

SPACE RESEARCH COORDINATION CENTER



CASE FILE  
COPY

EXCITATION OF THE WERNER BANDS  
OF H<sub>2</sub> BY ELECTRON IMPACT

BY

E. J. STONE AND E. C. ZIPF

SRCC REPORT NO. 164

UNIVERSITY OF PITTSBURGH  
PITTSBURGH, PENNSYLVANIA

FEBRUARY 1972

The Space Research Coordination Center, established in May, 1963, has the following functions: (1) it administers predoctoral and postdoctoral fellowships in space-related science and engineering programs; (2) it makes available, on application and after review, allocations to assist new faculty members in the Division of the Natural Sciences and the School of Engineering to initiate research programs or to permit established faculty members to do preliminary work on research ideas of a novel character; (3) in the Division of the Natural Sciences it makes an annual allocation of funds to the Interdisciplinary Laboratory for Atmospheric and Space Sciences; (4) in the School of Engineering it makes a similar allocation of funds to the Department of Metallurgical and Materials Engineering and to the program in Engineering Systems Management of the Department of Industrial Engineering; and (5) in concert with the University's Knowledge Availability Systems Center, it seeks to assist in the orderly transfer of new space-generated knowledge in industrial application. The Center also issues periodic reports of space-oriented research and a comprehensive annual report.

The Center is supported by an Institutional Grant (NsG-416) from the National Aeronautics and Space Administration, strongly supplemented by grants from the A. W. Mellon Educational and Charitable Trust, the Maurice Falk Medical Fund, the Richard King Mellon Foundation and the Sarah Mellon Scaife Foundation. Much of the work described in SRCC reports is financed by other grants, made to individual faculty members.

EXCITATION OF THE WERNER BANDS OF H<sub>2</sub> BY ELECTRON IMPACT

(The Journal of Chemical Physics)

E. J. Stone and E. C. Zipf

University of Pittsburgh

Pittsburgh, Pennsylvania 15213

"Approved for public release; distribution unlimited."

January 1972

# Excitation of the Werner Bands of $H_2$ by Electron Impact

E. J. Stone and E. C. Zipf

Department of Physics

University of Pittsburgh

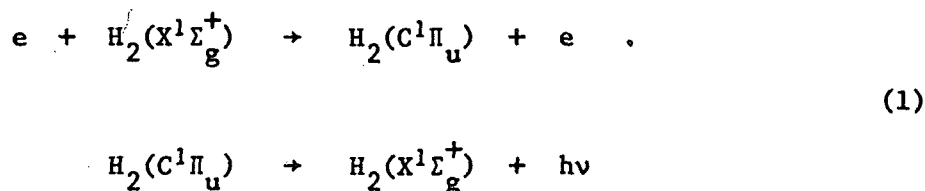
Pittsburgh, Pennsylvania 15213

## Abstract

Absolute cross sections for the excitation of the Werner band system  $H_2(C^1\Pi_u \rightarrow X^1\Sigma_g^+)$  have been measured from energy threshold to 300 eV for electron impact on  $H_2$ . The bands were observed in emission in the wavelength region 1100 $\overset{\circ}{\text{A}}$  - 1250 $\overset{\circ}{\text{A}}$ . The measured cross sections were compared with published transition probabilities, leading to the conclusion that the Werner bands are suitable as the basis for a relative spectral response calibration only when the bands are observed under sufficiently high resolution (FWHM  $\sim$  0.4 $\overset{\circ}{\text{A}}$ ). The effect of the perturbation between the  $C^1\Pi_u$  and  $B^1\Sigma_u^+$  states of the hydrogen molecule was clearly observed in anomalies in the rotational intensity distribution in bands of the (3,  $v''$ ) progression.

## INTRODUCTION

The Werner band system of molecular hydrogen [ $C^1\Pi_u \rightarrow X^1\Sigma_g^+$ ] is readily excited by electron impact,



The resulting vacuum ultraviolet bands appear as prominent emission features in the wavelength region  $800\text{\AA} - 1400\text{\AA}$ . The Werner system is particularly intense from  $1100\text{\AA}$  to  $1250\text{\AA}$  where it is accessible to optical instruments using lithium fluoride windows. In this wavelength region the Werner bands are reasonably free from spectral contamination and can generally be distinguished by a monochromator with a modest bandwidth ( $0.5\text{\AA}$  FWHM) from the overlapping hydrogen Lyman bands ( $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ ), which are relatively weak. Hence, it is tempting to use the relative intensities of the Werner bands excited by electron impact to determine the spectral sensitivity of an ultraviolet optical system in the  $1100\text{\AA} - 1250\text{\AA}$  region. Such measurements can be used in principal to augment atomic branching-ratio data<sup>1</sup> and to extend the molecular branching-ratio techniques based on the LBH system of  $N_2$ <sup>2</sup> to shorter wavelengths.

Calibration experiments of this kind have been carried out by Carriere and de Heer<sup>3</sup>, and by Aarts and de Heer<sup>4</sup>. In both of these studies the resulting spectral response curves showed a pronounced

dip near 1200Å. These calibration experiments involved measurements made at relatively low resolution, inviting contamination by Lyman-band radiation. This may account for the structure observed in these calibration curves.

There are, however, additional difficulties that complicate the use of the Werner bands in molecular branching-ratio measurements that should also be noted. Dieke<sup>5</sup> first pointed out that the levels of the  $C^1\Pi_u$  state of the hydrogen molecular are perturbed by nearby levels of the  $B^1\Sigma_g^+$  state. The effect of these perturbations on line positions has been analyzed by Monfils<sup>6</sup> and treated both experimentally and theoretically by Namioka<sup>7</sup>. Julienne<sup>8</sup> has calculated the extent of the mixing of some of the more strongly perturbed levels and his work shows that this mixing leads to significant intensity anomalies. Another complicating factor in the study of the Werner bands is the fact that the  $C^1\Pi_u$  state is populated to some extent by cascade transitions from more energetic states. These transitions have been discussed by Richardson<sup>9</sup> and Dieke<sup>5</sup>, but little is known quantitatively about the extent of the cascade process and its effects on an optical calibration experiment.

In this paper we describe an experiment that clarifies most of these points and shows under what conditions the Werner band system can be used in absolute calibration work. The intensity perturbations predicted by Julienne have been observed, and the absolute cross sections

for electron-impact excitation of the Werner bands are presented. These results are of direct importance in the study of the ultraviolet spectra of the Jovian planets and of the interstellar medium.

#### EXPERIMENTAL TECHNIQUES

The apparatus used in this work is nearly identical to that described in detail by Mumma and Zipf<sup>10,11</sup>. Hydrogen gas flowed into a small collision chamber located in a large vacuum chamber which was evacuated by two 1400  $\ell$ /sec diffusion pumps (Figure 1). An electron gun provided a monochromatic beam of electrons whose energy could be varied from 5 to 340 eV. The electron beam passed through the gas in the collision chamber and was collected by a positively-biased electron trap on the opposite side. The current to the electron trap, as well as stray currents to the top, bottom, and side wall of the collision chamber were monitored. Checks were made to ensure that effects due to secondary and reflected electrons were negligible. The resulting radiation was observed through windowless apertures with a one-meter, normal incidence vacuum monochromator and a solar-blind photomultiplier which was operated in a pulse-counting mode. The gas pressure in the collision chamber was monitored by measuring either the pressure in the gas flow line or the background pressure in the large vacuum chamber, and was maintained nearly constant by manual adjustment of the inlet leak valve. Variations due to drifts of various sorts were averaged by taking intensity measurements in repeated sequences.

The relative spectral response of the optical system was determined by the method of hydrogen deuteride fluorescence described by Becker et al<sup>12</sup>.

An argon light source with a lithium fluoride window was placed one inch from the optic axis, as shown in Figure 1. The large vacuum chamber was filled with HD to a pressure of few millitorr, and HD fluorescence was observed by the monochromator through an aperture in the back side of the collision chamber. Thus the photon collection geometries in the fluorescence and electron-impact experiments were virtually identical

The resulting spectral response curve, together with the data points on which it is based, is presented in Figure 2. The ordinate of the graph is the ratio of observed intensity to the predicted intensity. The solid line is a computer-generated least-squares third order fit to several sets of data.

The rotational line intensities of individual Werner bands were measured by scanning the monochromator slowly over the line with the slits set to achieve a resolution of  $0.44 \text{ \AA}$ . For each band, the intensity of the Q1 line was measured and taken as representative of the intensity of the whole band. This procedure was adopted for several reasons. The Q1 line is the strongest single feature in each band, and is well isolated from other rotational lines of the same band. Furthermore the Q-branch lines originate on levels of the C state which, due to their symmetry, are not subject to perturbation by levels of the B state. No attempt was made to integrate measured intensity over an entire Werner band, since doing so would have resulted in serious errors due to contamination by Lyman radiation and irrelevant rotational lines from overlapping Werner bands in the same spectral region. The problem of contamination is not entirely eliminated by confining intensity



measurements to single lines, but it is greatly reduced. The measured rotational intensities were converted into absolute excitation cross sections by comparison with the intensity of Lyman Alpha ( $1215.6\text{\AA}$ ) produced in dissociative excitation of  $\text{H}_2$  by electrons of 100 eV energy. The latter cross section was taken to be  $1.2 \times 10^{-17} \text{ cm}^2$  (see Mumma and Zipf<sup>11</sup>).

Excitation functions for the Werner bands were taken by setting the monochromator slits unequal and wide enough to include the R0, R1, R2, and Q1 lines of each band in the maximum pass band. The excitation function, defined as the number of photons collected per unit time per unit electron current per unit gas pressure within the experimental chamber as a function of electron energy, is thus directly proportional to the excitation cross section as a function of electron energy.

#### THEORY

Probabilities for radiative transitions from the C to the X state of the  $\text{H}_2$  molecule have been calculated by Allison and Dalgarno<sup>13</sup>. Relative probabilities for electron-impact excitation of the various levels of the C state from the X state may be deduced from these values by invoking the Born and Born-Oppenheimer approximations. In this approximation<sup>14</sup> a generalized oscillator strength may be defined in the expression for the differential scattering cross section. In the limit that the excitation energy for the transition is small compared to the electron impact energy, this generalized oscillator strength approaches the optical oscillator strength, and it follows that the cross section for electron-impact excitation is directly proportional to the probability of photon absorption from a continuum radiation field. Thus the probability for excitation to the  $v'$  vibrational level of the upper state is proportional to

$$P_{v'} \propto A_{v',0} / \nu_{v',0}^3 \quad (2)$$

where  $A_{v',0}$  is the radiative transition probability between the  $v'$  vibrational level of the upper state and the  $v'' = 0$  level of the ground electronic state, and  $\nu_{v',0}$  is the wave number of the corresponding radiation. The intensity of the  $(v', v'')$  band seen in emission will then be proportional to

$$I_{v',v''} \propto P_{v'} \frac{A_{v',v''}}{\sum_{v''} A_{v',v''}} \quad (3)$$

where  $A_{v',v''}$  is the radiative transition probability between the  $v'$  and  $v''$  vibrational levels of the upper and lower electronic states, respectively. If the C state is populated to a significant degree by cascade transition from higher-lying excited states, the use of the quantity  $P_{v'}$  is not justified, and bands originating on each upper level must be considered separately.

Werner band transition probabilities and predicted band intensities were also calculated from Franck-Condon factors, using published dipole transition moments and the r-centroid approximation. The appropriate formulae are given by Herzberg<sup>15</sup>. Arrays of Franck-Condon factors for the Werner bands have been calculated by Spindler<sup>16</sup> and by Halmann and Laulicht<sup>17</sup>. These two sets of numbers are based on RKR potential curves, and agree very well. R-centroids for the Werner bands have been calculated by Halmann and Laulicht<sup>18</sup>. The variation of dipole transition moment with internuclear distance was

taken from the work of Wolniewicz,<sup>19</sup> Other published transition moments for the Werner bands include the experimental result of Geiger and Schmoranzler<sup>20</sup> and the theoretical variation obtained by Miller and Krauss.<sup>21</sup>

The treatment of transition probabilities in H<sub>2</sub> using Franck-Condon factors and r-centroids must be regarded as somewhat inexact. Calculations have been reported by Halmann and Laulicht<sup>22</sup> and by Villarejo et al,<sup>23</sup> showing that the Franck-Condon factor for a band is not constant, but varies with rotational quantum number. Drake and Nicholls<sup>24</sup> report that the r-centroid approximation may fail for hydrogen. Nevertheless, as we will show later in this paper, the agreement between the experimental measurements and the results of a Franck-Condon calculation is quite good.

The distribution of intensity in the rotational structure of each band was calculated as follows, using the formulation of Herzberg<sup>16</sup>. The jth rotational level of the ground ( $X^1\Sigma_g^+$ , v'' = 0) state is populated in proportion to the quantity

$$W_j B_j = W_j \exp(-B_{v''} j(j+1) hc / KT) \quad (4)$$

where  $W_j$ , the statistical weight of the level, is 3 or 1 as j is odd or even,  $B_{v''}$  is the rotational constant of the v'' = 0 rotational level, h is Planck's constant, c is the speed of light, K is Boltzmann's constant, and T, the Kelvin temperature, is 295°. Each of the rotational levels of the upper ( $C^1\Pi_u$ , v') state is lambda doubled. The two parts of its kth rotational level will be populated according to

$$P_k^{(1)} = W_{k+1} S_{k+1}^P B_{k+1} + W_{k-1} S_{k-1}^R B_{k-1}, \quad (5)$$

$$P_k^{(2)} = W_k S_k^Q B_k, \quad k = 1, 2, 3, \dots$$

where  $P_k^{(1)}$  are the relative populations of the levels populated in P and R branches, and the  $P_k^{(2)}$  are the relative populations of the levels populated in Q branches. The  $S_k$  are the Honl-London Factors,

$$\begin{aligned} S_k^P &= k - 1 \\ S_k^Q &= 2k + 1 \\ S_k^R &= k + 2 \end{aligned} \quad (6)$$

except that

$$S_1^P = S_2^P = S_1^Q = 0.$$

The intensities of lines seen in emission will then be proportional to

$$\begin{aligned} I_j^P &= S_j^P P_{j-1}^{(1)} / (2j - 1) & j = 2, 3, 4, \dots \\ I_j^Q &= S_j^Q P_j^{(2)} / (2j + 1) & j = 1, 2, 3, \dots \\ I_j^R &= S_j^R P_{j+1}^{(1)} / (2j + 3) & j = 0, 1, 2, \dots \end{aligned} \quad (7)$$

where, for example,  $I_3^Q$  is the relative intensity of the Q3 line, and

where  $j$  designates the rotational level of the final state.

Julienne and Mies<sup>25</sup> have calculated transition probabilities in the P and R branches of the Werner bands of  $H_2$ , and report that the probabilities follow the Honl-London factors only approximately. While it is not clear what error has been incurred in our calculation of Q branch intensities by the use of the classical Honl-London factors,  $\pm 5\%$  seems to be a reasonable estimate.

### RESULTS

The observed intensity distribution in the Werner (1,3) and (2,5) bands is shown in Figures 3 and 4. The predicted distribution is shown for comparison; the agreement is seen to be good. However, the distribution of intensity in the (3,  $v''$ ) bands shows the effect of the perturbation interaction between the B and C states of the molecule.

Julienne<sup>8</sup> has calculated that the ( $v' = 3$ ,  $j = 1$  and  $2$ ) levels of the C state are 35% and 65% mixed, respectively, with the ( $v' = 14$ ,  $j = 1$  and  $2$ ) levels of the B state. This results in a reduction in the intensity of the R0, R1, R2, and P3 lines of the Werner (3,  $v''$ ) bands. Figure 5 compares the observed intensity distribution in the Werner (3,7) band with that expected in the absence of the perturbation. The effect of the intensity perturbation is unmistakable. The effect is less marked in the (3,6) band, apparently due to contamination by other VUV radiation.

The excitation functions for the  $v' = 0$  through  $v' = 4$  levels of the C state were measured from threshold to 340 eV. The total intensity observed was the sum of the R0, R1, R2, R3, and Q1 lines. The shapes of these excitation functions were found to be identical within the experimental

error (+ 3%), except near threshold. The excitation function curve for the (4,8) band is shown in Figure 6.

The experimental cross section  $\sigma(Q1)$  for the excitation of the Q1 lines of the prominent Werner bands in the spectral region 1100 $\text{\AA}$  - 1250 $\text{\AA}$  by electrons of 100 eV energy are given in Table I. The quantity (Q1/total) is the fraction of the intensity of the band which appears in the Q1 line. Predicted intensities, arbitrarily normalized and based on the transition probabilities of Allison and Dalgarno<sup>13</sup>, are given in the column marked A & D. Predicted relative intensities calculated from the Franck-Condon factors of Spindler<sup>16</sup>, the dipole transition moment of Wolniewicz<sup>19</sup>, and the r-centroids of Halmann and Laulicht<sup>22</sup> are given in the column marked FCF. The agreement between the measurements and both sets of predicted intensities is good, generally within + 5%.

#### DISCUSSION

The authors undertook the present measurements with the expectation of using the Werner-band intensities to determine the relative spectral response of laboratory and rocket-borne VUV optical systems. Our first measurements of the Werner-band rotational line intensities were made at resolutions of 0.88 $\text{\AA}$  and 0.66 $\text{\AA}$  (FWHM). The spectral response curves generated from these measurements contained unexplained structure near 1200 $\text{\AA}$ .

The spectral sensitivity calibration using HD fluorescence techniques was then carried out, demonstrating that the early Werner-band calibration was in error. The calibration experiment using hydrogen

deuteride has a twofold advantage: it has very few uncertainties in principle, and its spectral range overlaps the wavelength region that may be calibrated accurately using the LBH bands of  $N_2$ .

It is now clear from these measurements that certain of the Q1 line intensities, in particular those of the (3,6) and (1,5) bands, were contaminated by other lines of the hydrogen spectrum. Most of the contamination seems to have been eliminated by decreasing the monochromator bandwidth to 0.44Å.

Cascade excitation of the C state from high-lying states of the hydrogen molecule also seems to be small at the excitation energies used (100 eV and 300 eV) in this experiment and is not a source of significant error. Hence, the composite results of this study show that the Werner-band system can be used effectively as the basis of a molecular branching-ratio calibration of a VUV optical system, but care must be taken to use sufficient instrumental resolution while observing the Werner bands.

#### ACKNOWLEDGMENT

The authors wish to thank Dr. C. Bradley Moore of the University of California (Berkeley) for useful discussions of the technique of the HD calibration.

## FOOTNOTES

\*This work was supported by the NASA (NGL 39-011-030) and by the Advanced Research Projects Agency, The Department of Defense and was monitored by U. S. Army Research Office-Durham, Box CM, Duke Station, North Carolina 27706, under Contract No. (DA-31-124-ARO-D-440).

1. J. A. R. Samson, Techniques of Vacuum Ultraviolet Spectroscopy (Wiley, New York, 1967), pp. 288-290.
2. M. J. Mumma and E. C. Zipf, J. Opt. Soc. Am. 61, 83 (1971).
3. J. D. Carriere and F. J. de Heer, J. Chem. Phys. 55, 3829 (1971).
4. J. F. M. Aarts and F. J. de Heer, Physica 52, 45 (1971).
5. G. H. Dieke, Phys. Rev. 54, 439 (1938).
6. A. Monfils, Academie Royale de Belgique, Bulletin de la Classe des Sciences 47, 585 (1961).
7. T. Namioka, J. Chem. Phys. 40, 3154 (1964).
8. P. S. Julienne, private communication.
9. O. W. Richardson, Molecular Hydrogen and its Spectrum, (New Haven, 1934; University Microfilms, Ann Arbor, Michigan).
10. M. J. Mumma, Dissociative Excitation of Atmospheric Gases, Ph.D. Thesis, University of Pittsburgh (1970).
11. M. J. Mumma and E. C. Zipf, J. Chem. Phys. 55, 1661 (1971).
12. K. H. Becker, E. H. Fink, and A. C. Allison, J. Opt. Soc. Am. 61, 495 (1971).
13. A. C. Allison and A. Dalgarno, Atomic Data 1, 289 (1970).
14. H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena (Oxford, 1969), Vol. I, pp. 434-445 and Vol. II, p. 665 ff.



15. G. Herzberg, Spectra of Diatomic Molecules, (Van Nostrand Reinhold, New York, 1950), pp. 193-211.
16. R. J. Spindler, Jr., J. Quant. Spectrosc. Radiat. Transfer 9, 627 (1969).
17. M. Halmann and I. Laulicht, J. Chem. Phys. 46, 2684 (1967).
18. M. Halmann and I. Laulicht, private communication.
19. L. Wolniewicz, J. Chem. Phys. 51, 5002 (1969).
20. J. Geiger and H. Schmoranzler, J. Mol. Spec. 32, 39 (1969).
21. K. J. Miller and M. Krauss, J. Chem. Phys. 47, 3754 (1967).
22. M. Halmann and I. Laulicht, J. Quant Spectrosc. Radiat. Transfer 8, 935 (1968).
23. D. Villarejo, R. Stockbauer, and M. G. Inghram, J. Chem. Phys. 50, 1754 (1969).
24. Judith Drake and R. W. Nicholls, Chem. Phys. Letters 3, 457 (1969).
25. P. S. Julienne and F. H. Mies, private communication.

Table I

Band	$\lambda(Q1)$ Å	$\sigma(Q1)$ $10^{-19} \text{cm}^2$	$\frac{Q1}{\text{whole}}$	$\sigma(\text{band})$ $10^{-18} \text{cm}^2$	A & D	FCF
(0, 2)	1100	$8.47 \pm 5\%$	.322	2.63	2.77	2.88
(0, 3)	1146	$4.28 \pm 5\%$	.315	1.36	1.35	1.35
(1, 3)	1117	$8.55 \pm 5\%$	.316	2.71	2.65	2.79
(1, 4)	1161	$10.9 \pm 5\%$	.307	3.55	3.51	3.48
(1, 5)	1207	$4.39 \pm 3\%$	.299	1.47	1.53	1.46
(2, 5)	1176	$9.49 \pm 3\%$	.299	3.17	3.17	3.17
(2, 6)	1219	$7.32 \pm 3\%$	.288	2.54	2.50	2.35
(3, 6)	1190	$4.79 \pm 3\%$	.288	1.66	1.62	1.63
(3, 7)	1230	$6.79 \pm 3\%$	.278	2.44	2.56	2.37
(4, 8)	1240	$5.07 \pm 3\%$	.266	1.91	2.03	1.87
(5, 9)	1249	$3.53 \pm 3\%$	.253	1.40	1.44	1.53

## Figure Captions

- Figure 1 Diagram of the experimental apparatus.
- Figure 2 Relative spectral sensitivity of the experimental optics, based on observations of HD fluorescence.
- Figure 3 Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (1,3) band.
- Figure 4 Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (2,5) band. The P3 peak is contaminated.
- Figure 5 Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (3,7) band.
- Figure 6 Experimental excitation function for the Werner (4,8) band.

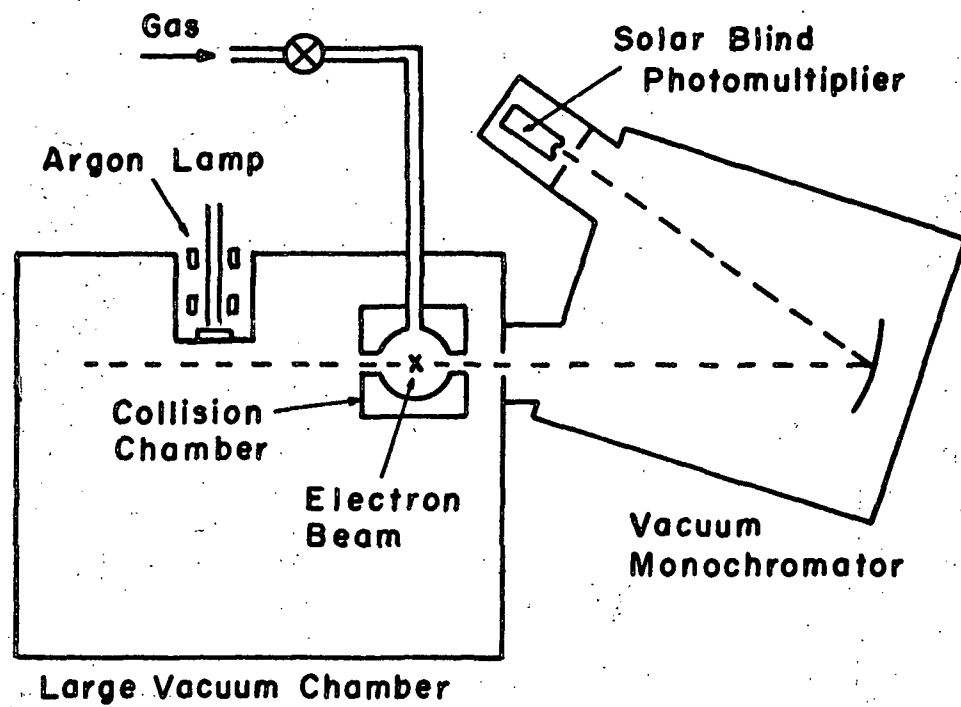


Figure 1

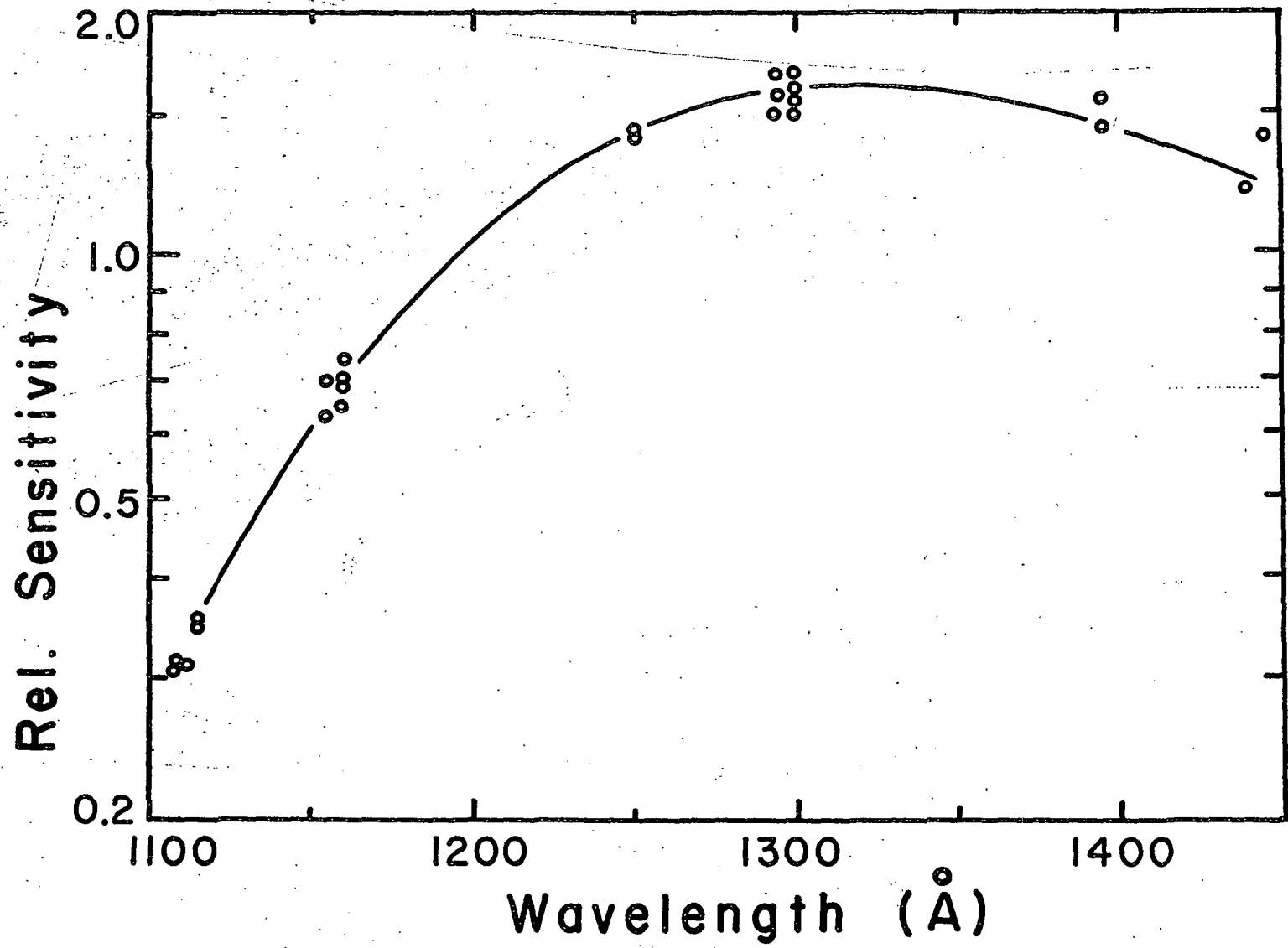


Figure 2

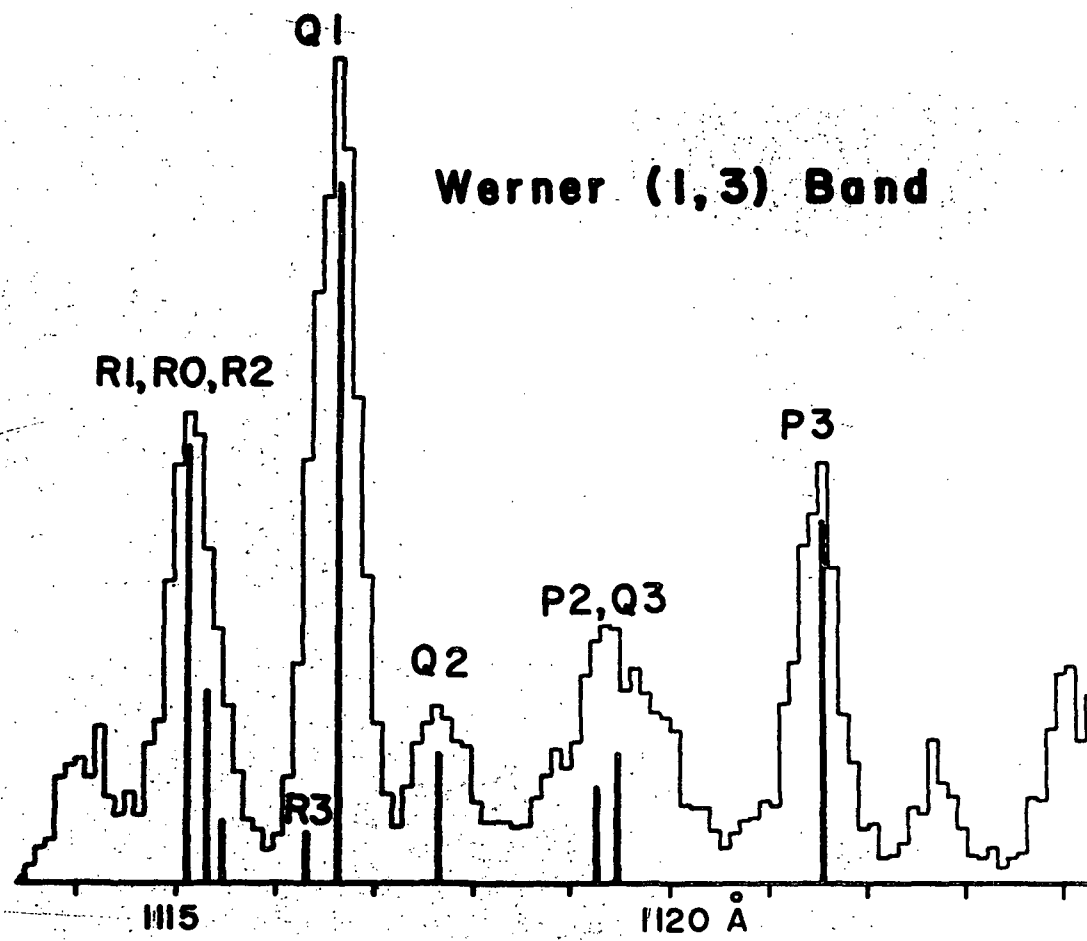


Figure 3

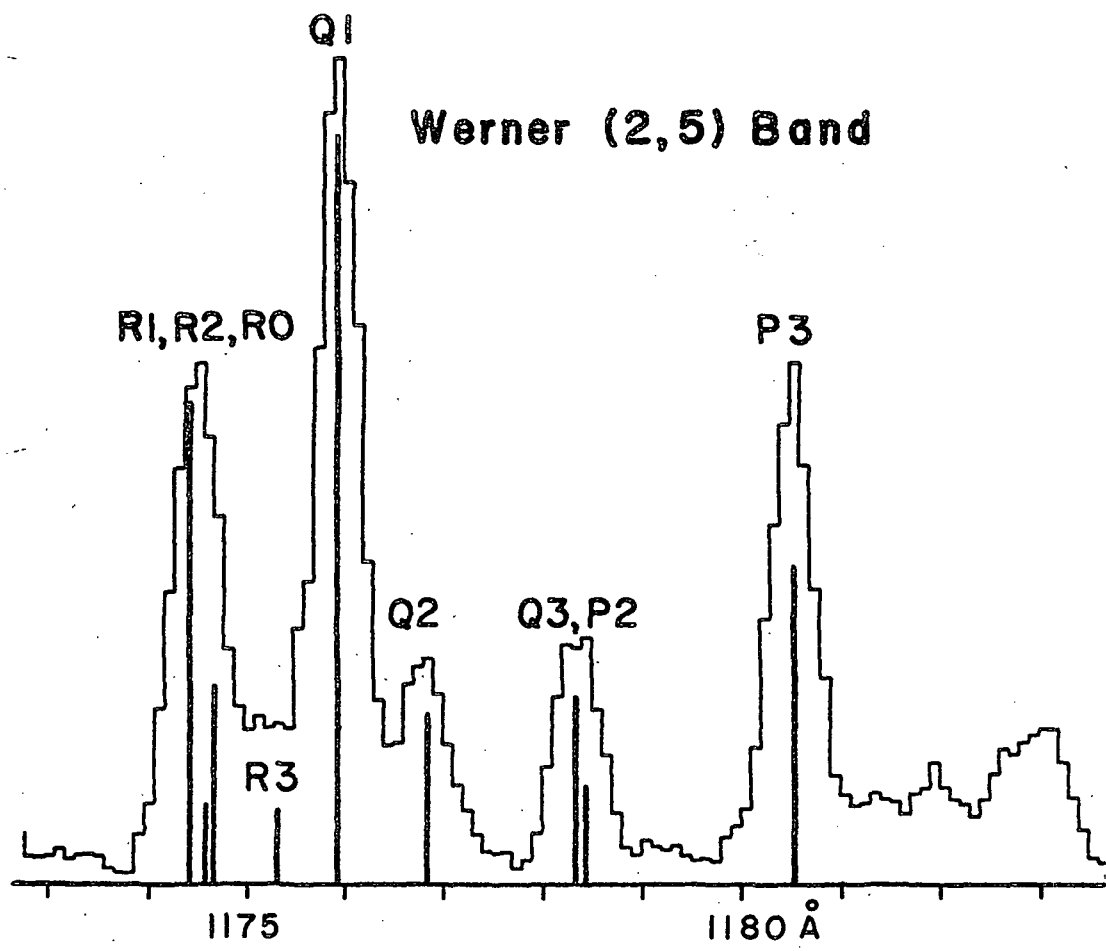


Figure 4

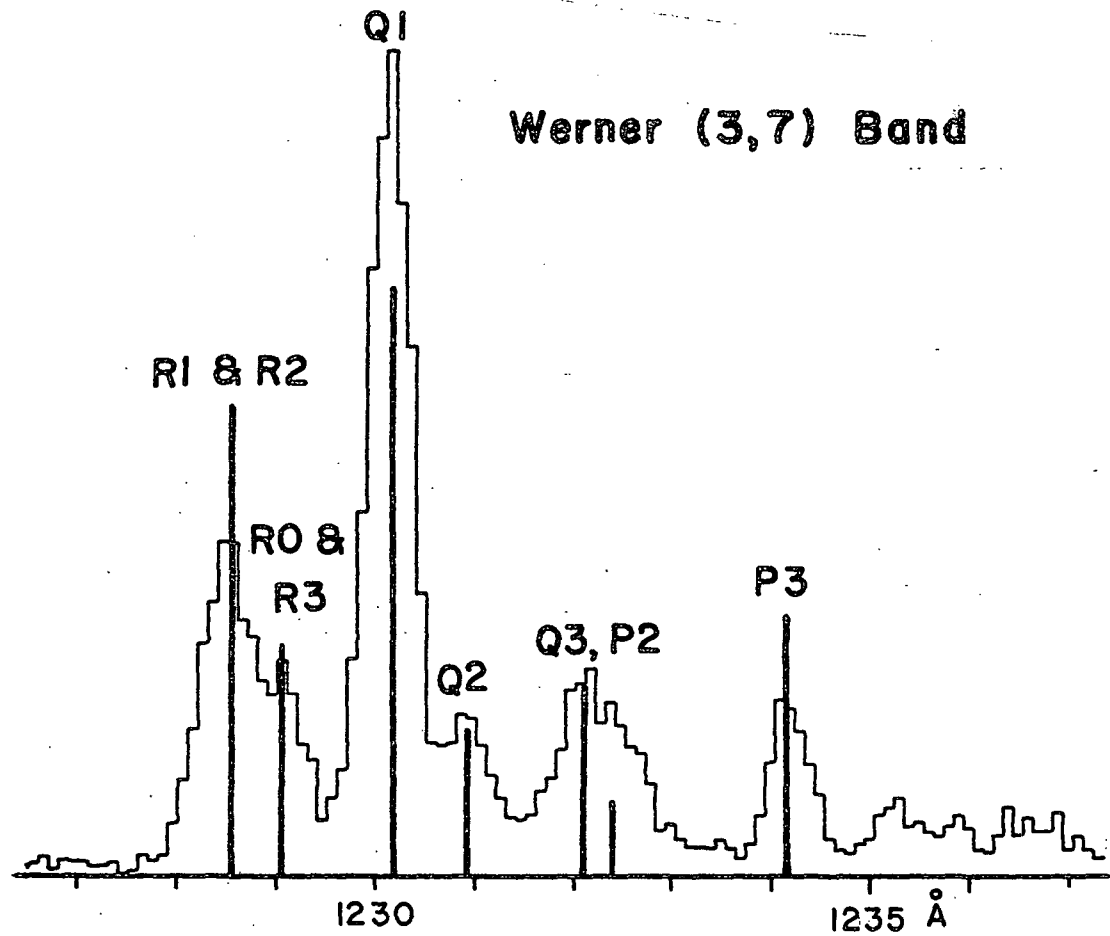


Figure 5



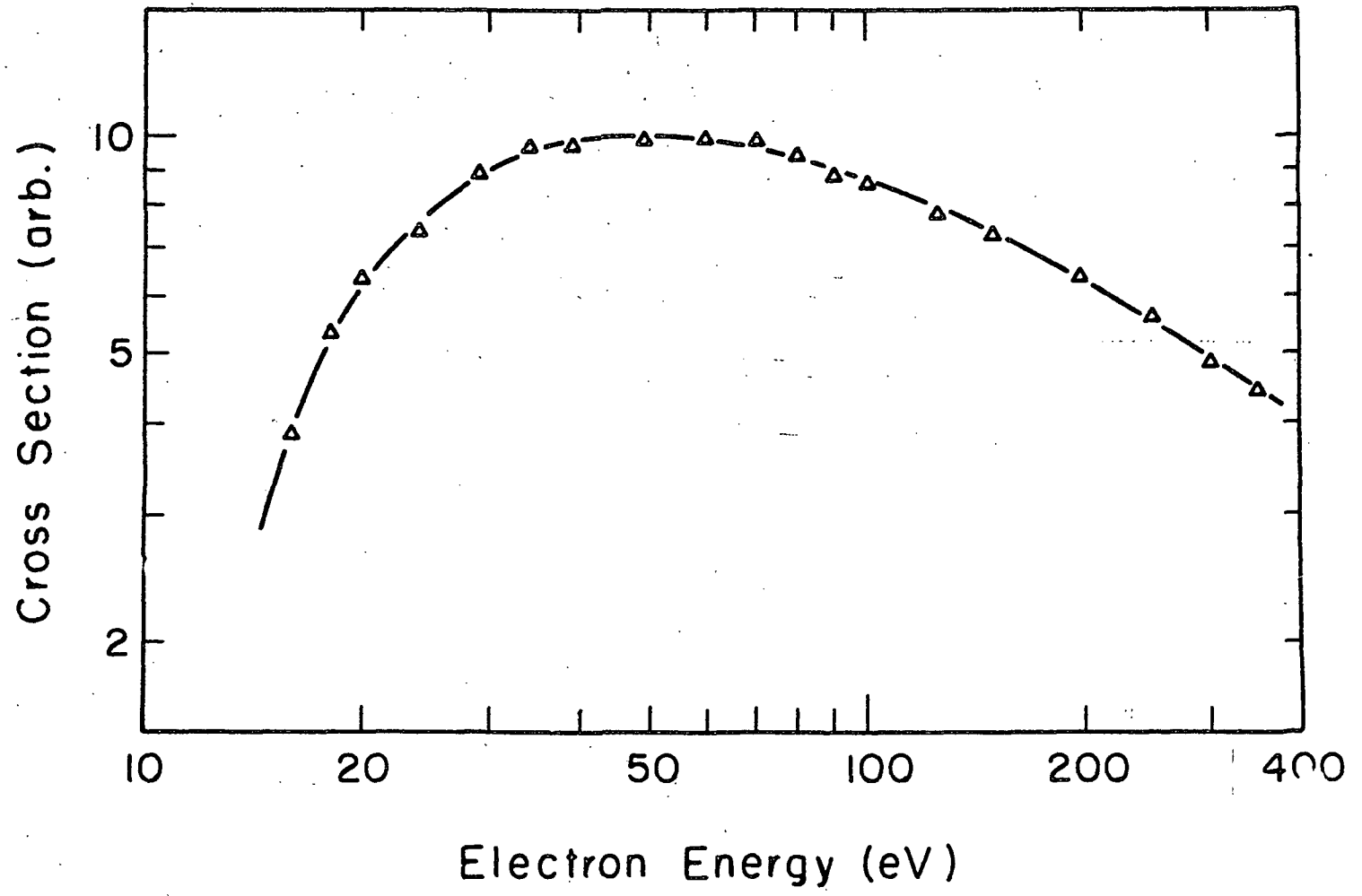


Figure 6