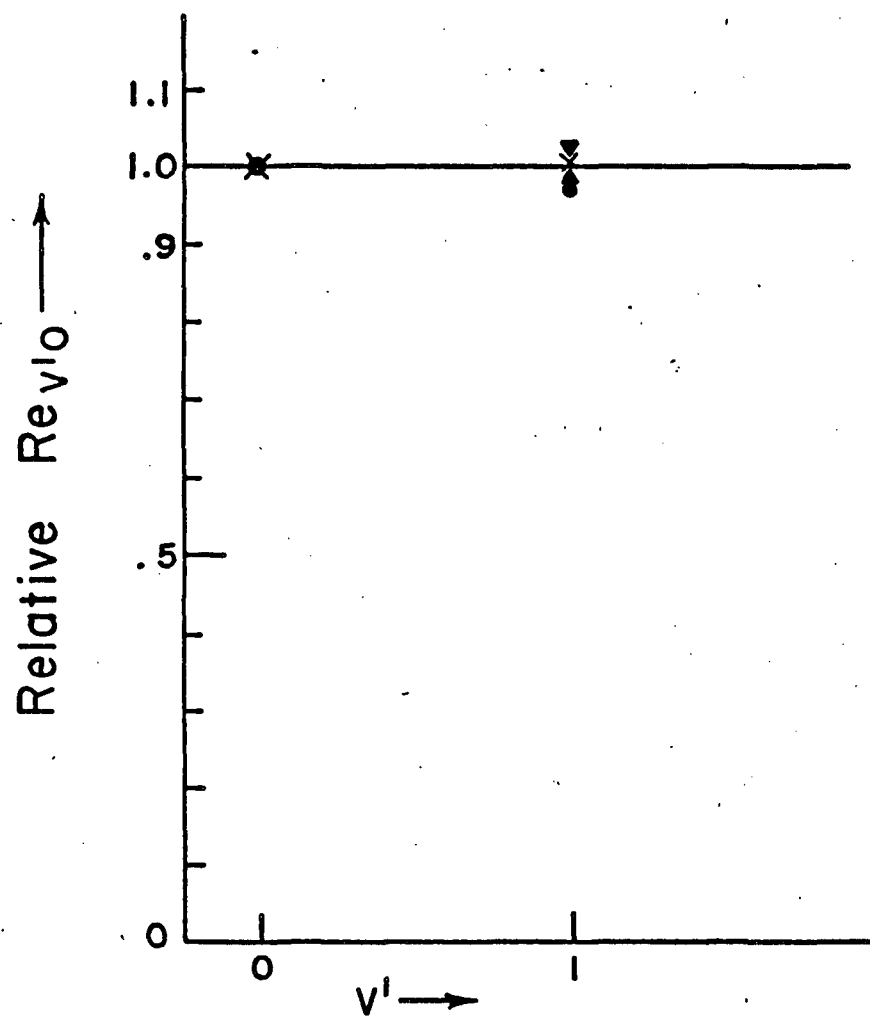


Fig. 10

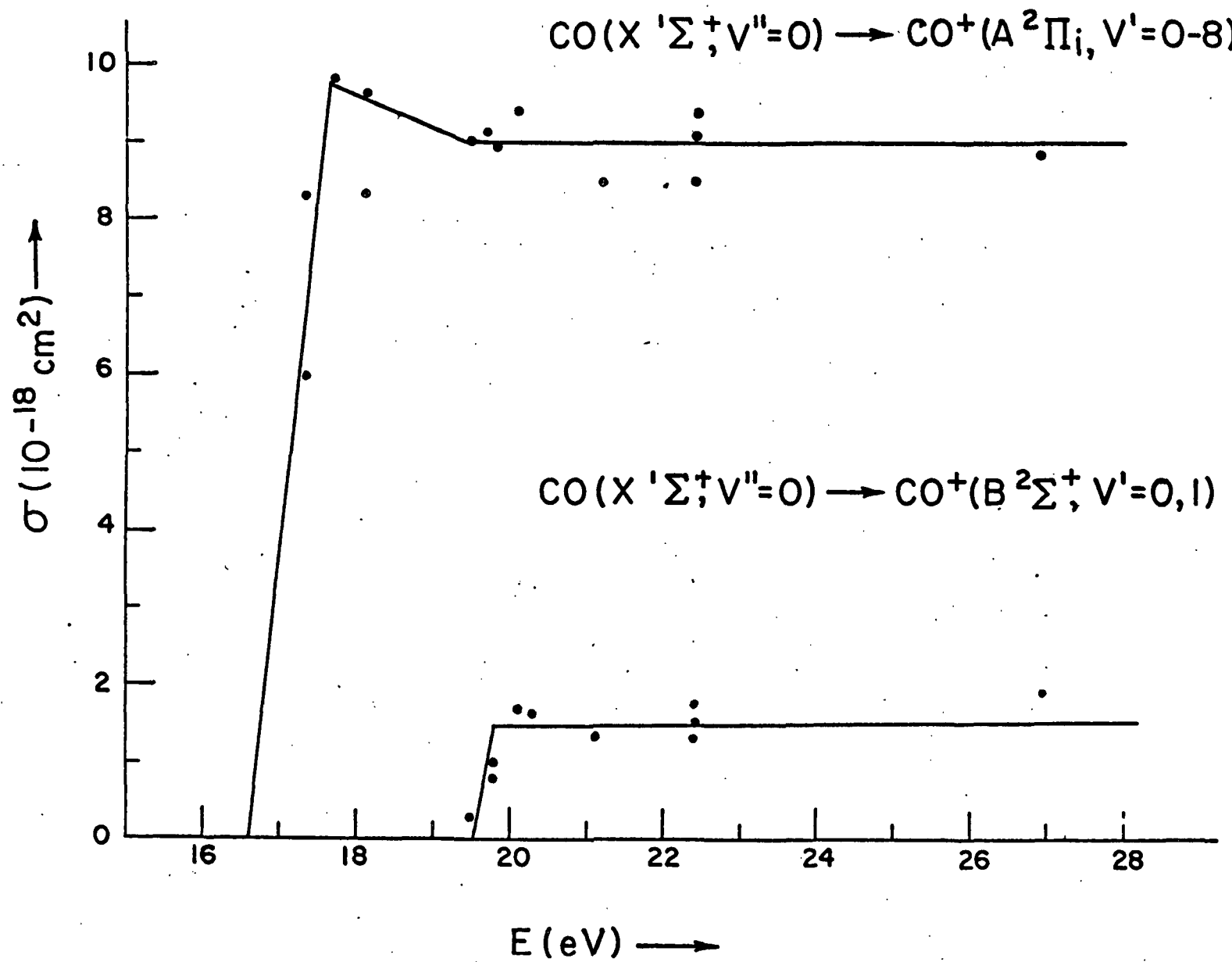


Fig. 11

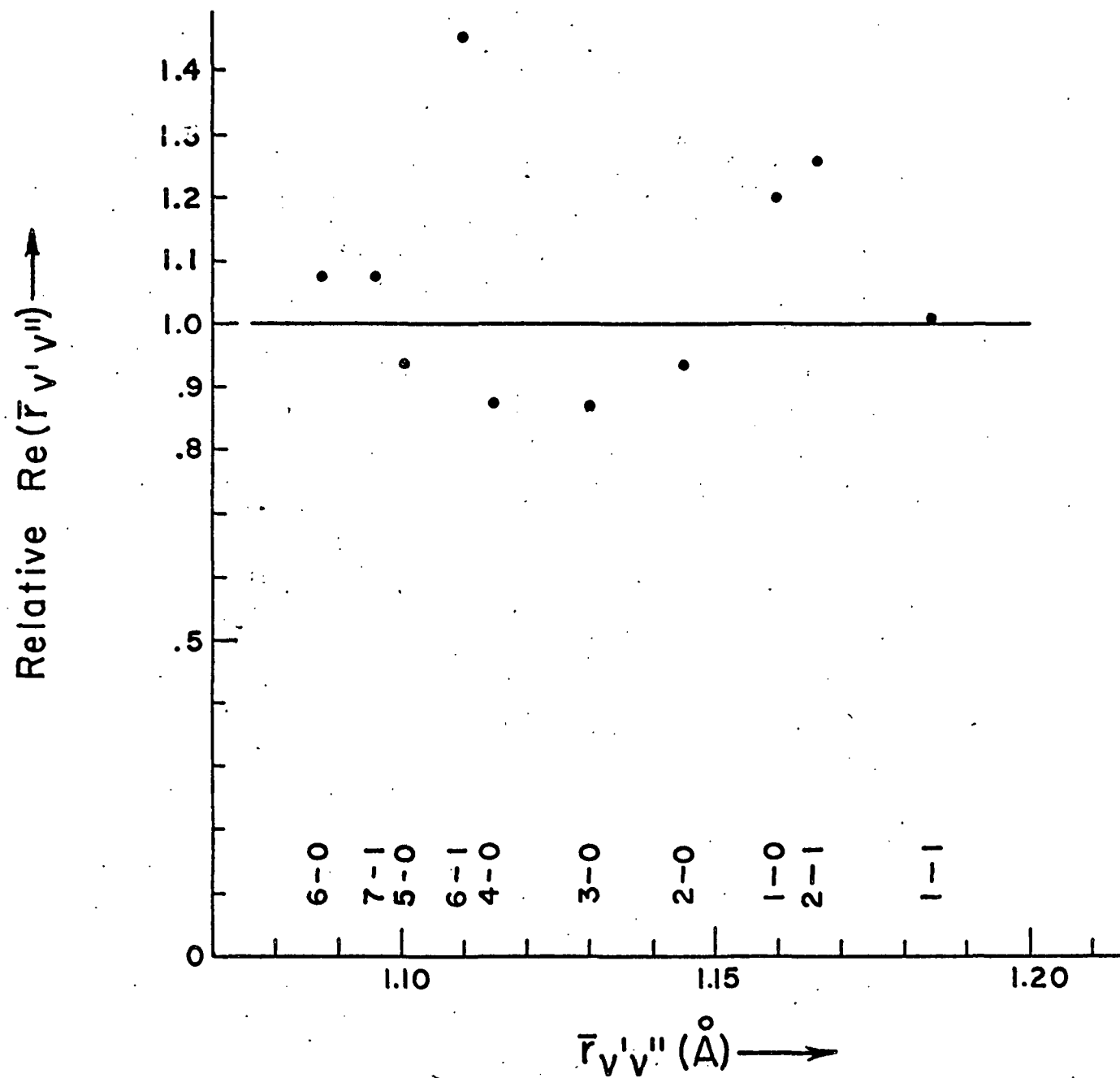


Fig. 12

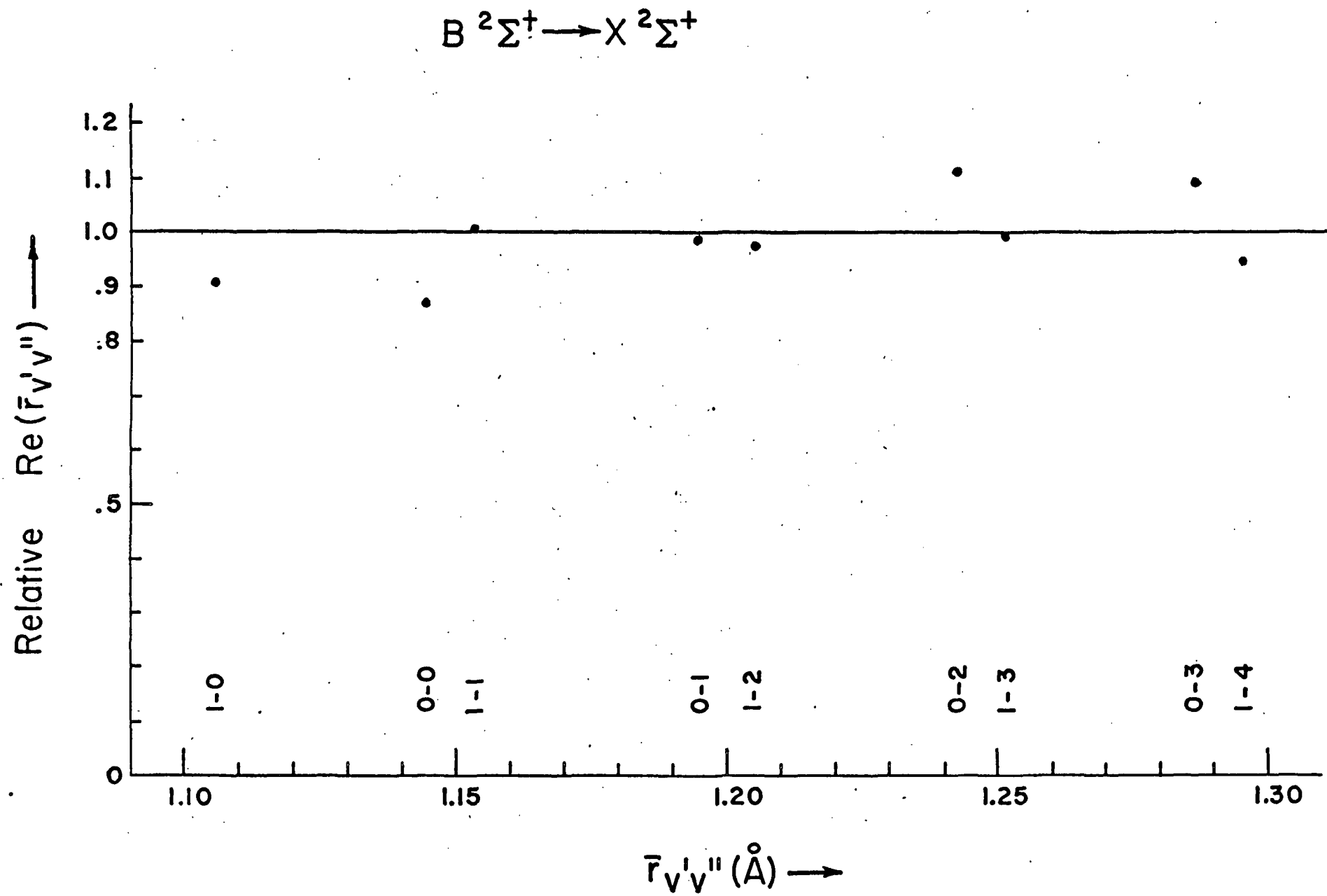


Fig. 13

ABSOLUTE SPECIFIC PHOTODISSOCIATION
CROSS SECTIONS OF CH₄ IN THE EXTREME ULTRAVIOLET*

A. R. Welch and D. L. Judge

Department of Physics
University of Southern California
Los Angeles, California 90007

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and # NGL 05-018-044.

ABSTRACT

The photodissociation of methane has been studied at 16 different incident wavelengths in the range 555-1242Å. Absolute partial cross sections have been determined for those processes yielding excited fragments which fluoresce in the range 3500-8000Å. The fluorescence was dispersed and found to result from the $A^2\Delta \rightarrow X^2\Pi$ and $B^2\Sigma \rightarrow X^2\Pi$ systems of CH, the $\tilde{b}^1B_1 \rightarrow \tilde{a}^1A_1$ system of CH_2 , and the H_α , H_β and H_γ transitions of H. Absolute cross sections have been assigned to the processes, $CH_4 + h\nu \rightarrow CH(A^2\Delta) + H_2(X^1\Sigma_g^+) + H(1^2S_{1/2})$, $CH_4 + h\nu \rightarrow CH(B^2\Sigma) + H_2(X^1\Sigma_g^+) + H(1^2S_{1/2})$ and $CH_4 + h\nu \rightarrow CH_2(\tilde{b}^1B_1) + H_2(X^1\Sigma_g^+)$. Emission cross sections have been assigned to the Balmer lines H_α , H_β and H_γ . The process $CH_4 + h\nu \rightarrow CH_3(\tilde{X}^2A_2'') + H^*$ is believed to be responsible for the Balmer lines. The largest cross section measured, $\sigma = 8 \times 10^{-20} \text{ cm}^2$, occurred at 923Å for the process leading to $CH(A^2\Delta)$. Cross sections of this magnitude are three orders of magnitude less than the total peak absorption cross section for methane.

INTRODUCTION

The investigation presented here is concerned with the dispersed fluorescence of fragments resulting from the dissociation of methane, irradiated by monochromatic vacuum ultraviolet photons. Since methane is a relatively small molecule there is some hope that if the fluorescence can be identified, simple energy arguments can be made to identify the photodissociation processes. Absolute cross sections can be assigned to specific processes using this approach, if the energy of the excited fragments is lost through radiative transitions.

The only other known study of the fluorescence from methane, in the region report here, has been made by Metzger and Cook¹. However, they only measured the relative total fluorescence over a portion of the range, making no attempt to disperse it, or suggest its source.

The total absorption cross section for methane has been established by previous experimenters. Notable papers include work by Wilkinson and Johnson², Moe and Duncan³, Sun and Weissler⁴, Ditchburn⁵, Metzger and Cook¹, and Rustgi⁶. Together their work assigns a cross section from 190Å to greater than 1400Å. It is known that between 400Å and 900Å this absorption is due primarily to photoionization^{4,5}. Dibeler, Krauss, Reese and Harlee⁷, have identified the processes $\text{CH}_4 + h\nu \rightarrow \text{CH}_4^+ + e$, $\text{CH}_4 + h\nu \rightarrow \text{CH}_3^+ + \text{H} + e$, and $\text{CH}_4 + h\nu \rightarrow \text{CH}_2^+ + \text{H}_2 + e$ over most of this region. These cross sections have also been calculated by Dalgarno, using self-consistent wave functions⁸. Other theoretical calculations for the decomposition of methane have been made by Lindholm⁹, using molecular orbital theory.

The processes responsible for the absorption at wavelengths greater than 900Å are not, however, well known. In view of the abundance of methane around Jupiter, these unknown processes would be valuable in forming a model for the Jovian atmosphere, especially those processes which occur at L_{α} (1216Å) ¹⁰. Furthermore, it is possible that other simpler molecules and atoms found in space could have their origin in methane, for example, the CH observed in comets.

II. EXPERIMENT

The experimental apparatus is illustrated in Fig. 1. The ultraviolet radiation was generated by a condensed spark discharge through a water-cooled boron nitride capillary containing hydrogen, nitrogen or oxygen. The discharge was operated at a rate of 38 pulses/second by means of a rotary spark gap. An evacuated 1-meter monochromator adjusted for 2Å resolution was used to disperse the source radiation. The intensity incident on the methane was detected at shorter wavelengths using a platinum photocathode, and at the longer wavelengths using sodium salicylate. An absolute calibration for the sodium salicylate was obtained by using the platinum since the response of these two detectors overlap. The intensity of the incident radiation ranged from 1.2×10^{10} photons/second for the strongest line, down to 8×10^8 photons/second for the weakest useful line.

The methane gas sample was admitted into the cell through a leak valve and was pumped out through the exit slit of the 1-meter monochromator. The cell pressure was maintained at 1.5×10^{-1} Torr. The fluorescence resulting from the photodissociation was viewed through a quartz window by a second monochromator.

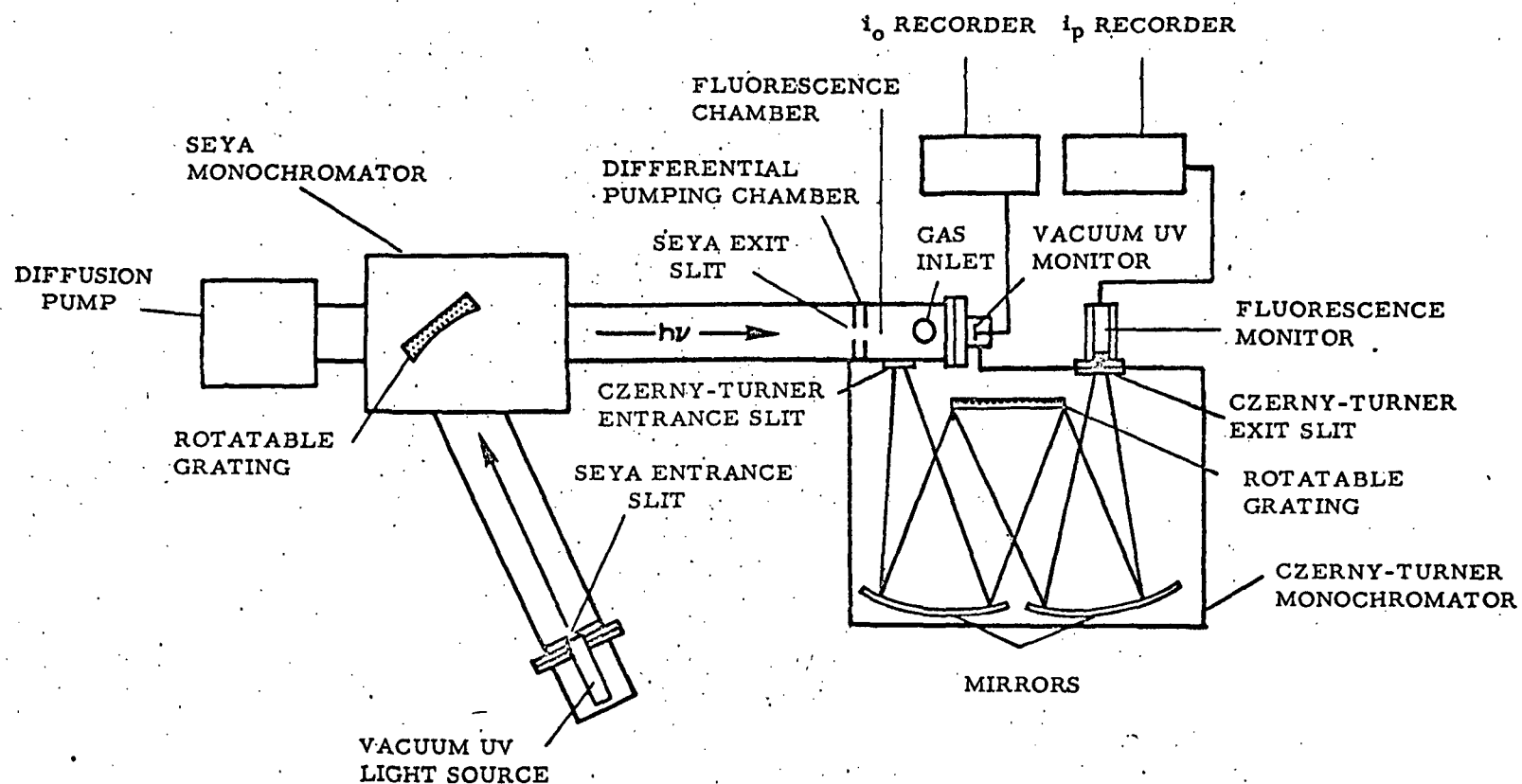


Fig. 1. Experimental Apparatus

Cooled EMI 9558QB and 9514S photomultiplier tubes were employed as part of a synchronous pulse counting system to detect the dispersed fluorescence. Only the signal received during the $10\mu\text{sec}$ discharge of the light source was detected. The small duty cycle and cooled detector limited the noise level to 0.3 dark counts/min.

The methane was obtained from the Matheson Company. It was specified as 99.5% pure, and was used without further purification. The impurities included ethane (C_2H_6), propane (C_3H_8), carbon dioxide (CO_2), nitrogen (N_2) and oxygen (O_2).

III. RESULTS

The dispersed fluorescence, resulting from the irradiated methane was recorded for 16 different incident energies with photon energies ranging from 10 eV ($1242\text{\AA}$) to 22.4 eV ($555\text{\AA}$).

For incident wavelengths less than $1032\text{\AA}$, the spectra were dominated by CH emission bands. These bands are well known and have been observed by other experimenters in hydrocarbon flames, discharge tubes containing carbon and hydrogen, carbon arcs in hydrogen, and the emission from comet heads¹¹. The $3900\text{\AA}$ system ($\text{B } ^2\Sigma \rightarrow \text{X } ^2\Pi$) and the $4300\text{\AA}$ system ($\text{A } ^2\Delta \rightarrow \text{X } ^2\Pi$) of CH were identified using Pearse and Gaydon band head data¹¹. The spectra taken at shorter incident wavelengths were of particular interest since they showed line emission resulting from excited atomic hydrogen. For these spectra the H_α , H_β and H_γ lines of the Balmer series were identified. The intensities of these lines were corrected for the system response, and compared with published oscillator strengths. They indicate the initial states were of nearly equal population. Fig. 2 shows the

Incident λ : 555 $\text{\AA}$

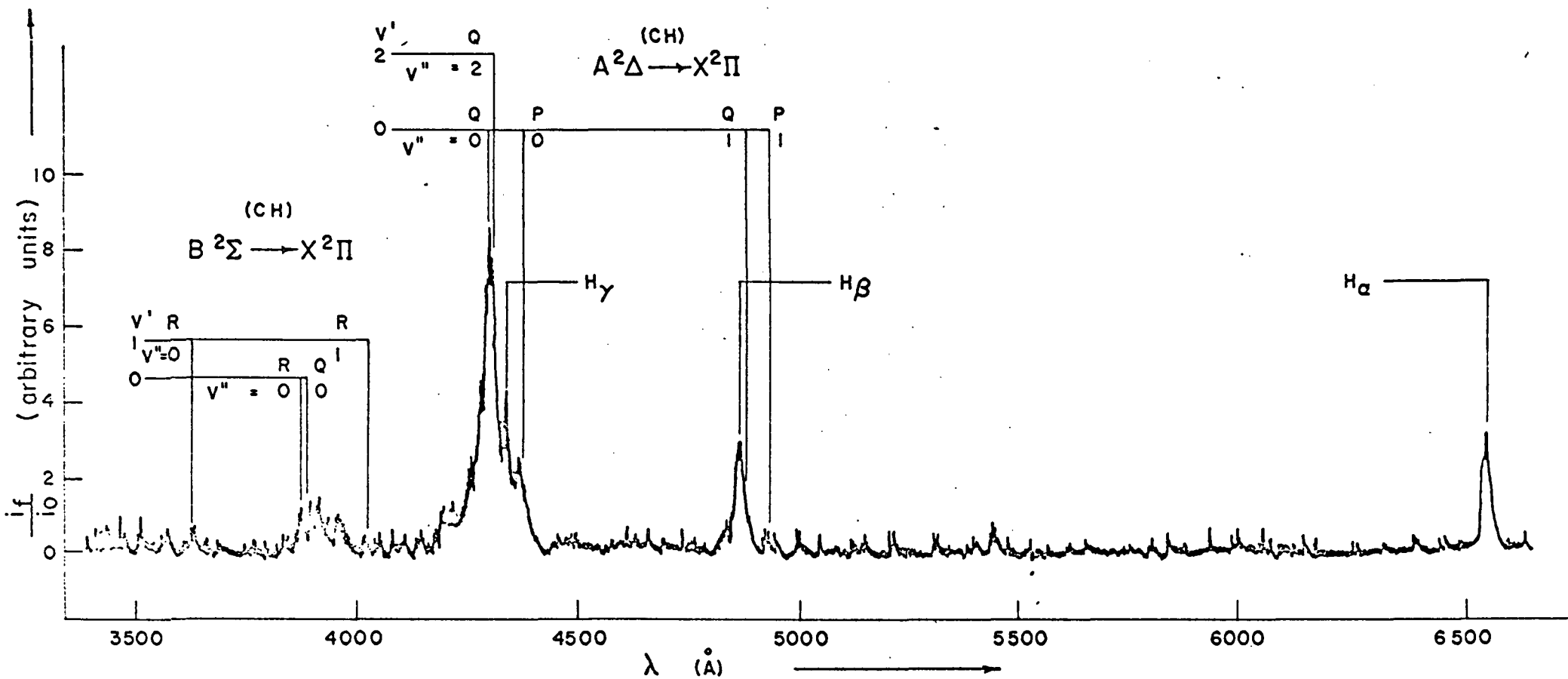


FIGURE 2

Fluorescence from CH and H, resulting from CH_4 irradiated by 555 $\text{\AA}$ photons.

resulting fluorescence spectrum taken at 555Å incident wavelength where most features of interest appear.

For incident wavelengths greater than 1032Å only the spectrum taken at L_α (1216Å) resulted in any significant fluorescence. This has been identified as the ($\tilde{b}^1B_1 \rightarrow \tilde{a}^1A_1$) system of CH_2 . This system has been seen previously only in absorption spectra, found to extend from 5000Å to 9000Å^{12,13}. The observed emission spectrum appears to cover nearly the same region, starting at 5500Å and extending beyond the 8000Å limit of this experiment. Since it was not possible to measure all the radiation resulting from the CH_2 only an estimate of the cross section for the responsible process could be made.

To obtain an absolute cross section for the observed processes, an emission spectrum of N_2^+ was taken. The emission spectrum of N_2^+ in the range 3500 to 5500Å following irradiation of N_2 by photons of wavelength 555Å (22.4 eV), was taken at the same scan speed and resolution as the photodissociation fluorescence spectra. By comparing the fluorescence from the first negative system of nitrogen ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) with the fluorescence yields for the various processes observed in CH_4 it was possible to assign absolute cross sections to these processes¹⁴.

The absolute cross sections versus incident wavelength for the processes resulting in the transitions $A^2\Delta \rightarrow X^2\Pi$, and $B^2\Sigma \rightarrow X^2\Pi$ of CH , H_α , H_β and H_γ of H and ($\tilde{b}^1B_1 \rightarrow \tilde{a}^1A_1$) of CH_2 are given in Fig. 3. The cross sections were found by integrating the area under the spectrum for each process, and at each incident wavelength, and comparing these areas with the area under the spectrum of N_2^+ for the process $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$. The radiation from these processes was assumed to be isotropic. Corrections

for system response were incorporated into these calculations; that is, photomultiplier and platinum detector efficiencies, incident intensities, optics, electronic amplification, scan speeds and pulse pile-up.

The calculated thresholds for many of the processes considered are identified in Fig. 3. They were found by adding together the energy necessary to dissociate the molecule and excite the labelled fragments. A discussion of the suggested dissociation processes is given below; their cross sections are given in Fig. 3.

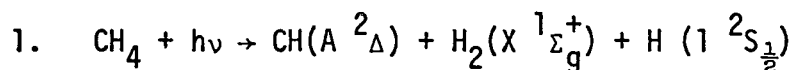


Fig. 3 strongly suggests the reaction $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{A } ^2\Delta) + \text{H}_2(\text{X } ^1\Sigma_g^+) + \text{H}(1 \text{ } ^2\text{S}_{\frac{1}{2}})$, since the threshold for the production of excited CH is observed within 0.05 eV of the calculated threshold at 1028Å.

There is also an energetically possible threshold for the process, $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{A } ^2\Delta) + 3\text{H}(1 \text{ } ^2\text{S}_{\frac{1}{2}})$ at 750Å. However no threshold appears at this wavelength. Thus, if this reaction is present, its threshold must occur at an energy higher than its calculated minimum value. This process could account for the increasing emission from $\text{CH}(\text{A } ^2\Delta \rightarrow \text{X } ^2\Pi)$ found between 555 and 626Å. If this process is absent, then the reaction $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{A } ^2\Delta) + \text{H}_2(\text{X } ^1\Sigma_g^+) + \text{H}(1 \text{ } ^2\text{S}_{\frac{1}{2}})$ must account for all excitation to the $\text{CH}(\text{A } ^2\Delta)$ state. The presence of the reaction $\text{CH}_4 + h\nu \rightarrow \text{CH}^* + \text{H}_2 + \text{H}$ and the absence of the reaction $\text{CH}_4 + h\nu \rightarrow \text{CH}^* + 3\text{H}$ would also suggest that upon photon impact the CH_4 molecule is distorted bringing at least two H atoms close enough together that when CH_4 dissociates these H atoms bond together forming H_2 .

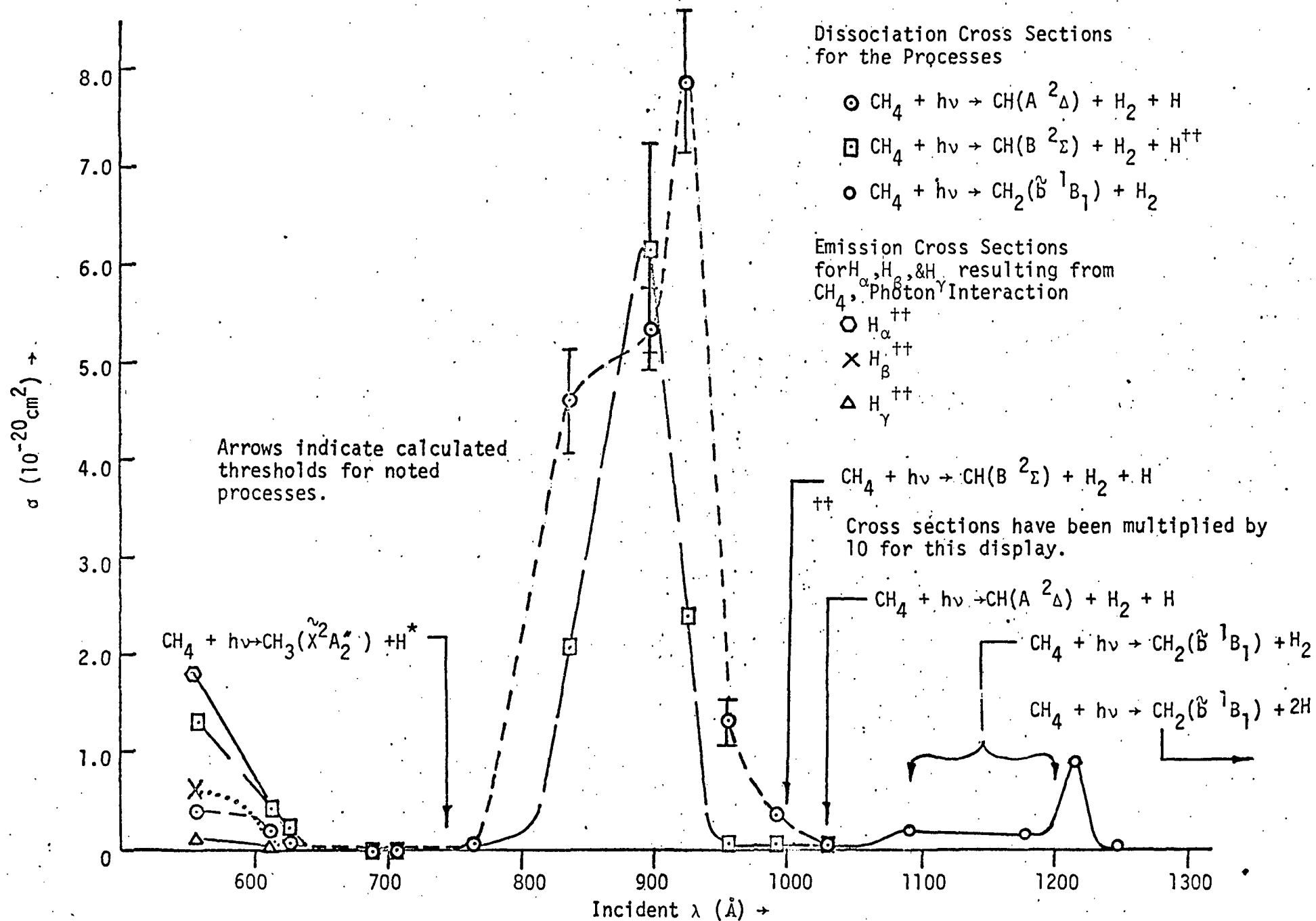
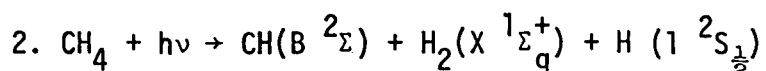
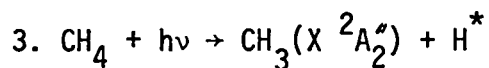


Fig. 3



From energy arguments, the threshold for the process $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{B } ^2\Sigma) + \text{H}_2(\text{X } ^1\Sigma_g^+) + \text{H}(1 ^2\text{S}_{\frac{1}{2}})$ cannot occur at wavelengths longer than 1005Å. For the process $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{B } ^2\Sigma) + 3\text{H}(1 ^2\text{S}_{\frac{1}{2}})$, the threshold must occur at wavelengths less than or equal to 736Å. The experimentally found threshold for the transition $\text{CH}(\text{B } ^2\Sigma) \rightarrow \text{CH}(\text{X } ^2\Pi)$ is near 950Å. Thus, of the above two processes the experimental data are consistent only with the process $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{B } ^2\Sigma) + \text{H}_2(\text{X } ^1\Sigma_g^+) + \text{H}(1 ^2\text{S}_{\frac{1}{2}})$. This is a reasonable process to expect since the process yielding $\text{CH}(\text{A } ^2\Delta)$ and ground state H_2 and H has also been identified. Here again, it is possible that the reaction $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{B } ^2\Sigma) + 3\text{H}(1 ^2\text{S}_{\frac{1}{2}})$ could account for the excitation to the $\text{CH}(\text{B } ^2\Sigma)$ state which results in the $\text{CH}(\text{B } ^2\Sigma \rightarrow \text{X } ^2\Pi)$ transition for incident photons between 555Å and 626Å.



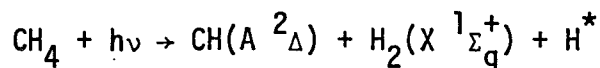
The threshold for production of H atoms in the fifth principal quantum state ($n = 5$), through the process $\text{CH}_4 + h\nu \rightarrow \text{CH}(\text{X } ^2\Pi) + \text{H}_2(\text{X } ^1\Sigma_g^+) + \text{H}^*$ is 559Å. From this state the third Balmer line H_γ is possible. The threshold decreases to 567Å for radiation resulting from the second Balmer line, H_β , and 585Å for H_α , the first Balmer line.

For the process $\text{CH}_4 + h\nu \rightarrow \text{CH}_2(\text{X } ^3\Sigma_g^-) + \text{H}(1 ^2\text{S}_{\frac{1}{2}}) + \text{H}^*$, the calculated threshold wavelength for H_γ is 564Å, H_β , 572Å and H_α , 590Å.

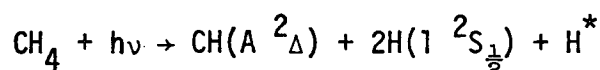
For the process $\text{CH}_4 + h\nu \rightarrow \text{CH}_3(\text{X } ^2\text{A}_2'') + \text{H}^*$, the calculated threshold wavelength for H_γ is 712Å, H_β 725Å, and H_α 754Å, respectively.

The experimental results show thresholds between 610-626Å for the first three Balmer lines. Thus, the process $\text{CH}_4 + h\nu \rightarrow \text{CH}_3(X^2A_2^*) + \text{H}^*$ appears to be a likely process for the production of excited H atoms.

Because the threshold for excited H atoms coincides with the "threshold" for fluorescence resulting from excited CH, the processes

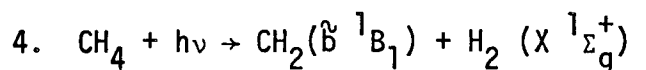


and



were considered. However, neither of these processes can occur for incident photon wavelengths longer than 500Å.

The possibility of secondary reactions giving rise to excited H atoms was checked by measuring the pressure dependence of the H_α line. The pressure dependence, over the range $10\text{-}300 \cdot 10^{-3}$ Torr, was linear at pressures less than $200 \cdot 10^{-3}$ Torr and showed quenching at the higher pressures.



Spectra for lower energy incident photons were taken at 1086Å, 1176Å, L_α (1216Å) and 1242Å. For incident photons at the three shorter wavelengths fluorescence resulted from $\text{CH}_2(\tilde{b}^1B_1 \rightarrow \tilde{a}^1A_1)$. This radiation was identified by comparison with the results of Herzberg and Johns for the absorption of CH_2^{13} . No fluorescence resulted at 1242Å. There are two possible processes to consider that yield CH_2^* : $\text{CH}_4 + h\nu \rightarrow \text{CH}_2^* + \text{H}_2(X^1\Sigma_g^+)$ and $\text{CH}_4 + h\nu \rightarrow \text{CH}_2^* + 2\text{H}(1^2S_{1/2})$. The first must be considered since the photodetachment of H_2 has been found to be a primary process

at 1236Å in studies made by Mahan and Mandel¹⁵ although their experiment was not capable of detecting excited states. The threshold for producing the lowest energy excited CH₂ fragment in the second process was calculated, using simple energy arguments, to be in the range 1090-1200Å. Only the range can be specified since the energy of the first singlet state of CH₂ above the triplet ground state is uncertain. Although Herzberg believes the energy to be less than one electron volt¹⁶. Thus the process $\text{CH}_4 + h\nu \rightarrow \text{CH}_2(\tilde{\text{b}}^1\text{B}_1) + \text{H}_2(\text{X}^1\Sigma_g^+)$ appears to be responsible for the CH₂^{*} radiation, since the other process would have to violate threshold arguments.

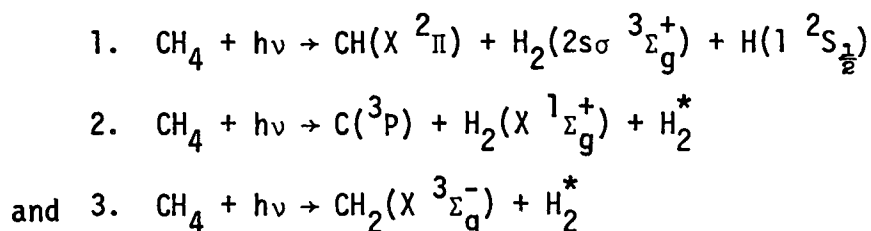
5. Other Possible Processes

The ($\text{A } ^2\Delta \rightarrow \text{X } ^2\Pi$) and ($\text{B } ^2\Sigma \rightarrow \text{X } ^2\Pi$) transitions of CH, the first three lines of the Balmer series and the ($\tilde{\text{b}}^1\text{B}_1 \rightarrow \tilde{\text{a}}^1\text{A}_1$) system of CH₂ appear to account for the total emission spectra resulting from CH₄ irradiated by vacuum UV photons over the observed range. The possibility of fluorescence from other fragments such as: C, H₂, CH⁺, CH₂⁺, CH₄, and CH₄⁺ resulting from dissociation and/or ionization processes was also considered. With the exceptions of C and H₂ fluorescence from these fragment is either not possible in the observed range or the incident energies used were not adequate to yield sufficient excitation of the fragments.

For carbon it is possible that emission could result from the process $\text{CH}_4 + h\nu \rightarrow \text{C}^* + 2\text{H}_2(\text{X}^1\Sigma_g^+)$. It is possible to ionize C through this process for incident photons of wavelength less than 636Å thus,

for longer wavelengths it is possible to excite those C transitions which fall within the observed range. However, no transitions corresponding to atomic carbon were observed.

Possible transitions resulting from excited H_2 could result from the primary processes



For the first of these processes, fluorescence would result from the transition $H_2(2s\sigma \ ^3\Sigma_g^+) \rightarrow H_2(2p\sigma \ ^3\Sigma_u^+)$. However, the $2p\sigma \ ^3\Sigma_u^+$ state is unstable and gives rise to a broad continuum thus, unless this process has a large cross section it is not expected that the fluorescence would be detectable.

For process 2) it is possible to excite higher singlet and triplet states of H_2 than were possible for process 1)

if the incident photon wavelength is less than 575Å. The same holds true for the third process if the incident photon is less than 697Å. However, if the H_2 is being highly excited the spectrum from 4000-6000Å should consist of many band systems, as reported by Gale, Monk and Lee¹⁷. Thus if any H_2 is excited upon dissociation of CH_4 , it has a small cross section compared to the processes observed.

IV. SUMMARY

Fluorescence, in the range 3500-8000Å is observed from the dissociation fragments of CH_4 when it is irradiated by vacuum ultraviolet light in

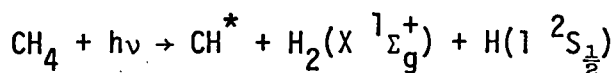
the range 555-1242Å. The fluorescence is due to the $A^2\Delta \rightarrow X^2\Pi$ and $B^2\Sigma \rightarrow X^2\Pi$ systems of CH, the $CH_2(\tilde{b}^1B_1 \rightarrow \tilde{a}^1A_1)$ system of CH_2 , and the first three Balmer lines of H. Other low intensity transitions may have been present, but were indistinguishable from the noise.

The irradiation wavelength threshold for electronically excited CH occurs near 1032Å, and results in the process $CH_4 + h\nu \rightarrow CH(A^2\Delta) + H_2(X^1\Sigma_g^+) + H(1^2S_{1/2})$. The calculated and measured threshold for the process agree to within 0.05 eV. The maximum absolute cross section occurs near 923Å and has a value of $7.8 \times 10^{-20} \text{ cm}^2$.

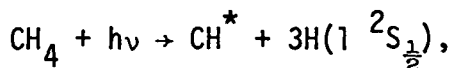
The threshold for exciting CH to the $B^2\Sigma$ state occurs near 950Å with a maximum absolute cross section of $6.1 \times 10^{-21} \text{ cm}^2$ near 898Å. It is suggested that this state results from the process, $CH_4 + h\nu \rightarrow CH(B^2\Sigma) + H_2(X^1\Sigma_g^+) + H(1^2S_{1/2})$.

The fluorescence, for all processes observed, approaches zero for incident photons between 626Å and 760Å.

A second measured "threshold" for excitation into the states $CH(A^2\Delta)$ and $CH(B^2\Sigma)$ occurs at 626Å. It has not been uniquely determined which of the two possible processes,



or



is responsible for the excitation at these shorter incident photon wavelengths. However, the absolute cross sections for the responsible process are down an order of magnitude from those associated with $CH_4 + h\nu \rightarrow CH^* + H_2(X^1\Sigma_g^+) + H(1^2S_{1/2})$, identified for incident photons of 900Å.

wavelength. In addition, 626Å corresponds approximately to the threshold for the process $\text{CH}_4 + h\nu \rightarrow \text{CH}_3(X^2A_2'') + \text{H}^*$ which is suggested as the process resulting in the first three Balmer lines. The process $\text{CH}_4 + h\nu \rightarrow \text{CH}_2(\tilde{b}^1B_1) + \text{H}_2(^1\Sigma_g^+)$ is suggested as the process responsible for the CH_2 fluorescence. Its maximum cross section is estimated to be $\sigma = 1 \times 10^{-20} \text{ cm}^2$.

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CONTINUOUS CHANNEL ELECTRON MULTIPLIERS

INTRODUCTION

Recognizing the substantial reduction in weight, size and power consumption that continuous channel electron multipliers offer over conventional discrete multipliers, a study of the life-time characteristics of the Bendix 4028 continuous channel electron multipliers has been undertaken. Among the characteristics studied are expected lifetime when operating in the "pulse counting mode", gain versus accumulated charge and count, gain degregation versus count rate, gain versus operating voltage, "resolution" versus operating voltage, multiplier load resistance, operation at atmospheric pressure, and secondary pulsing.

As a result of this work, criteria for selecting units which promise a long lifetime without significantly affecting their overall life has been found. The criteria are believed to be good since they result from an evaluation of 28 of these units under well controlled conditions. Using the criteria, given in the results section, 20% of the units tested here were identified as marginal or bad.

The experimental arrangement of this testing program and the terminology used are similar to that used by previous experimenters^{1, 2, 3}, including the manufacturer^{4, 5}.

In previous work, the "total accumulated count" has been used most often as the independent variable to identify the age of a multiplier. This has its shortcomings and, as will be shown, a better choice is the total accumulated charge.

The lifetime of a good multiplier can be divided into three regions. An idealized gain versus accumulated count curve furnished by the manufacturer, for their 4010 continuous electron multiplier is shown in Figure 1, with the three regions identified. These regions are:

1. Clean-up Region:

This region is characterized by an initial drop in the gain of the device due to desorption of gas molecules from the multiplier's surface. This same phenomenon can be repeated, if the multiplier is shut off and allowed to readsorb gas molecules. In the latter case it is called "gain recovery". Both the clean-up region and gain recovery are short lived.

2. Plateau Region

This region is characterized by a relatively stable gain and stable "resolution". For a good multiplier this region represents the major portion of the device's lifetime.

3. Fatigue Region

This region is characterized by an irreversible gain loss and ultimately results in the "death" of the device.

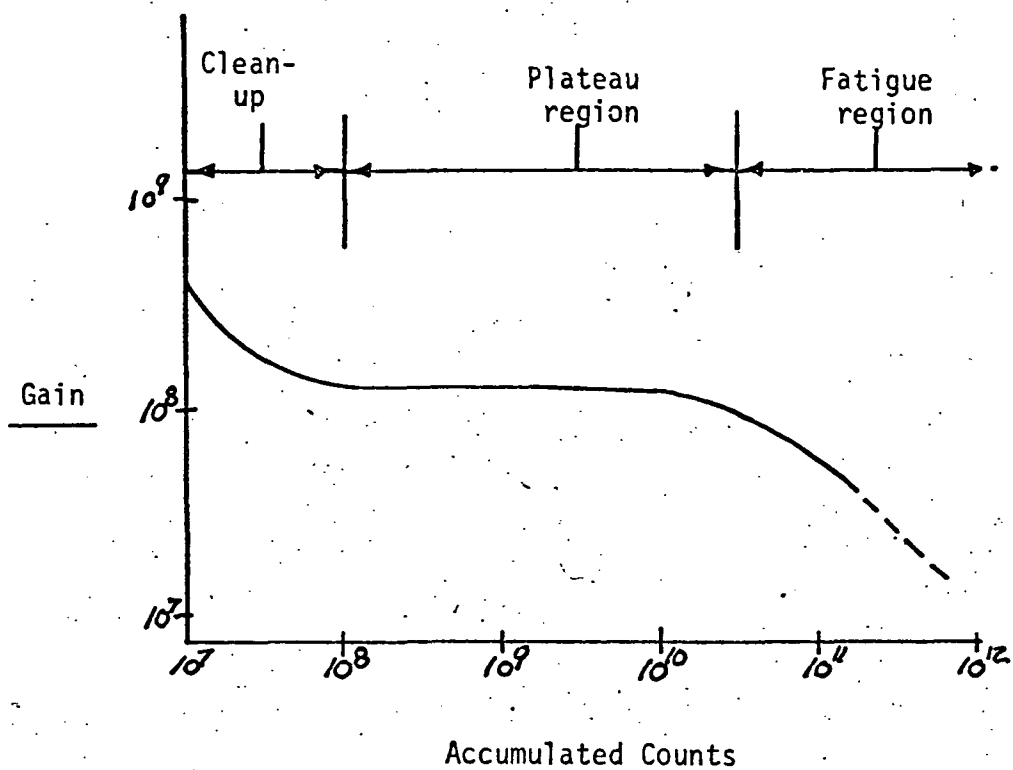


Fig. 1

Gain fatigue curve for Bendix CEM 4010

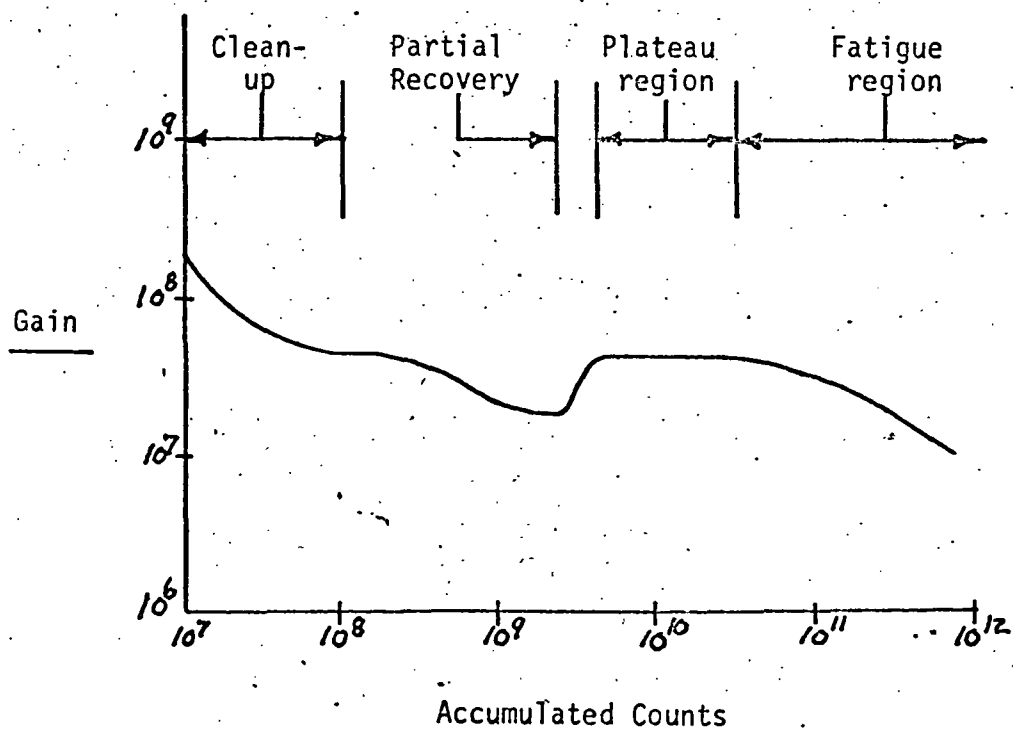


Fig. 2

Gain fatigue versus accumulated counts.

The lifetime data reported here and even earlier by Bakke et al.⁶ differ slightly from the Bendix gain fatigue curve of Fig. 1. Fig. 2 illustrates the difference. The gain drops due to clean-up, reaches a semi-level state then continues to drop further, reaches another level state and then recovers to its initial gain after clean-up. Bakke reports and it is here again verified that this partial recovery is not caused by readsorption of gas molecules inside the multiplier. This recovery only occurs once during the lifetime of the device. The response of Fig. 2 is typical of the "good" multipliers tested here.

EXPERIMENT

The source of electrons needed to stimulate the multipliers are furnished by thermal emission from a tungsten filament. The electrons are accelerated through 0.005 inch diameter apertures and impinge on the multiplier cathodes with 150 electron volts of energy.

The test fixture with mounted multipliers is shown in Fig. 3. The single filament supplies electrons to as many as eight multipliers around the circumference of the fixture. The number of electrons reaching the multipliers is adjusted by changing the filament temperature, and the accelerating grid voltage.

The tests were made in a clean, organic free, ion-pumped vacuum chamber operating at a pressure of 2×10^{-7} Torr. The system was roughed out by a pair of sorption pumps. Grounded screens

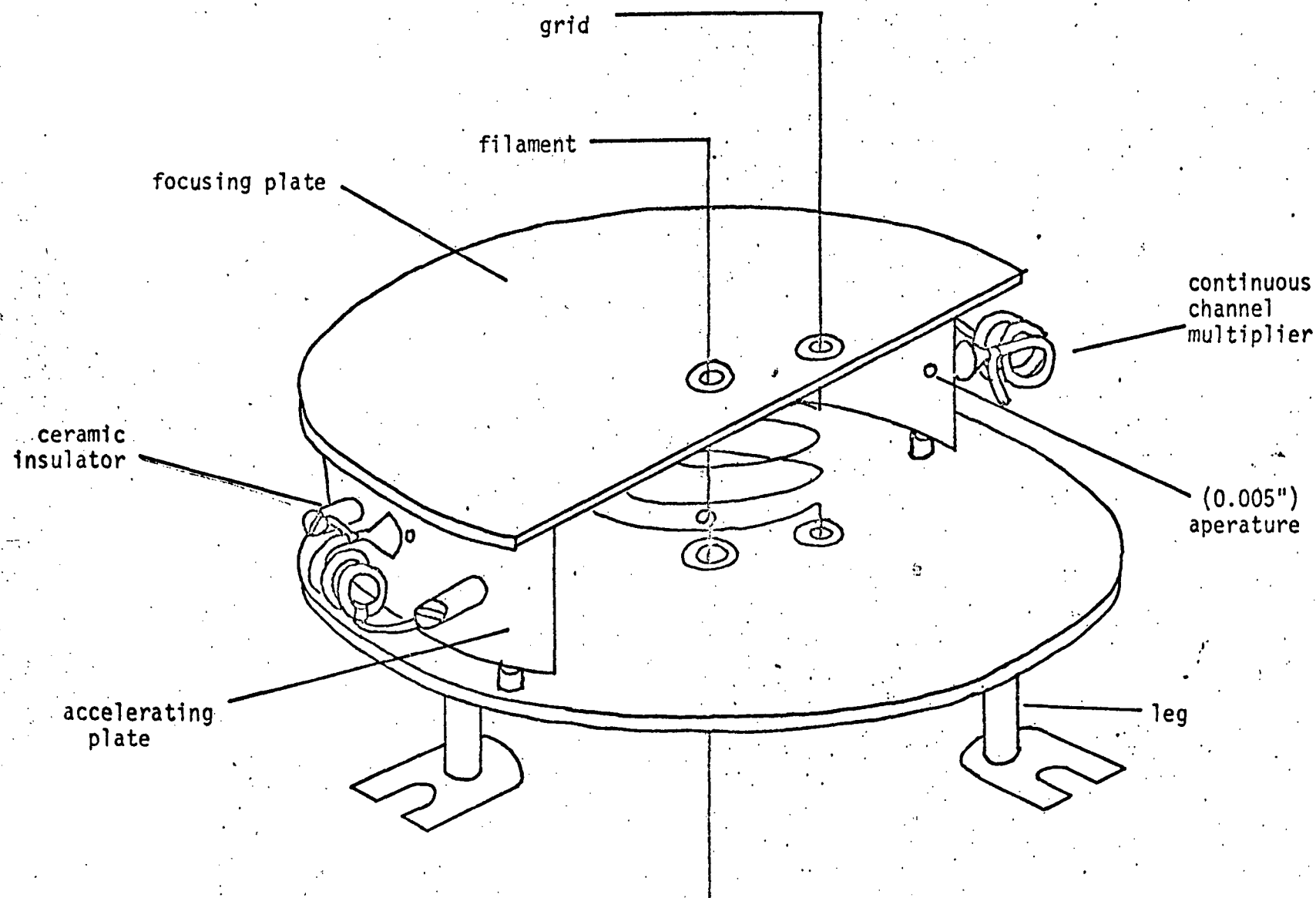


Fig. 3. Test Fixture

and baffles were used to prevent charged particles leaving the ion pump from reaching the multipliers.

The output from each multiplier was capacitively coupled to a separate BNC vacuum feedthrough. Fig. 4. shows a block diagram of the electronic system: charge sensitive amplifier, multichannel analyzer, etc.

RESULTS

Lifetime and Screening Criteria

The purpose of undertaking this study was twofold. The first was to determine if these devices had a sufficient lifetime for extended space exploration, such as the proposed Grand Tour Missions to the outer planets. Secondly, could criteria be developed whereby units could be screened and selected without significantly shortening their lifetime.

What constitutes a sufficient lifetime is of course a relative thing dependent upon the phenomena to be studied. Thus to meet the objective one must determine some expected "average lifetime" by operating a statistically sufficient number of these devices to destruction. At the present time seven units are under test to meet this objective. The total accumulated counts thus far are 6×10^{11} , 3×10^{11} and five at 1.5×10^{11} . Their gains are all greater than 5×10^7 . (Total accumulated count rather than charge is used here since it is probably the parameter

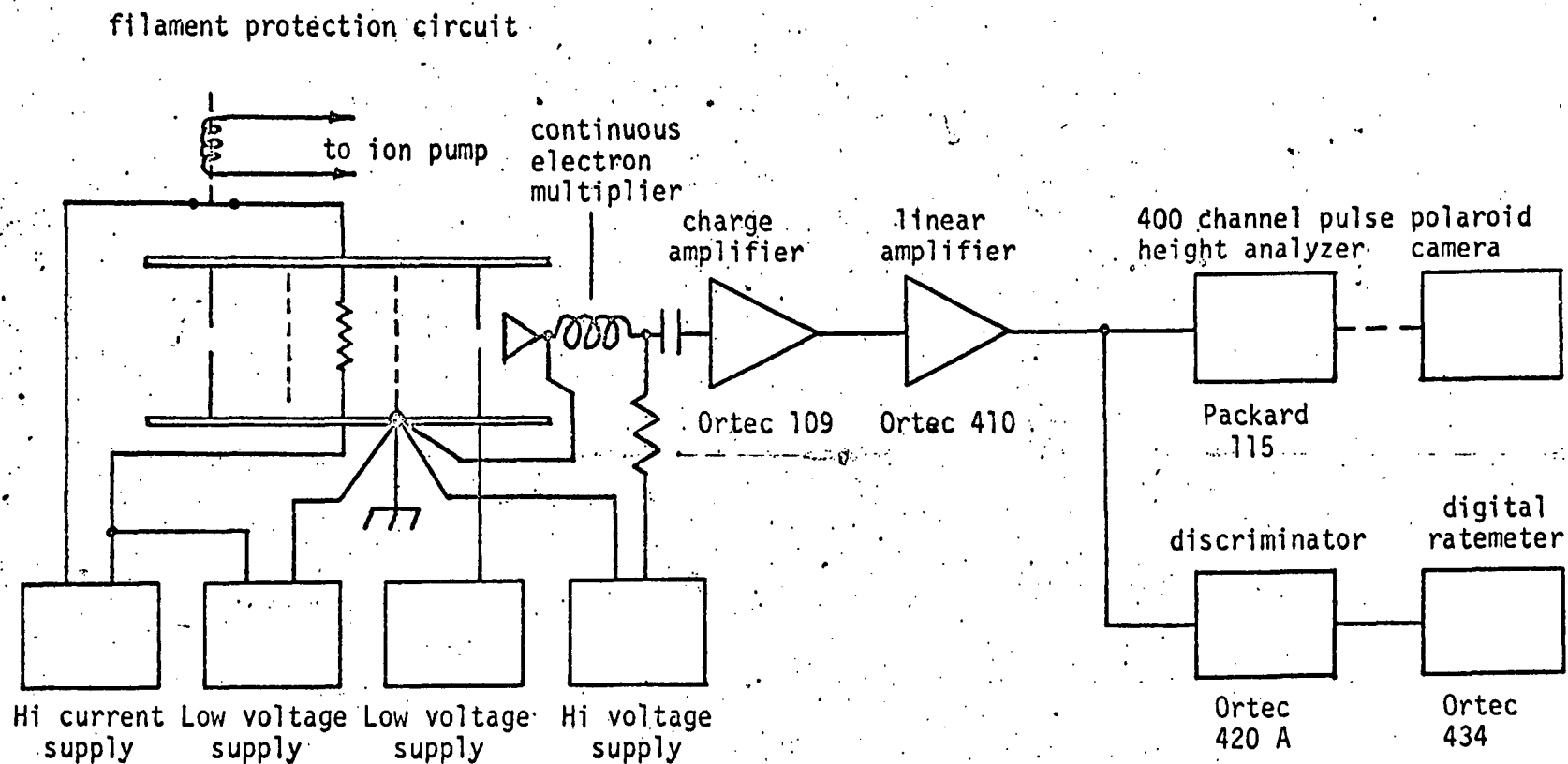


Fig. 4. Block diagram of electronic system.

most familiar to the reader.)

The criteria developed for the selection of these multipliers results in a yield approaching 100 percent in the selection of multipliers having a lifetime greater than 1×10^{11} counts (or 0.80 coulombs at an average gain of 5×10^7).

The multipliers tested were classified as either good, marginal or bad according to the following criteria.

A multiplier was classified as bad if:

1. it failed to meet the manufacturer's specifications,
2. it failed to reach a plateau level after clean-up,
3. it failed to produce a "gain recovery" phenomenon, or
4. it exhibited premature gain fatigue.

It was classified as marginal if it had a

1. low gain
2. poor pulse height distribution,

and

3. produced some unexpected behavior.

A good multiplier has

1. good gain distribution

and

2. good pulse height distribution,

and

3. does not exhibit any of the above symptoms(bad or marginal symptoms)

Twenty-eight (28) units were tested out to 5×10^9 counts. Of these 22 were classified as good, 2 as marginal and 4 as bad. Seven (7) of the good multipliers have been operated without any failure, to greater than 1×10^{11} counts. These are the seven being tested to determine an "expected average lifetime". The remaining 15 multipliers have not undergone any further testing under controlled conditions.

To summarize, if marginal multipliers are classified as unusable, one can expect an 80% yield of multipliers having lifetimes greater than 1×10^{11} counts. One can also expect a 100% yield out to 1.5×10^{11} counts after screening to 5×10^9 counts for the remaining good multipliers.

Variation of Parameters

When designing electronic circuits which incorporate these continuous electron multipliers, one should be aware of the many parameters which change as a function of lifetime, count rate, and operating voltage. Fig. 5 through Fig. 9 show respectively gain fatigue, gain degregation versus count rate, gain versus operating voltage, and resolution versus accumulated charge.

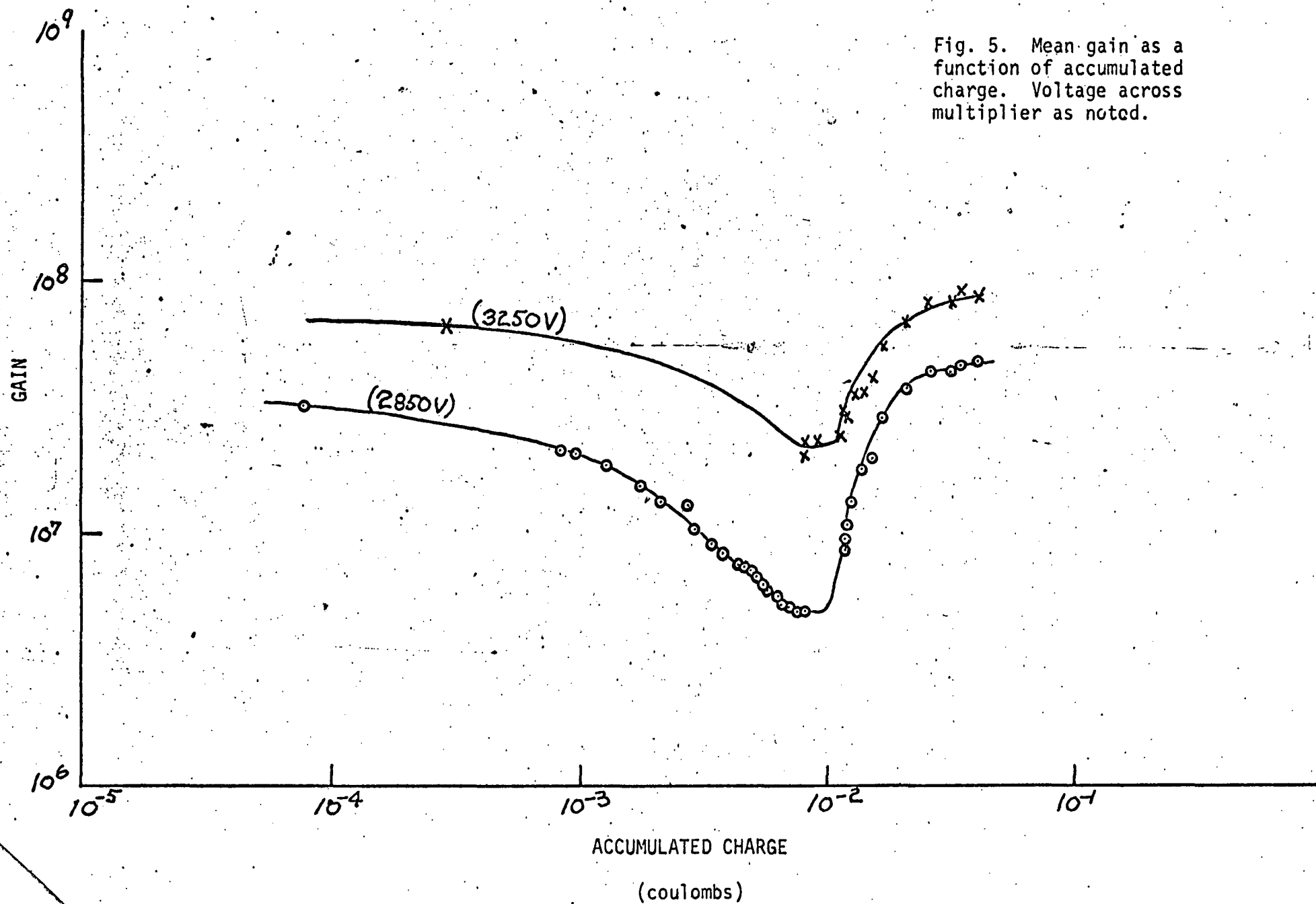
These curves are representative for the multipliers tested here.

Operation at atmospheric pressure, and after pulsing are also discussed.

Gain Fatigue:

It was mentioned earlier that our fatigue curves differed somewhat from those published by the manufacturer. That is, after

Fig. 5. Mean gain as a function of accumulated charge. Voltage across multiplier as noted.



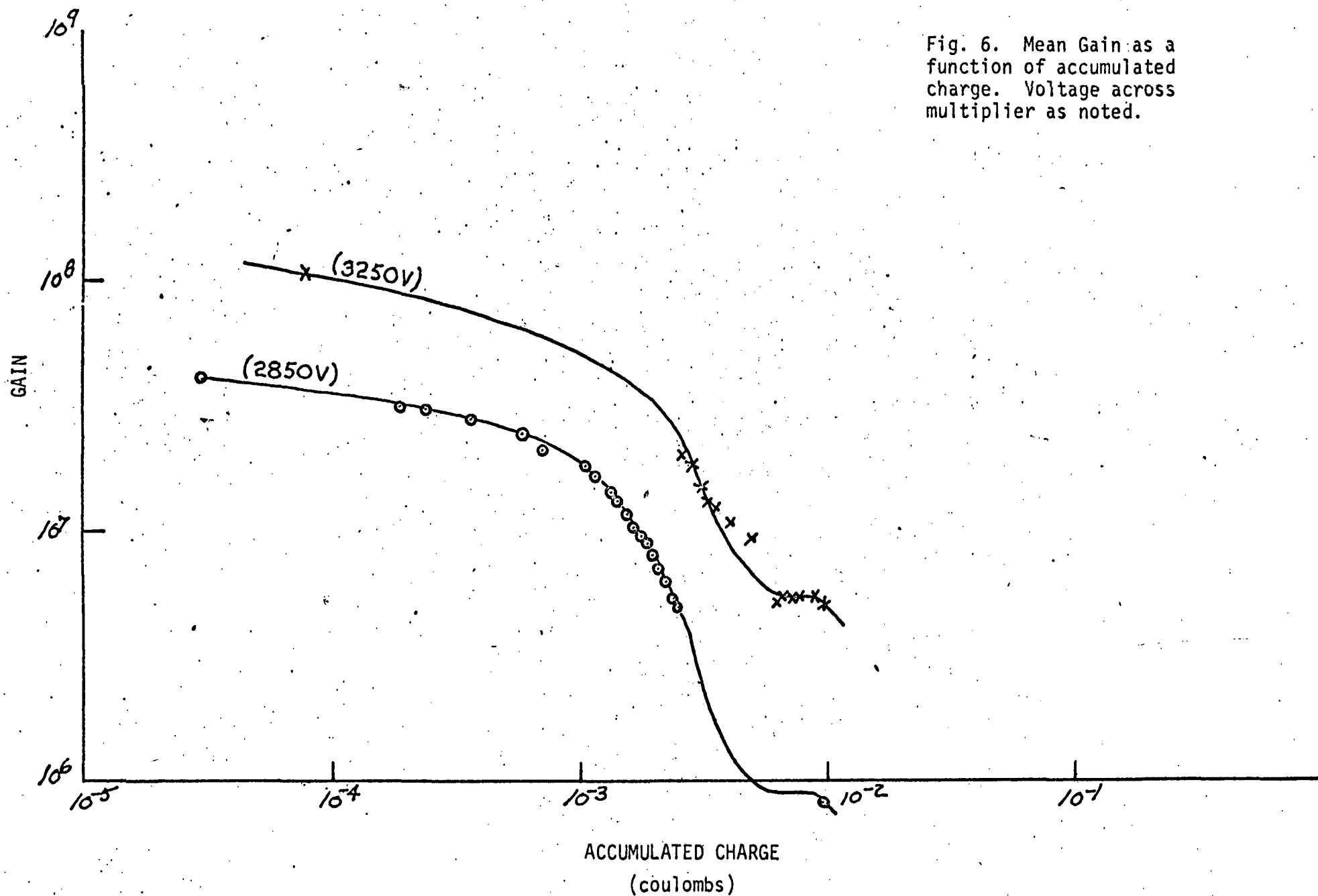


Fig. 7. Gain as a function of
count rate.
(3050 volts across multiplier)

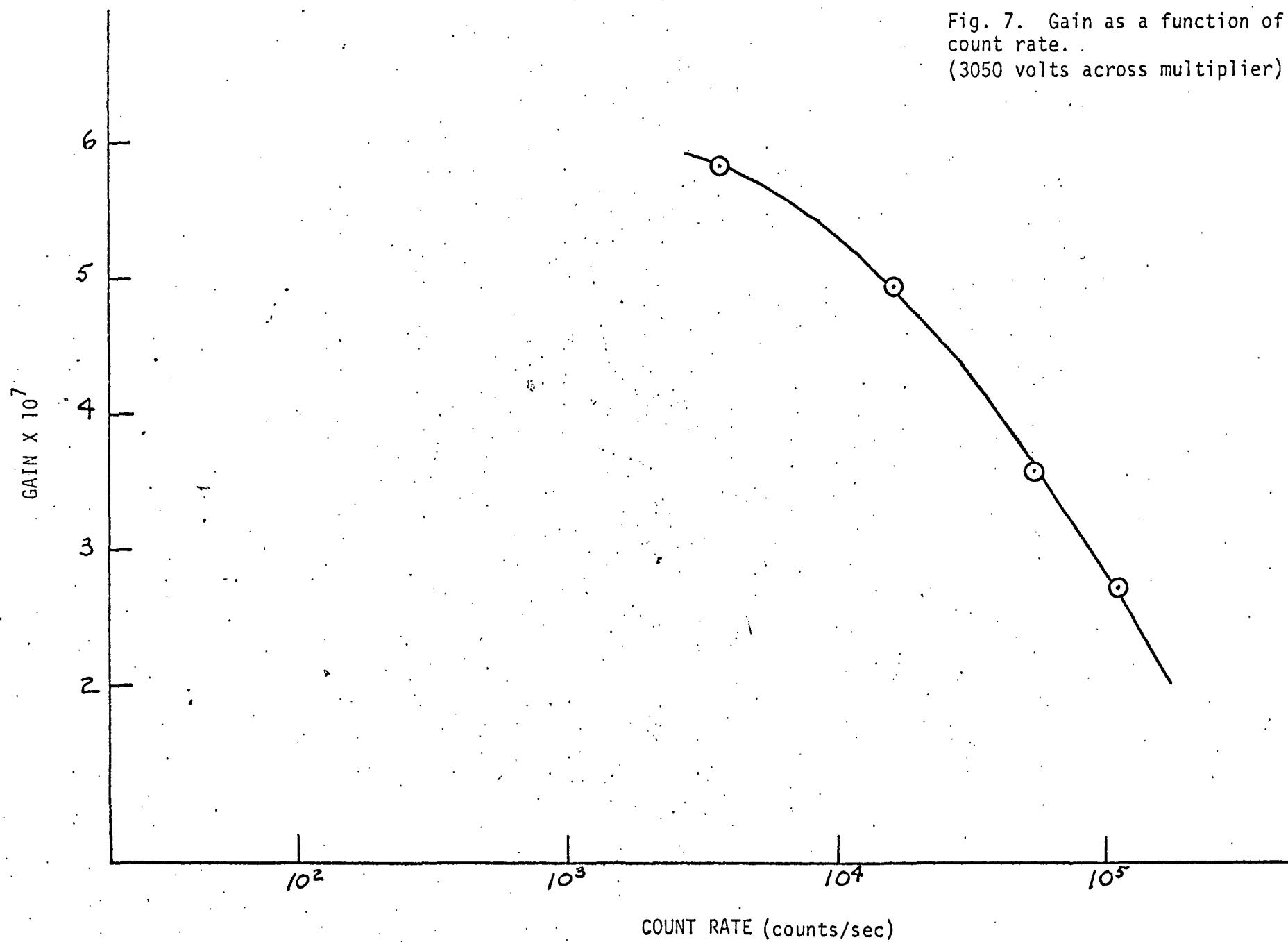


Fig. 8. Gain as a function of operating voltage across multiplier.

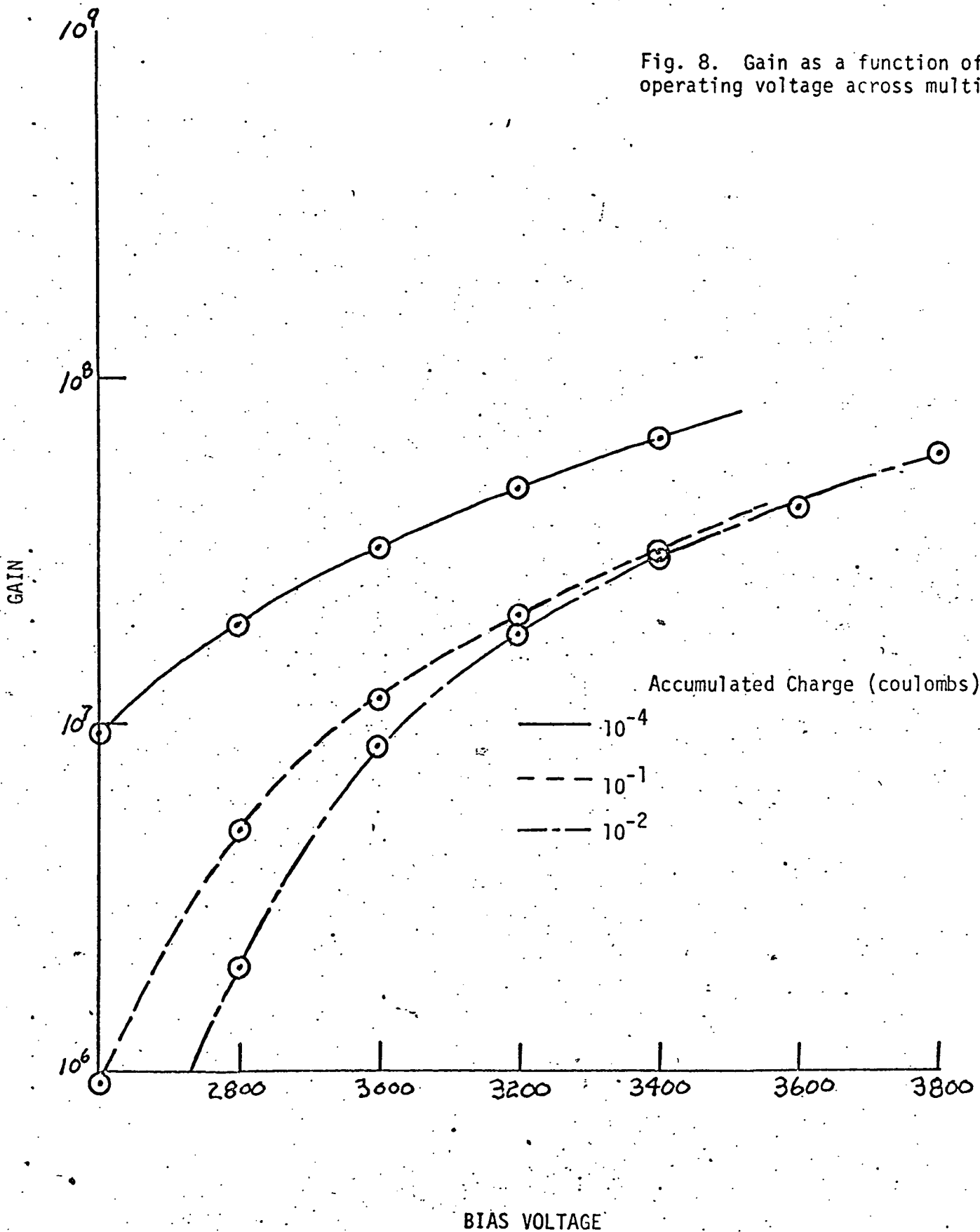
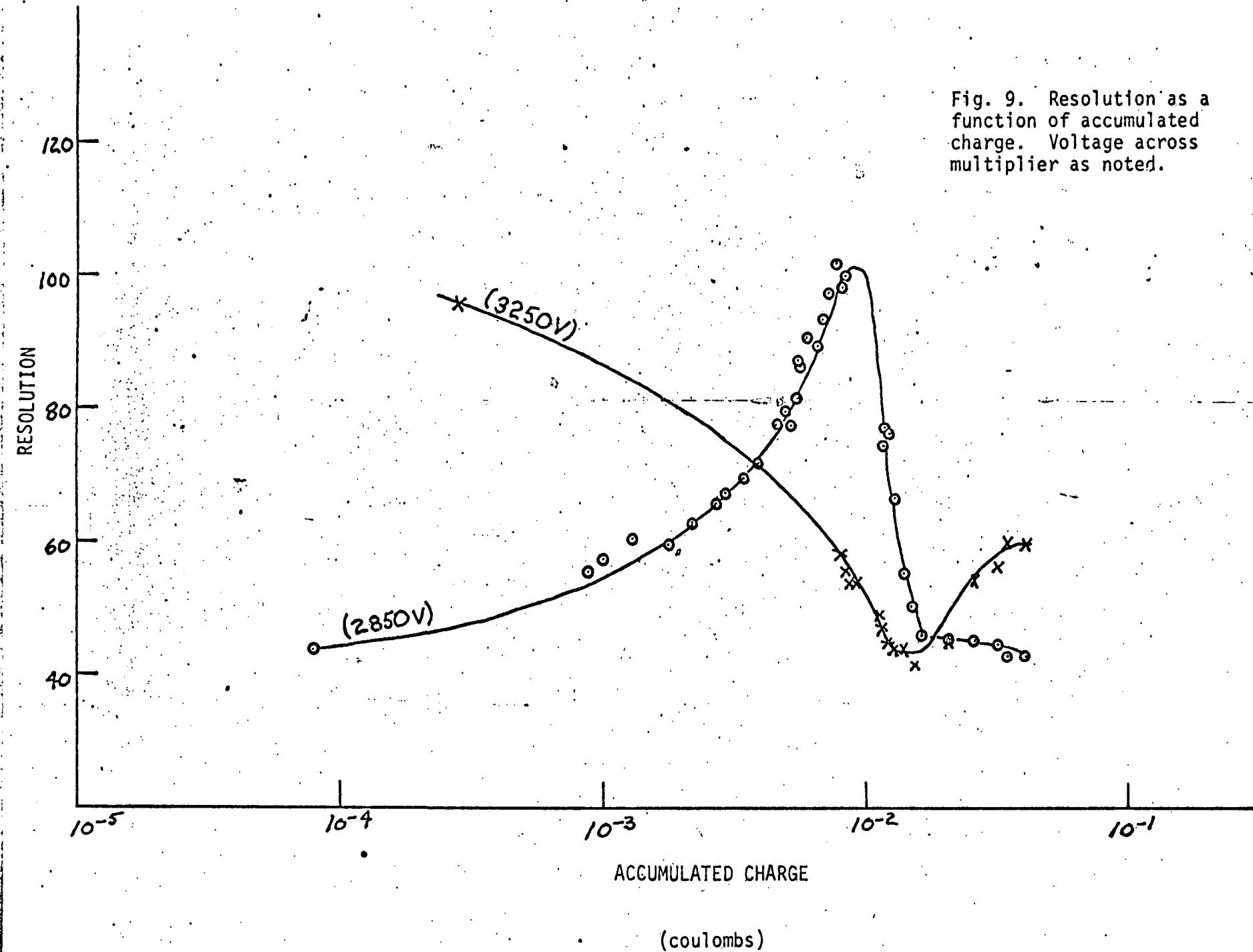


Fig. 9. Resolution as a function of accumulated charge. Voltage across multiplier as noted.



the initial clean-up period, and a small plateau region the multipliers suffered a gain loss which was always significantly recovered after the multiplier had supplied 10^{-2} coulombs of charge. Fig. 5 is the actual data taken for one of the good multipliers tested. Fig. 6 is included since it shows the gain recovery phenomenon occurring even for a bad multiplier.

It was this gain recovery feature which suggested that the total accumulated charge is the best choice of an independent variable to measure lifetime rather than the total accumulated counts, for there was no correlation between the total accumulated counts and the position of this gain recovery. However, the recovery always appeared very near the same total accumulated charge.

Gain Degregation Versus Count Rate:

Fig. 7 shows the gain as a function of count rate for one of the multipliers operating in the pulse counting mode. It agrees very favorably with the manufacturer's published findings. Notice that the count rates need not be very great before the gain is significantly effected. This is one of the reasons why the electronics detecting the multiplier output should have a wide dynamic range.

Gain Versus Operating Voltage & Count Rate

Just as for discrete multipliers, it is expected that continuous multipliers can be operated either in a linear or a nonlinear mode. For the "pulse counting mode" the multiplier is operated in the

nonlinear or saturation mode. Thus, the output pulse is less dependent on the initial input particles energy and the operating voltage.

Fig 8 shows a typical gain versus operating voltage curve for the multipliers tested here. The linear region extends from <2600 volts to ≈ 2900 volts, where the saturation region begins. It has been suggested that the multiplier can be thought of as an RC transmission line, and that as soon as all the available charge has been depleted no further gain can be realized. This transmission line model also helps to explain why the gain is degraded with increasing count rate. That is, there is some time constant associated with the multiplier during which the lost charge is replenished.

Resolution:

Resolution is defined here as the full width half maximum (FWHM) spread in gain about the mean gain, divided by the mean gain. The resolution is easily found from analyzing the pulse height distribution from the pulse height analyzer. Fig. 9 shows the resolution as a function of accumulated charge, with the operating voltage as a parameter. Resolution is affected by both lifetime and operating voltage. Here again, these effects can be minimized by using a system with a large dynamic range.

Load resistance:

The average resistance of these devices when new was measured to be 1.4×10^9 ohms. This resistance when measured after having accumulated a total charge of 0.80 coulombs, (10^{11} counts at an average gain of 5×10^7) was unchanged.

Secondary After Pulsing:

This phenomenon generates pulses which result from positive ions causing secondary electrons near the multiplier cathode. Some after pulsing was witnessed during the initial clean-up region, of these multipliers but then disappeared. The physical geometry of these multipliers is designed to prevent after pulsing. This, in addition to the low pressure of 2×10^{-7} Torr and a dead time of 3 microseconds is believed to have prevented any further appearance of after pulsing.

Operation at Atmospheric Pressure:

Eight good multipliers have been operated at atmospheric pressure and 3700 volts, some for as long as 24 hours. The multipliers failed to multiply of course. However, when returned to a vacuum environment they all operated satisfactorily.

SUMMARY AND CONCLUSIONS

The evaluation of "channeltron" electron multipliers is continuing. Attention is now being directed toward determining an "average lifetime expectancy" for units which are still operating satisfactorily after 5×10^9 accumulated counts at a gain of 5×10^7 or better. Since initiation of this study some 28 Bendix 4028 electron multipliers have been subjected to test. Of these about 20% have failed to operate correctly prior to the 5×10^9 total accumulated count. Seven of the good units are presently under test. They will be operated until they fail, in order to determine an average life expectancy. To date these

units range in total accumulated counts from 1.5×10^{11} - 6×10^{11} counts.

None of these seven has shown any sign of fatigue.

It can therefore be concluded that these multipliers can be screened to yield an average lifetime of greater than 1.5×10^{11} counts without significantly effecting their lifetime. That is the "bad or marginal" multipliers can be found prior to accumulating 5×10^9 counts. It is expected that some 20% will be found in this usable condition. Furthermore, the operating characteristics for these devices are predictable. Thus, any difference in operating parameters, as a function of lifetime can be compensated for in the electronics design.

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ABSORPTION SPECTRUM OF CO IN THE
HOPFIELD HELIUM CONTINUUM REGION, 600-1020Å *

M. OGAWA AND S. OGAWA

Department of Physics
University of Southern California
Los Angeles, California 90007

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18 pages of the manuscript
4 pages of figures
8 pages of tables

ABSORPTION SPECTRUM OF CO

Mailing Address:

Professor Masaru Ogawa
Department of Physics
University of Southern California
Los Angeles, California 90007

ABSTRACT

The absorption spectrum of CO has been reinvestigated in the Hopfield helium continuum region, 600-1020Å. Rydberg series converging to the B $2\Sigma^+$ state of CO^+ were extended to higher members, and a new group of Rydberg series converging to the A $2\Pi_{1/2}$ state of CO^+ was identified, it consists of eight vibrational series. Finally, another new Rydberg series converging to the X $2\Sigma^+$ ground state of CO^+ was also identified. The series limits obtained in the present study are 158664 cm^{-1} (B $2\Sigma^+$), 133484 cm^{-1} (A $2\Pi_{1/2}$), and 113029 cm^{-1} (X $2\Sigma^+$). The electron configuration of the upper state of the new series converging to the X $2\Sigma^+$ state is $(5\sigma)(np)$. The rotational structures of the $(5\sigma)(4p\sigma) 1\Sigma^+ - X 1\Sigma^+$ and $(5\sigma)(4p\pi) 1\Pi - X 1\Sigma^+$ bands were analyzed, and the molecular constants of these upper states are $\nu_0 = 103054.25 \text{ cm}^{-1}$, $B_0 = 1.9189 \text{ cm}^{-1}$, and $D_0 = 6.6 \times 10^{-5} \text{ cm}^{-1}$ for the $1\Sigma^+$ state and $\nu_0 = 103271.49 \text{ cm}^{-1}$, $B_0 = 1.9812 \text{ cm}^{-1}$, and $D_0 = 1.4 \times 10^{-5} \text{ cm}^{-1}$ for the 1Π state.

I. INTRODUCTION

The absorption spectrum of CO in the vacuum ultraviolet region, particularly below $1000\text{\AA}$, has been studied by several investigators (1-5). One Rydberg series converging to the $X\ 2\Sigma^+$ state was earlier identified by Takamine et al. (4). Another series, (α), converging to the $A\ 2\Pi$ state, and two farther ones (β), sharp and diffuse, converging to the $B\ 2\Sigma^+$ state were identified by Tanaka (3). In addition to Tanaka's two series, converging to the $B\ 2\Sigma^+$ state, two more series, (III and IV), converging to the same limit were also observed by one of us (M. O.) (5). Both previously identified series, converging to the $X\ 2\Sigma^+$ and $A\ 2\Pi$ states, are rather weak and most of strong bands still remain unclassified, although they are likely to be members of other Rydberg series.

Recently, Lindholm (6) grouped many previously known bands into Rydberg series according to his own theoretical prediction of the quantum defects of Rydberg states. He used the wavelengths and absorption intensities, obtained through the photographic work by the above mentioned authors (2-5), and also through the measurements of absorption coefficients by Huffman, Larrabee, and Tanaka (7) and by Cook, Metzger, and Ogawa (8).

We are reinvestigating the absorption spectrum of CO in the region, 600-1020Å, which was photographed with improved resolution. This paper presents part of the results of our analysis of the spectrum.

II. EXPERIMENTAL

A 3-m vacuum spectrograph equipped with a grating of 1200 lines/mm was used, which provided a reciprocal linear dispersion of 2.85Å/mm in the first order. The spectrum was taken in the first, second, and third orders. Depending on the order and its corresponding wavelength region, two gratings were employed, one blazed at 1550Å and the other at 2950Å. The Hopfield helium continuum was used as background to photograph the spectrum on Kodak SWR plates.

CO gas, of 99.9% purity, was obtained from Air Reduction, Inc. and was introduced into the spectrograph without a further purification.

III. RESULTS AND DISCUSSIONS

A. Series Converging to the B $2\Sigma^+$ State of CO^+

The absorption spectrum in the region from 620 to 700Å is reproduced in Fig. 1(a). The spectrum of this region shows rather simple features and the bands are classified into five Rydberg series (sharp, diffuse, III, IV, and V) converging to the B $2\Sigma^+$ state of CO^+ . Wavenumbers and assignments of the observed bands are listed in Table I. The running number m of each Rydberg state is defined by $\mu = m - n^*$, so that it gives a minimum positive value of μ , where n^* is the effective quantum number. The intensity of the sharp series decreases rapidly as m increases and its higher members merge into series III. Series III was extended to higher members ($m = 18$). Convergence limits of the sharp series and series III are 158665 cm^{-1} and 158663 cm^{-1} , respectively. An average value of 158664 cm^{-1} , or 19.671 eV, was adopted as their series limit. Wavenumbers of the sharp series and series III are, respectively, expressed by the following equations

$$\nu_m = 158664 - R/(m - 0.650 - 0.084/m - 0.13/m^2)^2, \quad (1)$$

$$\text{and} \quad \nu_m = 158664 - R/(m - 0.902 - 0.232/m)^2, \quad (2)$$

where R (109735 cm^{-1}) is the Rydberg constant. The calculated wave-

numbers for series III according to Eq. (2) are also listed in the table.

The diffuse series with $m = 5, 6,$ and 7 of $v' = 0$ are accompanied on the longer wavelength side by a band which has almost the same intensity as the diffuse series. The separation is $82, 63,$ and 59 cm^{-1} for $m = 5, 6,$ and $7,$ respectively. The band with $m = 4$ does not show such side-band, although its width is about 80 cm^{-1} (see Fig. 1). The bands with $m = 5$ and 6 of $v' = 1$ are also accompanied by a side-band with a separation of about 70 and 50 cm^{-1} , respectively. However, as seen in Fig. 1(a), the bands in question approach very rapidly the sharp series as m increases and then merge into the sharp series. This suggests that the bands form an independent series, called series V henceforth, and their upper states are probably triplet which originate from the same electron configuration as that of the sharp series.

A band at $672.4\text{\AA}$, $m = 4$ of the sharp series, shows double heads in the second and third order spectrum, which seem likely to be R and Q heads. Therefore an upper state of this band is probably a $^1\Pi$ state rather than a $^1\Sigma^+$ state which is suggested by Lindholm (6). Recently, Betts and McKoy (9) suggested that Rydberg orbitals of the upper states of the diffuse and sharp

series are $np\sigma$ and $np\pi$, respectively. The latter gives a 1π state as an upper state of the sharp series.

Approximate values of the quantum defects, μ , observed in the present work, and the Rydberg orbitals, previously suggested for each series, are listed in Table IV.

It should be noticed that toward the shorter wavelength side of any of the member bands of series III there is exhibited slight darkness representing weak absorption, when compared to other parts in Fig. 1(a). This indicates that this part forms a Fano-type profile of preionization together with series III.

B. Series Converging to the A 2π State of CO^+

Rydberg series converging to the A 2π state of CO^+ are located mainly in the wavelength region from 690 to 880Å. The spectral features of this region are very complex due to the overlapping of many series consisting of several vibrational series. Henning (2) classified two progressions in this region and Tanaka (3) three progressions and one Rydberg series (α -series) which consists of three vibrational series.

We attempted to classify the bands first into progressions and then into Rydberg series. As a result, we have been able to

organize these bands into many progressions and then reclassified them tentatively into five Rydberg series, all of which consist of several vibrational series. In the present paper, we report a series of high intensity. This series consists of eight vibrational series and is different from the α -series which shows weak intensity. Most of both Henning's progression (1) and Tanaka's progressions (1) and (3) are reclassified as the $m = 3, 4$, and 6 progressions of the series, respectively. Early members of this series ($m = 3$ and 4) coincide exactly with those of the $1\pi \rightarrow n\sigma$ series ($n = 4$ and 5), suggested by Lindholm, but the higher members are different even though they are located at almost the same wavelengths. Observed wavenumbers, effective quantum numbers, and assignment of the member bands of the series are listed in Table II. The reproduction of the spectrum is also shown in Figs. 1(b) and 2(a).

Due to the large shift of the potential minimum of the $A^2\Pi$ state of CO^+ ($r_e = 1.2438\text{\AA}$) from that of the $X^1\Sigma^+$ state of CO ($r_e = 1.1283\text{\AA}$), the observed progression is well developed and its intensity maximum occurs around $v' = 2$. This fact agrees well with the intensity distribution of photoelectrons observed by Turner and May (10). Wavenumbers of the $v' = 2$ series are approximately represented as follows

$$\nu_m = 136530 - R/(m - 0.077 + 0.0725/m)^2, \quad (3)$$

which indicates that the quantum defect increases slowly with m .

Wavenumbers calculated according to Eq. (3) are listed in the parenthesis, next to the row of values of $v' = 2$ in Table II.

ΔG values of the $A^2\Pi$ state, calculated from both the series limits and the known vibrational constants obtained from CO^+ emission bands (Baldet-Johnson and Comet tail bands), are listed in Table IV. These two sets of the values agree very well. The difference between the series limits for the $B^2\Sigma^+$ and $A^2\Pi$ states is 25180 cm^{-1} , $(158664 \text{ (B)} - 133486 \text{ (A)} \text{ cm}^{-1})$, which is very close to the $\nu_{00} = 25167 \text{ cm}^{-1}$ of the $B^2\Sigma^+ - A^2\Pi_{1/2}$ band (Baldet-Johnson)(11). The difference between the series limits for the $A^2\Pi$ and $X^2\Sigma^+$ states (see next section) is 20455 cm^{-1} , $(133484 \text{ (A)} - 113029 \text{ (X)} \text{ cm}^{-1})$, which is also very close to the $\nu_{00} = 20466 \text{ cm}^{-1}$ of the $A^2\Pi_{1/2} - X^2\Sigma^+$ band (comet-tail)(11). Therefore, the new series converges to the $^2\Pi_{1/2}$ component of the $A^2\Pi_1$ state of CO^+ .

The band with $m = 3$ is the lowest member of the series and their quantum defect μ is about 0.05. If the value of m is one unit smaller than the true value of n , the actual quantum defect is 1.05. Then the possible electron configuration of the upper state is $(1\pi)^3(nd)$ or $(1\pi)^3(ns\sigma)$ according to $\mu = 0.05$ or

1.05, respectively. If the latter one ($ns\sigma$) is the case, the first member ($m = 2$ or $n = 3$) is located in the wavelength region $\sim 960\text{\AA}$. In this region, there are several bands which are degraded toward longer wavelengths but whose ΔG values do not vary smoothly. Therefore, at this moment we are not sure that the band $m = 3$ is the first member of the series.

C. Series Converging to the $X^2\Sigma^+$ State of CO^+

Rydberg series converging to the $X^2\Sigma^+$ ground state of CO^+ are located in the region from 860 to 1195 $\text{\AA}$. The appearance of the spectrum in this region is markedly different from that of N_2 which is isoelectronic to CO . By glancing at the spectrum, we get the impression that in contrast with the N_2 spectrum, the majority of the bands belong to several Rydberg series converging to the $X^2\Sigma^+$ state, and the remainder of the bands are non-Rydberg bands, though some of them may be first member bands of the Rydberg series converging to the $A^2\Pi$ state.

Many of the prominent bands have been classified into two Rydberg series converging to the $X^2\Sigma^+$ state. The upper states of these series are $(5\sigma)(np\sigma)^1\Sigma^+$ and $(5\sigma)(np\pi)^1\Pi$ complex whose first members, $C^1\Sigma^+$ and $E^1\Pi$, are already well known. Lindholm (6)

identified the $(5\sigma)(np\sigma)$ and $(np\pi)$ series, (np complex series), which includes the series observed by Takamine et al. (4) as its higher members. But the series newly classified here as the $(np\sigma)$ and $(np\pi)$ complex series do not include them (See Fig. 2(b)).

A reproduction of the spectrum is shown in Figs. 2(b) and 3(a), while wavenumbers and effective quantum numbers are listed in Table III.

At the location of the second member of $v' = 0$ series, $n = 4$ or $n^* = 3.35$, there is a group of three bands forming four distinct heads. According to the analysis of the rotational structure the one at the longest wavelength, shading toward longer wavelength, corresponds to the $4p\sigma \ ^1\Sigma^+ - X \ ^1\Sigma^+$ transition, and the one at the shortest wavelength, shading towards shorter wavelength, corresponds to the $4p\pi, \ ^1\Pi - X \ ^1\Sigma^+$ transition. The middle one shades towards longer wavelengths and is probably a $\Pi - \Sigma$ type band, but the present resolution was not enough to analyze its rotational structure.

At the location of the third member $n = 5$ or $n^* = 4.35$, there are five distinct heads, none of which shows clear shading towards shorter wavelengths and their spectral features are rather complex. The n^* values of the first and second heads from the longer wavelength are close to the expected values of the $5p\sigma$

$1\Sigma - X\ 1\Sigma^+$ and $5p\pi\ 1\Pi - X\ 1\Sigma^+$ bands, respectively. It is not possible to assign them definitely as members of the series without rotational analysis. The bands of $m = 6, 7$, and 8 show the double heads whose separation is $19, 21$, and 7 cm^{-1} , respectively. The intensity of the shorter wavelength head is weaker than that of the longer one. The head of the longer wavelength of the $m = 7$ band seems to be hidden by an NI emission line at $906.428\text{\AA}$. The shorter wavelength heads with $m \geq 9$ merge into the longer wavelength heads.

Around the position of $m = 13$ there are two line-like bands with wavenumbers of 112323 cm^{-1} ($n^* = 12.46$) and 112314 cm^{-1} ($n^* = 12.39$). From their intensities, the former band has been temporarily assigned to be the $m = 13$ band, although an effective quantum number of the other band is preferable as a member band. The intensities of bands with $m \geq 18$ become suddenly weak compared with those of the lower members. But in this study we did not attempt to analyze all lines in this region to explain the anomalous intensity distribution of the series. The intensities of member bands with $m \geq 26$ are rather strong due to overlapping with a band which has a head at about 112990 cm^{-1} .

The convergence limit of the $v' = 0$ series is $113029 \pm 2\text{ cm}^{-1}$, which is exactly the same as that obtained by Takamine et al.

although their series is different from the present one.

The excitation energy of the $np\sigma$ series is approximately given by the equation

$$v_n = 113029 - R/(n - 0.615 - 0.263/n - 0.165/n^2)^2. \quad (4)$$

Calculated values from Eq. (4) are listed in Table III.

The $v' = 1$ vibrational series was also identified. It is very weak compared with the $v' = 0$ series. Observed wavenumbers and effective quantum numbers of the member bands are also listed in Table III.

D. The $(5\sigma)(4p\sigma) \ ^1\Sigma^+$ and $(5\sigma)(4p\pi) \ ^1\Pi$ States

As mentioned in the last section, at the location of the $(5\sigma)(4p) - X \ ^1\Sigma^+$ bands there are three bands (970.2, 968.6, and 968.1 Å). The structures of these bands under low resolution spectrum are of the type $^1\Sigma^+ - ^1\Sigma^+$, $^1\Pi - ^1\Sigma^+$, and $^1\Pi - ^1\Sigma^+$, respectively. However, the band in the middle is very complex under high resolution. We have been able to analyze the rotational structure of two bands at both of its sides. An enlarged spectrum of these bands is shown in Fig. 3(b). Observed wavenumbers, assignment of rotational lines, and $\Delta_2 F''$ values (both observed and calculated from the known constants (12) are listed in Table VI.

The band at 970.2Å has a single P and R branch and is due to the transition $1\Sigma^+ - X\ 1\Sigma^+$. The molecular constant obtained for the upper $1\Sigma^+$ state are $\nu_0 = 103054.25\text{ cm}^{-1}$, $B_0 = 1.9189\text{ cm}^{-1}$, and $D_0 = 6.6 \times 10^{-5}\text{ cm}^{-1}$.

The 968.1Å band consists of P, Q, and R-branches, and most of the Q-lines are located within 16 cm^{-1} of the Q head due to the small difference of the rotational constants of the upper and lower states. The higher members of the P-branch merge into the 968.6Å band, and their wavelengths could not be measured. The intensity of the P-branch is much weaker than that of the R-branch. This band is due to the $1\Pi - X\ 1\Sigma^+$ transition, and the molecular constants obtained for the $1\Pi^+$ component are $\nu_0 = 103271.49\text{ cm}^{-1}$, $B_0 = 1.9812\text{ cm}^{-1}$, and $D_0 = 1.4 \times 10^{-5}\text{ cm}^{-1}$. The excitation energy of the $1\Pi^+$ state (consequently Λ -type doubling of 1Π state) is obtained by using the Q-branch. However, the resolution was not enough to separate the rotational lines of the Q-branch, and even the numbering of those several lines which were not overlapped by R-lines is not available.

The separation of the 1Π and 1Σ state of the $4p\sigma$ and π electrons is 217.2 cm^{-1} . Therefore, we expect the ℓ -uncoupling phenomenon. The large rotational constant of the $1\Pi^+$ state ($B = 1.9812\text{ cm}^{-1}$) and the small rotational constant of the $1\Sigma^+$ state

($B = 1.9189 \text{ cm}^{-1}$) may be mainly the result of the ℓ -coupling phenomenon, though we were not able to get the Λ -type doubling of the $^1\Pi$ state because of poor resolution.

The total energies of the p-complex are given by the expressions (13)

$$\Sigma^+ : T_1 = T_0 + B [\alpha/2 + J(J+1) + 1 - \sqrt{\alpha(\alpha-4)/4 + (2J+1)^2}], (5)$$

$$\Pi^- : T_2 = T_0 + B [\alpha + J(J+1)], (6)$$

$$\Pi^+ : T_3 = T_0 + B [\alpha/2 + J(J+1) + 1 + \sqrt{\alpha(\alpha-4)/4 + (2J+1)^2}], (7)$$

where $\alpha = C/B$ and C is the coupling constant, as characteristic of the coupling between the vector L and the internuclear axis. Adding Eqs. (5) and (7),

$$T_1 + T_3 = 2T_0 + C + 2B + BJ(J+1) (8)$$

is obtained. From the observed T_1 and T_3 energies and the eq. (8), and by considering the small centrifugal correction, the following constants have been obtained

$$T_0 = 103050.2 \text{ cm}^{-1}, C = 221.28 \text{ cm}^{-1}, B = 1.9494 \text{ cm}^{-1}, D = 3.46 \times 10^{-5} \text{ cm}^{-1}.$$

The calculated values for the Σ^+ , Π^- , and Π^+ states according to these constants and equations (5), (6), and (7) are shown in Fig. 4 together with the observed values of Σ^+ and Π^+ . In the figure,

$BJ(J+1) - DJ^2(J+1)^2$ values have been subtracted. The calculated and observed curves agree qualitatively. However, the observed Q-lines, which are not blended with other lines, do not agree with the calculated ones. These discrepancies may be caused by the perturbation between these states, $^1\Pi$ and $^1\Sigma^+$, and the upper state ($^1\Pi?$) of a band at $968.6\text{\AA}$, which is located between these two bands.

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Table I Wavenumbers of $B^2\Sigma^+ \leftarrow X^1\Sigma^+$ Rydberg Series

R_B - Sharp Series								
m	$v' = 0$			$v' = 1$			$v' = 2$	
	$\nu(\text{cm}^{-1})$	n^*	ΔG	$\nu(\text{cm}^{-1})$	n^*	ΔG	$\nu(\text{cm}^{-1})$	n^*
3	137835	2.295	1713	139548	2.297	1655	141233	2.301
4	148715	3.321	1688	150403	3.323	1586	151989 [†]	3.317
5	142809 [†]	4.329	1693	154502	4.335	1658	156160	4.349
6	154819	5.342	1663	156482	5.332	1638	158120 [†]	5.344
7	155925	6.329	1658	157583 [†]	6.307	1657	159240	6.348
8	156631	7.343	1684	158288 [†]	7.358	1608	159923	7.334
9	157082	8.327	1690	158782	8.387	1629	160411	8.409
10	157406	9.339	1676	159082	9.332	1612	160694	9.299
11	157638	10.34	1678	159316	10.34	1611	160927	10.29
12	157808	11.33	1682	159490	11.35			
13	157942	12.33						

R_B - Diffuse Series								
4	149070	3.382	1670	150740	3.381	1610	152350	3.379
5	153037	4.416	1664	154701	4.416			
6	154957	5.441	----	-----				
7	156041	6.468	1603	157644	6.379			
8	156708	7.490						
9	157144	8.497						

R_B - V Series					
5	152955	4.384	1676	154631	4.383
6	154894	5.396	1670	156564	5.389
7	155982	6.396			

† - Blend

Table I (continued)

R_B - III Series									
m	$v' = 0$				$v' = 1$			$v' = 2$	
	$\nu(\text{cm}^{-1})$	n^*	$\nu_{\text{cal}}(\text{cm}^{-1})$	ΔG	$\nu(\text{cm}^{-1})$	n^*	ΔG	$\nu(\text{cm}^{-1})$	n^*
3			131797						
4	146810	3.041	146790	1636	148446	3.037	1614	150060	3.036
5	151989 [†]	4.055	152004	1686	153675	4.057			
6	154394	5.069	154376	1647	156041	5.051			
7	155690	6.075	155681	1646	157336 [†]	6.042	1616	158952	6.037
8	156472	7.075	156468	1648	158120 [†]	7.027	1582	159702 [†]	6.967
9	156979	8.071	156980	1667	158646	8.044	1628	160274	8.060
10	157336 [†]	9.089	157332	1665	159001	9.046	1618	160619	9.036
11	157583 [†]	10.07	157583	1675	159261	10.08			
12	157769	11.07	157770	1682	159451	11.10			
13	157914	12.09	157912	----	over emission line				
14	158028	13.13	158023	1670	159702 [†]	13.09			
15	158120 [†]	14.20	158111	1679	159790	14.09			
16	158184	15.11	158182	1680	159864	15.15			
17	158238	16.05	158240	1683	159923	16.18			
18	158288 [†]	17.08	158288						

R_B - IV Series									
3	144718	2.815		1680	146398	2.805	1625	148023	2.806
4	151059	3.799		1750	152809 [†]	3.817			
5	153892	4.795		1689	155581	4.801			
6	155405	5.803							
7	156298	6.809							
8	156870	7.821							
9	157259	8.838							
10	157522	9.803							

Table II Wavenumbers of R_A -I Series ($A^2\Pi \leftarrow X^1\Sigma^+$)

v'	$\nu(\text{cm}^{-1})$	ΔG	n^*	$\nu(\text{cm}^{-1})$	ΔG	n^*
$m = 3$				$m = 5$		
0	120837	1548	2.946	128992	1527	4.943
1	122385	1510	2.947	130519	1505	4.938
2	123895	1495	2.947	132024	1489	4.935
	(123896)		(2.947)	(132029)		(4.938)
3	125390	1459	2.949	133513	1452	4.940
4	126849	1428	2.950	134965	1429	4.940
5	128277	1373	2.950	136394		4.940
6	129650	1396	2.947	a		
7	131046	1352	2.950	139152	1372	4.934
8	132398 [†]	1331		140524		
9	133729	1301				
10	135030					
$m = 4$				$m = 6$		
0	126424	1541	3.942	130366	1545	5.932
1	127965	1499	3.944	131911	1508	5.941
2	129464	1485	3.941	133419	1476	5.939
	(129465)		(3.941)	(133415)		(5.935)
3	130949	1449	3.942	134895	1449	5.936
4	132398	1431	3.941	136344		5.932
5	133829	1393	3.942	a		
6	135222	1376	3.942			
7	136598	1368	3.942			
8	137966					

a - Masked by other strong band

† - Blend

Table II (Continued)

v'	$\nu(\text{cm}^{-1})$	ΔG	n^*	$\nu(\text{cm}^{-1})$	ΔG	n^*
$m = 7$				$m = 10$		
0	131205	1535	6.939	a		
1	132740	1513	6.938	133899	1515	9.894
2	134253	1485	6.942	135414	1486	9.916
	(134247)		(6.933)	(135417)		(9.930)
3	135738	1443	6.951	136900	1456	9.947
4	137181	1438	6.936	138356	1427	9.961
5	138619	1387	6.951	139783		9.956
6	140006	1370	6.939			
7	141376	1366	6.933			
$m = 8$				$m = 11$		
0	131739	1548	7.930	132564		10.92
1	133287 [†]	1507	7.957	a		
2	134794	1478	7.951	135609	1487	10.92
	(134786)		(7.932)	(135612)		(10.93)
3	136272	1456	7.948	137096	1452	10.96
4	137728	1424	7.955	138548	1425	10.96
5	139152		7.946	139973		10.94
$m = 9$						
0	132116	1537	8.956			
1	133653	1508	8.960			
2	135161	1477	8.953			
	(135185)		(8.931)			
3	136638	1445	8.947			
4	138083	1431	8.921			
5	139514	1397	8.930			
6	140911	1378	8.937			
7	142289		8.950			

Table III Wavenumbers of R_x -I Series ($X^2\Sigma^+ \leftarrow X^1\Sigma^+$)

$v' = 0$					$v' = 1$		$v' = 0$			
n	$\nu_{\text{obs}} (\text{cm}^{-1})$	n*	$\nu_{\text{calc}} (\text{cm}^{-1})$	ΔG	$\nu_{\text{obs}} (\text{cm}^{-1})$	n*	n	$\nu_{\text{obs}} (\text{cm}^{-1})$	n*	$\nu_{\text{calc}} (\text{cm}^{-1})$
3	91919	2.280	91935	2145	94064	2.278	16	112561	15.31	112564
	92930	2.337		2150	95080	2.329	17	112616	16.30	112620
4	103054	3.317	103007	-----	-----	-----	18	112666	17.39	112665
	103272	3.353		2181	105453	3.353	19	112702	18.32	112704
5	107162 ^a	4.325	107165	-----	-----	-----	20	112738	19.42	112737
	107215 ^a	4.344		2271	109486	4.378	21	112766	20.4	112765
6	109185	5.342	109176	2160	111345	5.326	22	112788	21.3	112789
	109204	5.356		2152	111356	5.334	23	112809	22.3	112810
7	110310 ^a	6.353	110302	2190	112500	6.360	24	112828	23.4	112828
	110331	6.378		2182	112513	6.375	25	112844	24.4	112844
8	110999	7.352	110999	2177	113176	7.347	26	112859	25.4	112859
	111006	7.365		-----	-----	-----	27	112872	26.4	112871
9	111457	8.357	111457	2187	113644	8.366	28	112883	27.4	112883
10	111767	9.325	111776	2190	113957	9.350	29	112892	28.3	112893
11	112000	10.33	112007	2193	114193	10.38	30	112901	29.3	112902
12	112175	11.34	112179	2182	114357	11.33	31	112908	30.2	112910
13	112323 ^a	12.46	112311	2161	114484	12.28	32	112916	31.1	112918
14	112416	13.39	112415	2172	114588	13.25				
15	112496	14.32	112497							

a - See text.

Table IV Observed Rydberg States and Suggested Rydberg Orbitals

CO^+	Series	Quantum Defect	Rydberg orbital	
			Lindholm	Betts & McKoy
$\text{B } ^2\Sigma^+$	$\text{R}_\text{B} - \text{III}$	0.93	$\text{ns}\sigma$	$\text{ns}\sigma$
	Sharp	0.67	$\text{np}\sigma$	$\text{np}\pi$
	$\text{R}_\text{B} - \text{V}$	0.61		
	Diffuse	0.55	$\text{np}\pi$	$\text{np}\sigma$
	$\text{R}_\text{B} - \text{IV}$	0.19	$\text{nd}\sigma$	$\text{nd}\pi$
$\text{A } ^2\Pi$	$\text{R}_\text{A} - \text{I}$	0.06 (or 1.06)	$\text{ns}\sigma^{\text{a}}$	
	α	0.67	$\text{np}\sigma, \pi$	
$\text{X } ^2\Sigma^+$	$\text{R}_\text{x} - \text{I}$	0.66	$\text{np}\sigma, \pi^{\text{b}}$	$3\text{p}\sigma, \pi$
	T. T. I.	0.89	$\text{np}\sigma, \pi^{\text{c}}$	

a- Lower members of $\text{R}_\text{A} - \text{I}$ series. See text and ref. (6).

b- Lower members of $\text{R}_\text{x} - \text{I}$ series. See text and ref. (6).

c- Higher members of T. T. I. series. See text and ref. (6).

Table V Series Limits of Observed CO Rydberg Series (cm^{-1})

CO ⁺	v'	Present		CO ⁺ Emis. B.	Previous
		Series Limit	ΔG	ΔG	Series Limit
		R _B - Sharp, Diffuse, III, IV, V			R _B - Sharp, Diffuse (3)
B 2 _Σ ⁺	0	158664	1678	1678.3	158692
	1	160342	1621	1622.5	160353
	2	161963			161983
		R _A - I			R _A - α (3)
A 2 _Π	0	133484	1536	1535.2	133380
	1	135020	1510	1507.8	
	2	136530	1479	1481.1	
	3	138009	1453	1454.6	
	4	139462	1428	1427.7	
	5	140890	1395	1401.1	
	6	142285	1374	1374.6	
	7	143659			
		R _x - I			R _x - T. T. I. (4)
X 2 _Σ ⁺	0	113029	2184	2183.9	113029
	1	115213			115190

Table VI Wavenumbers for the $1\Sigma^+ \leftarrow X^1\Sigma^+$ and $1\Pi \leftarrow X^1\Sigma^+$ Bands

$4p\sigma \ 1\Sigma^+ - X^1\Sigma^+$				$4p\pi \ 1\Pi - X^1\Sigma^+$			
J	P	R	$\Delta_2 F''_{\text{obs}}$	P	R	$\Delta_2 F''_{\text{obs}}$	$\Delta_2 F''_{\text{calc}}$
0		103058.0			103275.6		
1	103050.5	061.9	11.4		279.3	11.9	11.5
2	046.6	065.7	19.1	103263.7	283.6	19.8	19.2
3	042.8	069.4	26.8	259.8	288.0	27.1	26.9
4	038.9	073.1	34.4	256.3	292.5	34.8	34.6
5	035.0	077.1	42.0	253.2	297.0	42.2	42.3
6	031.1	081.0	50.0	250.3	301.7	50.4	50.0
7	027.1	084.7	57.9	246.6	306.5	57.9	57.7
8	023.1	088.2	65.6	243.8	311.3	65.5	65.3
9	019.1	091.3	73.2	241.0	316.3	72.9	73.0
10	015.0	094.7	80.5	238.4	321.3	80.2	80.7
11	010.8	098.4	88.1	236.1	326.5		88.4
12	006.6	101.3	96.1		331.8		96.0
13	002.3	104.4	103.4		337.2		103.7
14	102997.9	107.3	111.1		342.7		111.4
15	993.3	110.2	118.7		348.3		119.0
16	988.6	112.9	126.8		353.9		126.7
17	983.4	115.4	134.8		359.5		134.3
18	978.1	117.6	142.7		365.1 ⁿ		142.0
19	972.7		150.1		371.4		149.6
20	967.5	a			377.4		157.2
21	961.5						
22	955.7						
23	948.9						
24	941.6						
25	934.7						

a - R-head, calc. = 103122.4 cm^{-1}
 R-head, obs. = 103121.4 cm^{-1}

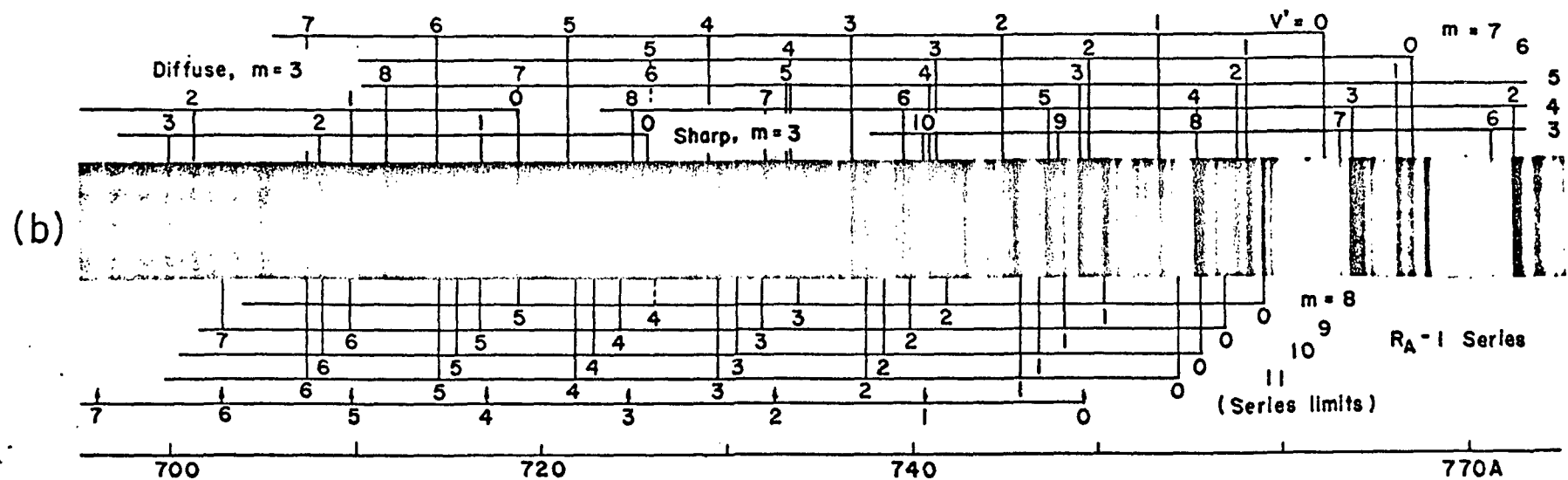
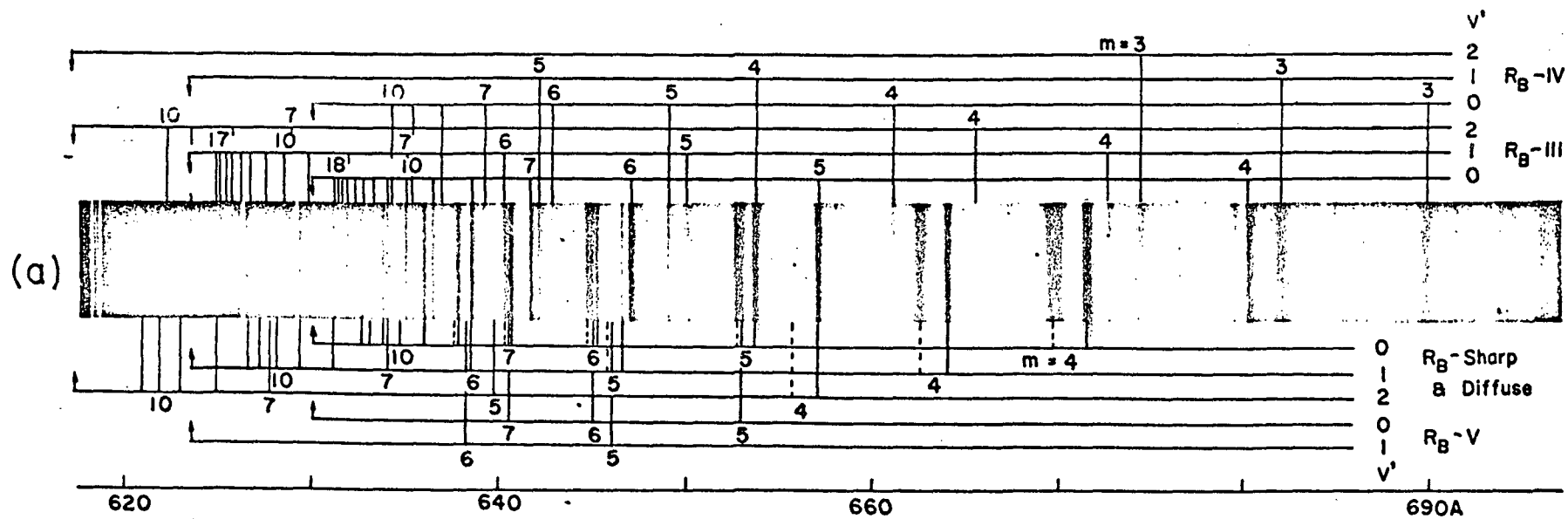
n - Blended with N_2 -line
 Q-head, obs. = 103272 cm^{-1}

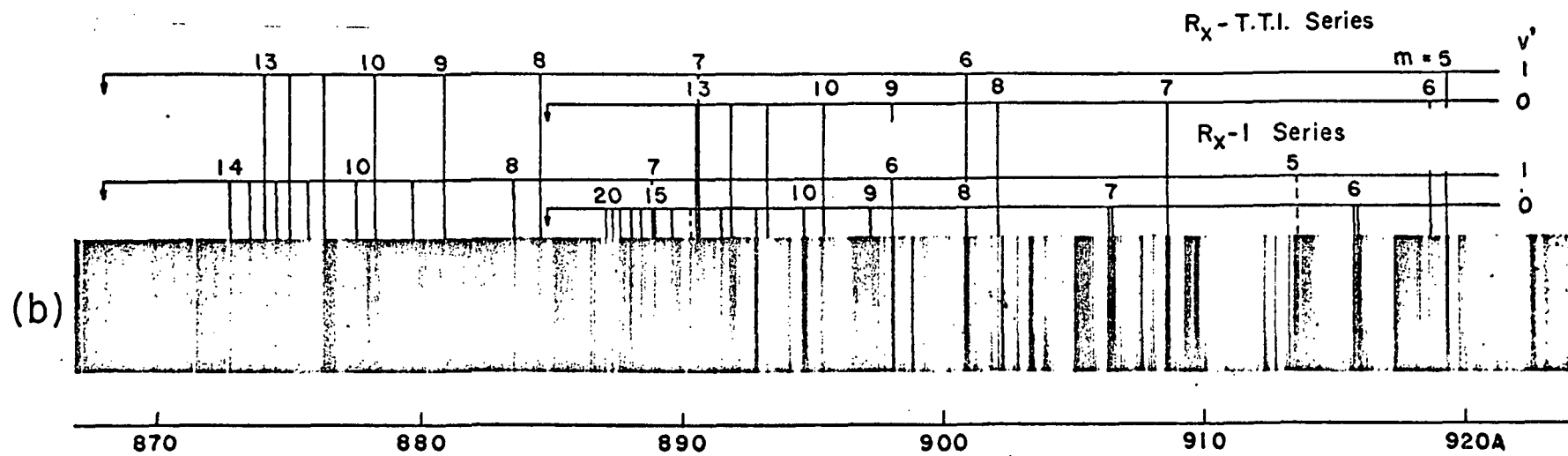
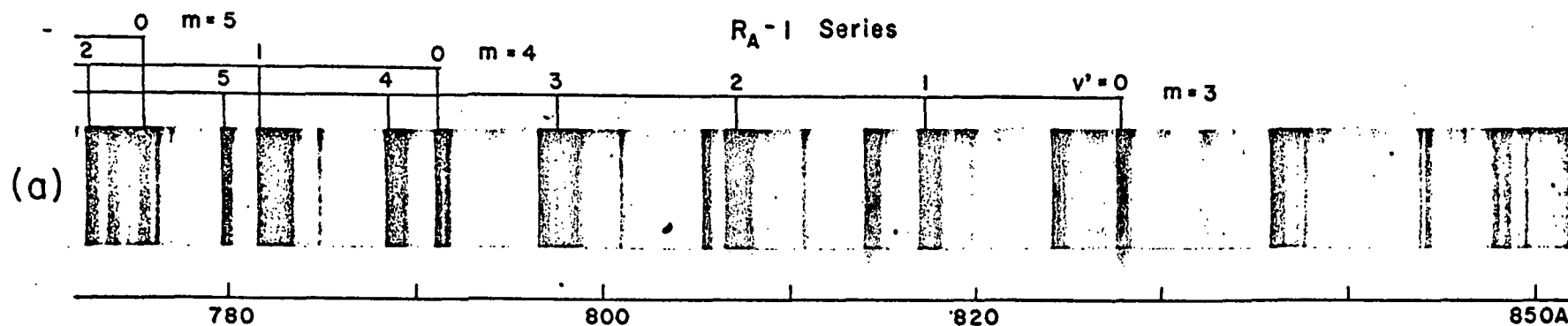
$$\begin{aligned} \nu_0 &= 103054.25 \pm 0.04 \text{ cm}^{-1} \\ B_0 &= 1.9189 \pm 0.0001 \text{ cm}^{-1} \\ D_0 &= (6.6 \pm 0.1) \times 10^{-5} \text{ cm}^{-1} \end{aligned}$$

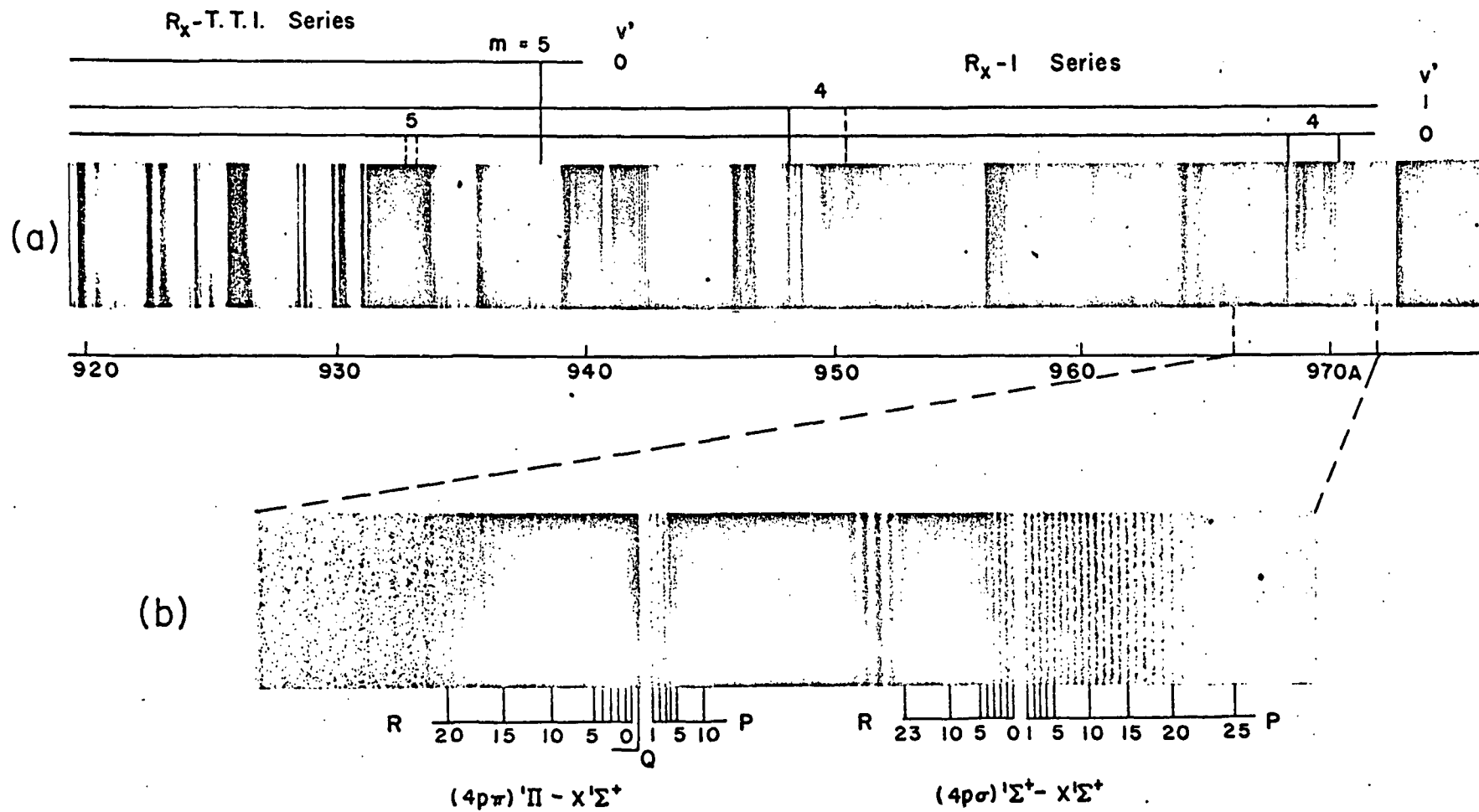
$$\begin{aligned} \nu_0 &= 103271.49 \pm 0.04 \text{ cm}^{-1} \\ B_0 &= 1.9812 \pm 0.0001 \text{ cm}^{-1} \\ D_0 &= (1.4 \pm 0.1) \times 10^{-5} \text{ cm}^{-1} \end{aligned}$$

FIGURE CAPTIONS

- Fig. 1. Absorption spectrum of CO in the region, 620-775Å.
Horizontal lines in (a) indicate the vibrational series.
Vertical broken lines in (a) indicate the diffuse series.
Horizontal lines in (b) indicate the progressions.
- Fig. 2. Absorption spectrum of CO in the region, 770-925Å.
- Fig. 3. Absorption spectrum of CO in the region, 920-975Å.
- Fig. 4. Differences between total energies of 4p-complex (Eqs. 5, 6, and 7) and $BJ(J+1) - DJ^2(J+1)^2$.







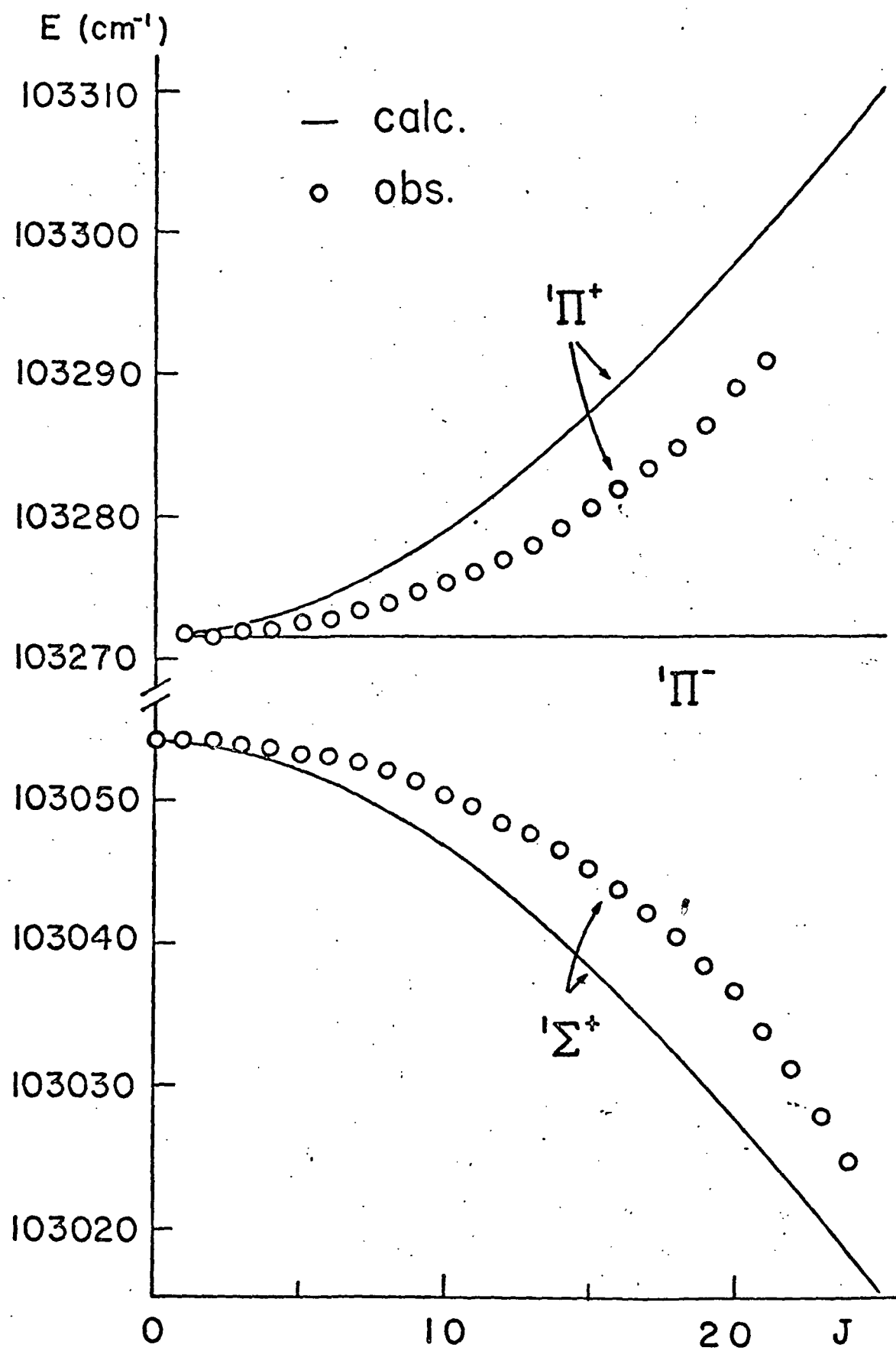


Fig. 4.

Absorption Cross Sections of O₂ and CO₂ Continua in the Schumann and Far-uv Regions*

M. OGAWA

Department of Physics, University of Southern California, Los Angeles, California 90007

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By means of a photoelectrical technique used in conjunction with a 3-m vacuum monochromator, the absorption cross section of the O₂ continuum in the region 2350–1814 Å and the absorption cross section of CO₂ in the region 2160–1718 Å have been measured. The cross section of the O₂ continuum is 3.8×10^{-24} cm² at 2350 Å; it slowly increases towards shorter wavelengths and reaches 10.7×10^{-24} cm² at about 1980 Å, then increases very rapidly and reaches 7.1×10^{-22} cm² at about 1814 Å. In the case of CO₂, numerous discrete bands were found overlapping a weak continuum in the wavelength region below 1980 Å. The absorption cross section of the CO₂ continuum is about 2×10^{-24} cm² at 2100 Å; it gradually increases toward the shorter wavelength side, and reaches about 4×10^{-24} cm² at 2000 Å. The continuum rises rapidly at 2000 Å and its value is 1.19×10^{-20} cm² at 1718 Å. Origins of the continua of both O₂ and CO₂ are briefly discussed.

INTRODUCTION

Absorption coefficients of the O₂ continuum in the wavelength region from 2423.6 Å, the dissociation limit of the $X^3\Sigma_g^-$ ground state, to 1750.5 Å, the dissociation limit of the $B^3\Sigma_u^-$ state, have been measured by several investigators: Wilkinson and Mulliken,¹ Ditchburn and Young,² Hudson, Carter, and Stein,³ and Shardanand.⁴ The continuum between 2423.6 and 2000 Å corresponds to the dissociation continuum associated with the forbidden band systems from the $X^3\Sigma_g^-$ state to the $c^1\Sigma_u^-$, $C^3\Delta_u$, and $A^3\Sigma_u^+$ states, but mainly to the $A^3\Sigma_u^+$ state. However, the major part of the continuum in the wavelength region 2000–1750 Å is probably due to the $^3\Pi_u(\sigma^2\pi^4\pi\sigma, \text{repulsive})-X^3\Sigma_g^-$ transition, which may reach a maximum around 1400 Å.¹ The $^3\Pi_u$ repulsive state, originating from the lowest dissociation limit ($^3P+^3P$), causes predissociation of the $B^3\Sigma_u^-$ state, the upper state of the Schumann-Runge bands.^{1,5,6} Many diffuse absorption bands of O₂ have been observed in the wavelength region 1350–1130 Å.^{7,8} Price and Collins⁷ suggested that the observed strong and diffuse bands predissociate into a $^3\Sigma_u^-$ state or other states predicted from the $\sigma^2\pi^3\pi^3$ electron configuration. Tanaka⁸ also suggested the weak and very broad bands at 1290, 1334, and 1349 Å probably predissociate into the $^3P+^1S$, or $^1D+^1D$ separated atoms. But the latter combination is unlikely from spin consideration.⁹ However, the repulsive $^3\Pi_u$ state may also cause the predissociation of the upper state of the observed diffuse bands. Therefore, it is important to measure the absorption cross section of the underlying continuum of the Schumann-Runge bands in order to provide information on not only the magnitude of the photodissociation cross section but also on the species and potential curve of the upper state(s) of the dissociation continuum.

According to the measurement of liquid CO₂ by Eiseman and Harris,¹⁰ CO₂ is transparent down to 2100 Å. This has been confirmed by Herzberg¹¹ who used the high-pressure and multireflection absorption method to seek possible absorption. Inn, Watanabe,

and Zelikoff¹² measured absorption coefficients in the region 1800–1050 Å. They found that an absorption starts at about 1750 Å and reaches a maximum at 1475 Å. They also found that the absorption consists of rather diffuse bands overlapping a continuum. Almost the same results were reported by Wilkinson and Johnston.^{13a} Thompson, Harteck, and Reeves^{13b} reported the absorption coefficients in the region 1850–1960 Å.

The absorption spectrum of CO₂ in the wavelength region shorter than 1215 Å has been studied by Price and Simpson¹⁴ and by Tanaka, Jursa, and LeBlanc.¹⁵ They found strong bands (Rydberg bands) which start at 1129.5 Å and extend towards shorter wavelengths. Absorption and photoionization coefficients of CO₂ in the region 1000–600 Å have been reported by Cook, Metzger, and Ogawa.¹⁶ There are no reported measurements of the absorption coefficient of CO₂ in the wavelength regions 1750–1850 Å and above 1960 Å.

This paper presents results of a remeasurement of the absorption coefficients of the O₂ continuum in the region 2350–1800 Å and also a new measurement of the absorption coefficients of CO₂ in the region 2160–1718 Å.

EXPERIMENTAL PROCEDURE

A 3-m vacuum monochromator equipped with a grating of 1200 lines/mm blazed at 2950 Å was used to determine the wavelength dependence of the cross sections. The reciprocal linear dispersion was 2.84 Å/mm in the first-order spectrum. The discharge tube was an ordinary water-cooled π -shaped tube with a quartz (Suprasil) window. A hydrogen continuum background was excited in the tube by a 900-W, 15-kV neon sign transformer.

The monochromator itself was used as an absorption cell whose path length was 618 cm. Ultrapure O₂ gas or ultrapure CO₂ gas, obtained from Air Reduction Incorporated, was introduced into the monochromator, and the pressure was measured by a mercury or an oil manometer. Maximum pressures were 745 torr for O₂ and 596 torr for CO₂.

The transmitted light was measured behind an exit slit by a photomultiplier tube, type EMI 9514S, attached behind a quartz window coated with sodium salicylate on the surface adjacent to the photomultiplier. For the measurement of the cross sections of O₂, the widths of both the entrance and exit slits were adjusted to 25 μ which gave a bandwidth of 0.075 $\text{\AA}$. For the measurement of the cross sections of CO₂ the widths of both slits were 20 μ , which gave a bandwidth of 0.057 $\text{\AA}$.

Absorption coefficients, k , are defined by the relation $\ln(I_0/I) = kx$, where I_0 and I are light intensities before and after absorption in a path length x reduced to the standard condition of 0°C and 760 torr. The reduced path is given by $x = lpT_0/Tp_0$, where l is the actual cell length and the subscript 0 refers to standard conditions. Absorption cross sections, σ , are calculated from $\sigma = k/n_0$, where n_0 is Loschmidt's number (2.687×10^{19} molecules/cm³).

RESULTS AND DISCUSSIONS

Oxygen

Since an object of the experiment was to obtain absorption coefficients of the dissociation continuum of O₂, the coefficients were measured at minima between the well-separated rotational lines of the Schumann-Runge bands when the measurement was carried out in the region of $\lambda < 2025$ $\text{\AA}$. In the pressure range and

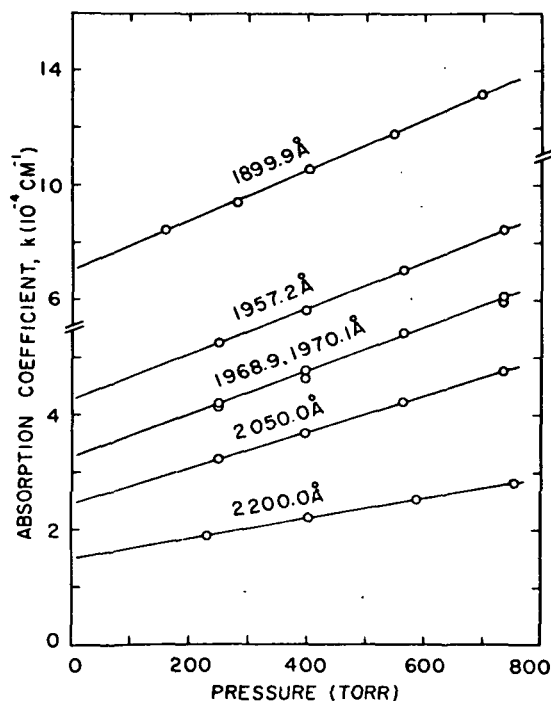


FIG. 1. Pressure dependence of the absorption coefficients of the O₂ continuum.

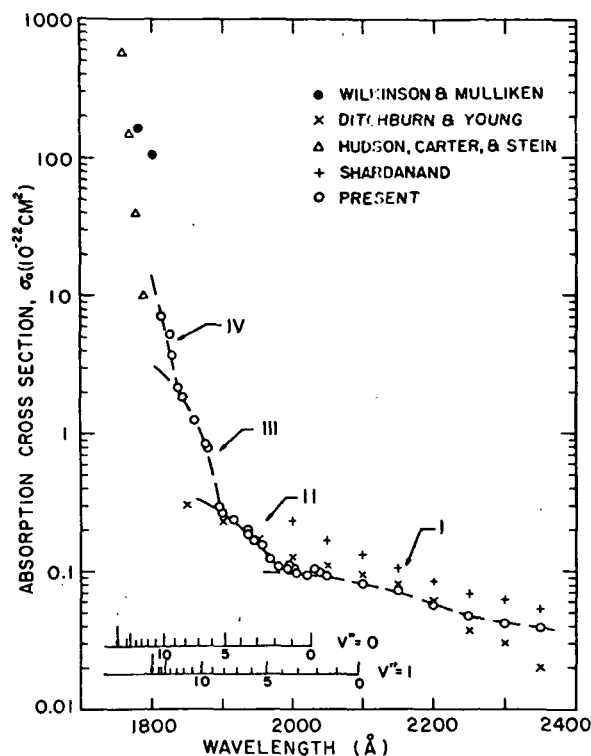


FIG. 2. Absorption cross sections, σ_0 , of the O₂ continuum. Positions of the calculated band origins of the Schumann-Runge absorption bands from $v''=0$ and 1 are also indicated by vertical lines.

the wavelength range of the present experiment, the absorption coefficients of O₂ do not follow Beer's law, but increase linearly with pressure and can be represented by $k = k_0 + \alpha p$, where k_0 is the coefficient at zero pressure and α is the rate of change of the coefficient. The pressure dependence at several wavelengths is shown in Fig. 1. The values of k_0 and α were obtained from linear plots such as these and are listed in Table I. The corresponding cross sections are given by $\sigma = \sigma_0 + \beta p$, and values of both σ_0 and β are also listed in the same table. In the last column of the table are listed the vibrational assignments of the bands which are located in the region of measurement.

The cross section, σ_0 , and the rate of change of the cross section, β , are plotted in Figs. 2 and 3, respectively, which also show previously reported values.¹⁻⁴ The linear increase in the cross section with pressure has been ascribed by Ditchburn and Young² to the absorption of O₄ and has been studied in some detail by Shardanand.⁴

The present values of the cross sections agree well with those of Ditchburn and Young in the region 1900–2200 $\text{\AA}$, but become larger at wavelengths in the region $\lambda > 2200$ $\text{\AA}$. Below 1900 $\text{\AA}$ these workers measured the cross section only at one wavelength, 1850 $\text{\AA}$,

TABLE I. Absorption coefficients and cross sections of the O₂ continuum in the region 2350-1814 Å.

λ_{vac} (Å)	Coefficients, $k = k_0 + \alpha p$		Cross sections, $\sigma = \sigma_0 + \beta p$		$v' - v''$
	k_0 (10^{-4} cm^{-1})	α (10^{-7} $\text{cm}^{-1}/\text{torr}$)	σ_0 (10^{-24} cm^2)	β (10^{-26} cm^2/torr)	
2350	1.03	0.86	3.8	0.32	
2300	1.13	1.07	4.20	0.40	
2250	1.26	1.42	4.68	0.53	
2200	1.52	1.72	5.65	0.64	
2150	1.91	2.50	7.09	0.93	
2100	2.16	2.92	8.04	1.09	
2050	2.44	3.17	9.1	1.18	
2040	2.60	3.23	9.7	1.20	
2032	2.73	3.23	10.2	1.20	2-1, 0-0
2025.4	2.59	3.47	9.6	1.29	3-1 1-0
2023.0	2.49	3.47	9.3	1.29	
2021.0	2.49	3.47	9.3	1.29	
2007.8	2.65	3.67	9.9	1.37	4-1 1-0
2005.9	2.58	3.67	9.6	1.37	
2004.0	2.78	3.62	10.4	1.35	
1997.5	2.95	3.77	11.0	1.40	4-1 2-0
1996.5	2.84	3.77	10.6	1.40	
1994.0	2.84	3.77	10.6	1.40	
1981.7	2.88	4.02	10.7	1.50	5-1 2-0
1979.9	2.88	4.02	10.7	1.50	
1970.1	3.28	3.77	12.2	1.40	5-1 3-0
1968.9	3.28	3.77	12.2	1.40	
1966.8	3.34	3.83	12.4	1.43	
1959.2	4.13	4.04	15.4	1.50	6-1 3-0
1957.2	4.28	4.00	15.9	1.49	
1946.0	4.43	4.73	16.5	1.76	6-1 4-0
1944.0	4.48	4.73	16.7	1.76	
1938.5	5.01	5.72	18.4	2.13	7-1 4-0
1937.8	5.31	6.18	19.8	2.30	
1935.8	5.43	6.61	20.2	2.46	
1918.7	6.40	7.57	23.8	2.82	8-1 5-0
1916.6	6.40	7.57	23.8	2.82	
1899.9	7.03	8.87	26.2	3.30	9-1 6-0
1896.8	7.73	8.92	28.8	3.32	
1880.5	20.7	14.8	77.0	5.50	10-1 7-0
1878.6	22.4	15.6	83.3	5.79	
1878.2	22.4	15.6	83.3	5.79	
1860.8	33.8	25.6	126	9.52	11-1, 8-0 13-1, 9-0
1842.8	49.3	39.7	184	14.8	
1828.7	99.3	88.5	370	32.9	14-1 10-0
1827.1	143	136	532	50.6	
1814.1	190	174	707	64.7	16-1, 11-0

and obtained $\sigma_0 = 30 \pm 6 \times 10^{-24}$ cm². However, we could not measure the cross section at 1850 Å or near this wavelength because of its large cross section. The wavelength 1850 Å is between two strong rotational lines, $R_2(11)$ at 1849.40 Å and $P_2(11)$ at 1850.46 Å, of the (8-0) band. Between these two lines there are several other weak lines: $R(27)$ of (9-0) at 1849.68 Å, $P_2(13)$ of (12-1) at 1849.89 Å, $R_2(23)$ of (13-1) at 1849.95 Å, $R_1(23)$ of (13-1) at 1850.06 Å, and $P_2(27)$ of (14-1) at 1850.43 Å. In the present experiment, the incident radiation between 1950.9 and 1847.0 Å was absorbed almost completely at 10 torr pressure of O₂. The present value even at 1860.8 Å is 126×10^{-24} cm² which is much higher than Ditchburn and Young's value at 1850 Å. Their value, therefore, at 1850 Å is probably too small even if they intended to give only the approximate wavelength.

The present values are smaller than all of Shardanand's values (2000-2400 Å), but are almost the average between Shardanand's and Ditchburn and Young's in the wavelength region 2250-2350 Å.¹ However, both the present cross sections and those of Shardanand decrease slowly toward longer wavelengths compared to Ditchburn and Young's results (see 2200-2400-Å range in Fig. 2).

The shortest wavelength in the present measurement is limited to 1814.1 Å, because the proper pressure of O₂ for the measurement of the cross sections below

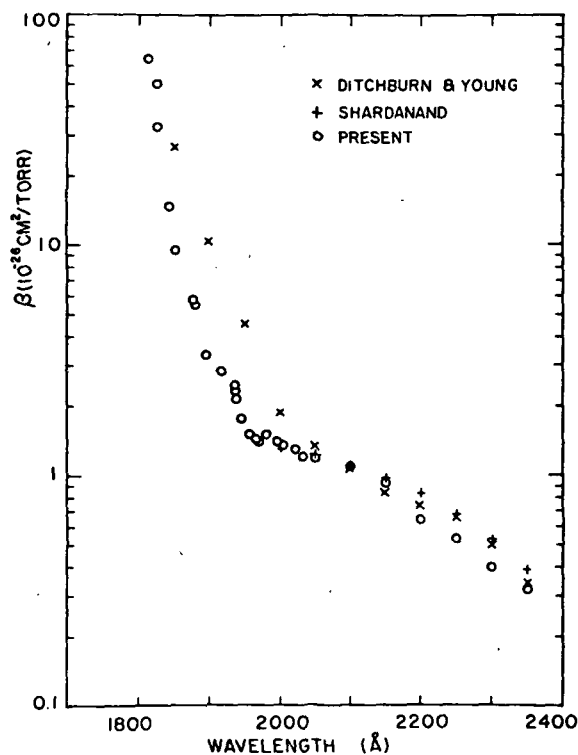


FIG. 3. Rate of change of the absorption cross sections, β , of the O₂ continuum.

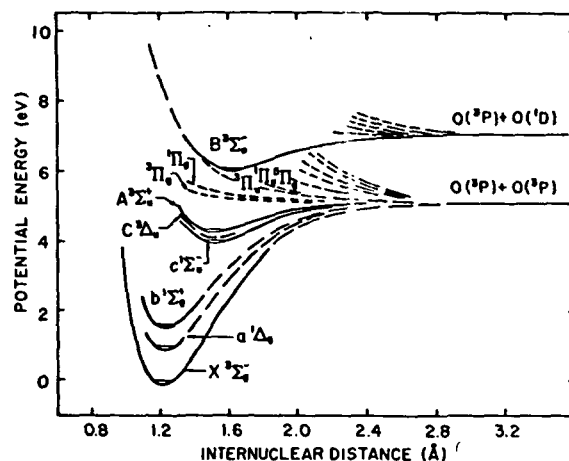


FIG. 4. Potential-energy diagram of O₂. This is a reproduction of the diagram given by Gilmore.¹⁸ The potential curve of the $c^1\Sigma_u^-$ state have been redrawn according to the new values of the molecular constants given by Degen [V. Degen, Can. J. Phys. 46, 783 (1968)]. Potential curves of the $^3\Pi_u$ and $^1\Pi_u$ states given by Schaefer and Harris are quite different from those shown in this figure (see Ref. 19).

1814 Å was too low to measure accurately with an oil manometer. However, Hudson *et al.*³ have measured the coefficients at 1790, 1780, and 1760 Å. The cross section at 1790 Å was 10×10^{-22} cm² which was their minimum detectable value. Wilkinson and Mulliken have also measured the cross section of the continuum at two wavelengths (1781 and 1796 Å) by a photographic method and their values are higher than Hudson *et al.*'s values.

In the Schumann-Runge band region, we must expect that the measured values include more or less the absorption by tails of rotational lines. Therefore, the present values or any previous values will give only an upper limit of the dissociation continuum.

The continuum gradually increases towards shorter wavelengths and almost levels off around 1980 Å. Then it increases rapidly towards shorter wavelengths and its value at 1814 Å is 7.1×10^{-22} cm² which is still a very small value. The curve of the cross sections is not simple and seems to be divided into four sections, I-IV, although section IV is not so distinctive from section III as shown in Fig. 2. Section I corresponds mainly to the $A^3\Sigma_u^+ - X^3\Sigma_g^-$ transition^{2,17} and probably in part to the $c^1\Sigma_u^- - X^3\Sigma_g^-$ transition in the long wavelength region.

According to the potential curve diagram of O₂ given by Gilmore¹⁸ (see Fig. 4, a reproduction), there are three repulsive states, $^3\Pi_u$, $^1\Pi_u$, and $^3\Pi_u$ between the $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ states and according to Schaefer and Harris¹⁹ there are two repulsive states, $^3\Pi_u$ and $^3\Pi_u$. We are not certain whether each of these states corresponds to each of the sections, II, III, and IV or not. However, it is certain that none of these sections corresponds to the $^3\Pi_u - X^3\Sigma_g^-$ transition if the $^3\Pi_u$ curve

TABLE II. Absorption coefficients and cross sections of the CO₂ continuum in the region 2160–1718 Å.

λ_{vac} (Å)	Coefficients k (10^{-3} cm^{-1})	Cross sections σ (10^{-22} cm^2)	λ_{vac} (Å)	Coefficients k (10^{-3} cm^{-1})	Cross sections σ (10^{-22} cm^2)
2160	0.054	0.020	1850.0	7.52	2.80
2140	0.061	0.023	1848.6	7.79	2.90
2120	0.069	0.026	1844.7	9.58	3.56
2100	0.076	0.028	1830.3	14.6	5.43
2080	0.076	0.028	1827.9	15.0	5.58
2060	0.081	0.030	1823.3	20.6	7.67
2040	0.092	0.034	1806.3	28.4	10.6
1995	0.131	0.049	1787.8	50.5	18.8
1990	0.133	0.049	1783.5	59.4	22.1
1972.8	0.222	0.083	1775.6	80.0	29.8
1948.7	0.422	0.157	1774.1	81.0	30.1
1936.4	0.589	0.219	1768.5	100	37.2
1926.9	0.714	0.266	1765.8	106	39.4
1913.1	1.04	0.387	1763.0	115	42.8
1906.2	1.40	0.520	1757.2	129	48.0
1890.2	2.06	0.767	1752.3	153	56.9
1887.4	2.36	0.878	1747.7	178	66.2
1870.9	4.15	1.54	1737.2	215	80.0
1865.7	4.62	1.72	1732.9	253	94.1
1852.0	7.25	2.70	1717.8	319	119

intersects the right limb of the $B^3\Sigma_u^-$ state between $v=3$ and 4 (see curve II, Carroll⁵), because in such a case, the Franck-Condon factor of the $^3\Pi_u-X^3\Sigma_g^-$ transition (allowed) is too small to permit observation of the continuum in the wavelength region of the present experiment. If the potential curve of the $^3\Pi_u$ state intersects the left limb of the $B^3\Sigma_u^-$ state as shown in Gilmore's diagram, it is possible that section IV and an appreciable part of the Schumann-Runge continuum

may be due to the $^3\Pi_u-X^3\Sigma_g^-$ transition. The $^3\Pi_u$ curve which is given by Gilmore is based on the predissociation of the $B^3\Sigma_u^- (v \geq 3)$ state, agrees with that given theoretically by Schaefer *et al.* and is slightly different than Carroll's curve I. However, Murrell and Taylor²⁰ studied the potential curve of the $^3\Pi_u$ state in order to explain the vibrational dependence of the predissociation of the $B^3\Sigma_u^-$ state observed by Carroll. They found that the observed vibrational dependence could be explained if the predissociation is caused only by the $^3\Pi_u$ state and the $^3\Pi_u$ state intersects the right limb of the $B^3\Sigma_u^-$ state like Carroll's curve II. They also found that the Franck-Condon factors of the $B^3\Sigma_u^- \rightarrow ^3\Pi_u$ radiationless transition are very sensitive to the shape

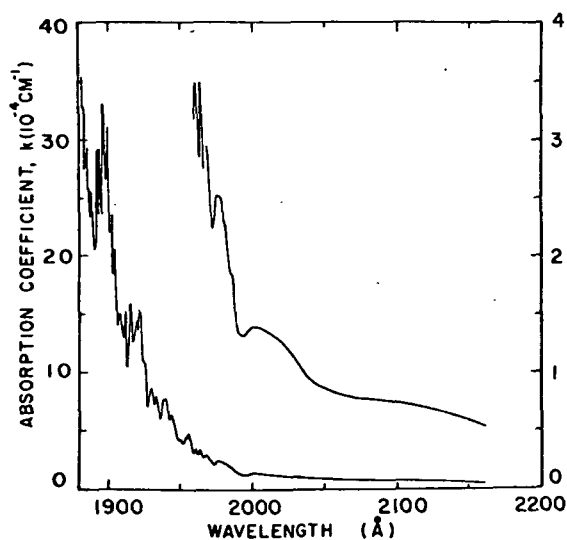


FIG. 5. Absorption coefficients of CO₂ in the region 2160–1880 Å. The right and left curves correspond to the right and left scales, respectively.

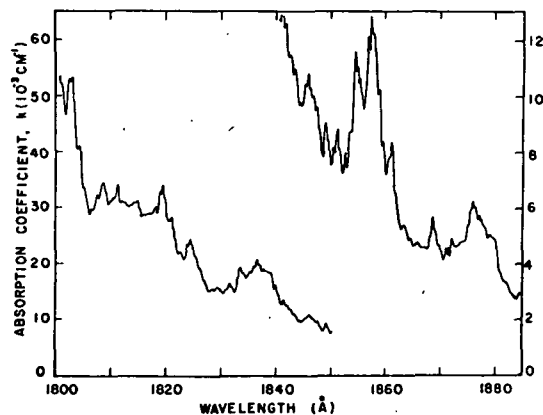


FIG. 6. Absorption coefficients of CO₂ in the region 1885–1800 Å.

of the repulsive potential curve. Thus they support Carroll's curve II.

The rate of change of the absorption cross section (β) vs wavelength is shown in Fig. 3. These values also increase towards shorter wavelength almost in the same manner as observed for the cross sections, σ_0 . Agreement between the present values and those previously reported is rather good except below 2000 Å. As already mentioned, the linear increase in the cross section with pressure has been ascribed to the absorption caused by O₄.^{2,4}

2. Carbon Dioxide

By using the 3-m vacuum spectrograph the absorption spectrum of CO₂ was photographed in the region 2300–600 Å; in addition photoelectric measurements of the absorption coefficients were made. Numerous bands were observed even above 1750 Å up to 1980 Å when high pressures of CO₂ were used; the maximum pressure was 700 torr. The spectrum reveals fine structure in the region $\lambda > 1650$ Å. For the measurement of the coefficients, both the minor peaks and minima due to the fine structure have been ignored.

Absorption coefficients in the regions, 2160–1880 Å, 1885–1800 Å, and 1805–1720 Å are shown in Figs. 5–7, respectively. These figures show the complicated structure of the spectrum. Notable band structure starts around 1980 Å and overlaps a weak continuum. Coefficients of both the bands and continuum increase towards shorter wavelengths. By taking the values at deep minima, an upper limit of the underlying continuum has been defined. The values at those minima are listed in Table II and are plotted in Fig. 8. Wavelengths listed in the table are corrected to those in the vacuum. This correction was achieved by measuring the wavelength shift with the pressure of CO₂.

Approximate absorption coefficients of the bands are 1×10^{-4} , 1×10^{-3} , 1×10^{-2} , and 1×10^{-1} cm⁻¹ around 1980, 1900, 1800, and 1730 Å, respectively. A possible

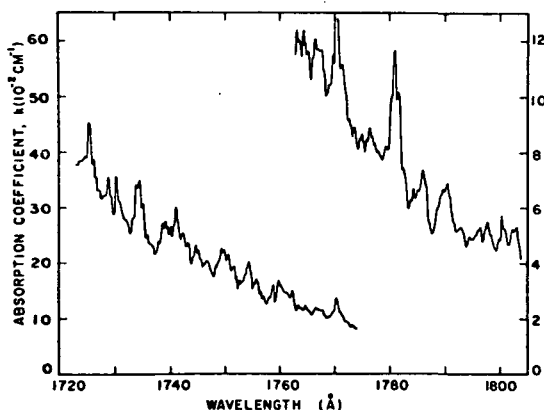


FIG. 7. Absorption coefficients of CO₂ in the region 1805–1720 Å.

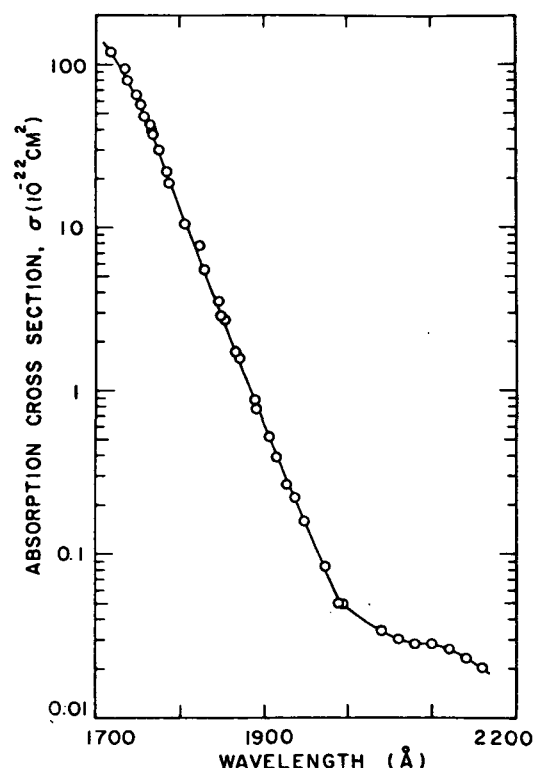


FIG. 8. Absorption cross sections of CO₂ continuum.

upper state of the bands is the $\tilde{A}^1B_2$ state which dissociates into the CO($X^1\Sigma^+$)+O(1D) combination.

The cross section of the continuum is 2×10^{-24} cm² at 2160 Å and slowly increases towards 2000 Å. Below 2000 Å, the cross section increases almost exponentially down to about 1780 Å. Below 1780 Å, the increase is slower and the cross section at 1718 Å is 1.2×10^{-20} cm² which is still a very small value. A possible origin of the continuum is the dissociation continuum of the $^3B_2-\tilde{X}^1\Sigma_g^+$ transition. The 3B_2 state dissociates into the CO($X^1\Sigma^+$)+O(3P) products. An energy diagram for the CO₂↔CO+O system in the energy region of the present interest has been given by Lin and Bauer.²¹

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