

## ELECTRON IMPACT EXCITATION OF H<sub>2</sub>: RYDBERG BAND SYSTEMS AND THE BENCHMARK DISSOCIATIVE CROSS SECTION FOR H LYMAN-ALPHA

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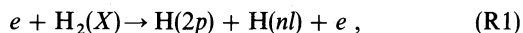
### ABSTRACT

The cross section  $\sigma_{R1}(2p)$  for H Ly $\alpha$  line production by electron dissociation of H<sub>2</sub>, widely used as a calibration reference standard in the EUV, has been calculated using two methods. The first method involves reexamination of the original experimental measurement with an accurate model of molecular and atomic hydrogen emissions. The second method establishes the H Ly $\alpha$  cross section on the basis of its value relative to the H<sub>2</sub> Rydberg band systems. The cross sections of the H<sub>2</sub> Rydberg systems are, in turn, established by a combination of theory and experimental measurement of excitation shape functions. In our analysis the cross sections derived from the first method must be reduced, but the factor is somewhat uncertain. The second method provides an intrinsically more accurate value. The mean of two estimates gives  $\sigma_{R1}(2p) = (8.18 \pm 1.2) \times 10^{-18} \text{ cm}^2$  at 100 eV. This cross section is a factor of 0.69 below the value used universally over the past 14 years. The cross section at 200 eV is  $\sigma_{R1}(2p) = 5.78 \times 10^{-18} \text{ cm}^2$ . In the process of deriving the  $\sigma_{R1}(2p)$  cross section, we also obtain accurate H<sub>2</sub> Rydberg excitation functions from threshold in an easily integrable analytic form.

*Subject headings:* laboratory spectra — transition probabilities — ultraviolet: spectra

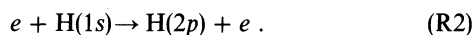
### I. INTRODUCTION

The cross section for dissociative excitation of H<sub>2</sub> producing the H(2p) state is an important quantity for astrophysics and laboratory research in the VUV. The reaction



which gives rise to the H 1s–2p Ly $\alpha$  line, has been used by many experimentalists as a convenient transfer standard for estimating cross sections for other gases. This technique of obtaining absolute cross sections has been carried on for more than 10 years, at least in part because the H Ly $\alpha$  cross section for reaction (R1) [ $\sigma_{R1}(2p)$ ] has been considered a relatively well-established quantity. Because of this usage we apply the term “benchmark” to reaction (R1), since it serves as a point of reference to many measured cross sections. The main purpose of this paper is to establish a more accurate value for the  $\sigma_{R1}(2p)$  benchmark. The preferred method of establishing the cross section in this work requires measurement of the electron impact excitation functions of the H<sub>2</sub> Rydberg band systems. The analysis therefore includes the establishment of accurate cross sections for the H<sub>2</sub> bands. The results are provided in a form allowing analytic model calculations in an energy regime which includes the threshold region of the excitation transitions.

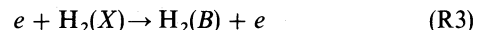
The cross section  $\sigma_{R1}(2p)$  established in earlier work is derived from the cross section  $\sigma_{R2}(2p)$  for the reaction



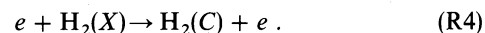
The ratio  $\sigma_{R1}(2p)/\sigma_{R2}(2p)$  was first estimated from pioneering laboratory research with atomic beams (Fite and Brackmann 1958). However, an uncertainty enters the measurement of  $\sigma_{R1}(2p)$  in that a LiF–O<sub>2</sub> filter was utilized in separating the H<sub>2</sub>

Rydberg bands from H Ly $\alpha$  in the molecular beam experiment, requiring an estimation of the fractional amount of molecular and atomic emissions in the signal. The only estimate of this fractional quantity considered to be reasonably accurate in the intervening period was that of Carrière and de Heer (1972, hereafter CdH). Although we believe an accurate cross section ( $\sigma_{\text{CUV}}$ ) has been established for the total signal transmitted by the LiF–O<sub>2</sub> filter in the experiment (Kaupila *et al.* 1971), we suggest that the estimated ratio  $\sigma_{\text{CUV}}/\sigma_{R1}(2p)$  (CdH) was not as well determined as has been generally assumed. A reexamination of the CdH experiment described below indicates that the derived  $\sigma_{R1}(2p)$  should be revised downward.

Another method of establishing  $\sigma_{R1}(2p)$  is examined in this work, based on relating reaction (R1) to the reactions



and



Reactions (R3) and (R4) produce the H<sub>2</sub> Lyman (B–X) and Werner (C–X) band systems with cross sections  $\sigma_{R3}(B)$  and  $\sigma_{R4}(C)$ . Recent measurements combined with model calculations (Ajello *et al.* 1984) have established the ratios  $\sigma_{R1}(2p)/\sigma_{R3}(B)$  and  $\sigma_{R1}(2p)/\sigma_{R4}(C)$ . Measured relative excitation functions for reactions (R3) and (R4) are used in this work to establish  $\sigma_{R3}$  and  $\sigma_{R4}$  through the Born approximation. This latter method produces two estimates of  $\sigma_{R1}(2p)$ , based on modern experimental techniques, that we consider to be the most accurate values to date. Some very recent work by Van Zyl, Gealy, and Neumann (1985) using an independent means of establishing  $\sigma_{R1}(2p)$  shows good agreement with the results reported here. The recommended cross section  $\sigma_{R1}(2p)$  ( $8.2 \times 10^{-18} \text{ cm}^2$  at 100 eV) is a factor of 1.44 below the pre-

viously accepted value, requiring a substantial downward revision of a large number of cross section measurements based on the reaction (R1) benchmark. A number of instances are cited in which cross sections dependent on this benchmark show much better agreement with published independent measurements. We give the revised cross sections for the astrophysically important  $H_2$  Rydberg systems below, in an accurate analytic form allowing direct calculation of rate coefficients.

The new estimate of  $\sigma_{R1}(2p)$  depends on application of the first Born approximation using the measured relative excitation function of the  $H_2$   $B$  and  $C$  states. Cross sections determined using the Born relation for allowed transitions have generally been obtained by extrapolation in a Fano plot (see Donaldson, Hender, and McConkey 1972). We propose a method of determining cross sections which eliminates the need for extrapolation through a process of fitting an analytic function to the entire experimental excitation function. The method is described in detail in the accompanying paper (Shemansky *et al.* 1985, hereafter Paper II). The method has the advantage of providing information on the physics of the excitation process, for example, of the contribution of exchange reactions.

## II. THE DISSOCIATIVE $H\ I$ (121.6 nm) CROSS SECTION

The basic difficulty in estimating the cross section for reaction (R1),  $\sigma_{R1}(2p)$ , lies in the involvement of blended  $H_2$  Rydberg band transitions near the location of the  $H\ Ly\alpha$  line. Blending with  $H_2$  transitions is also a problem in attempts to measure cross sections with low-resolution experimental apparatus, using reaction (R1) as a reference standard. We provide the means for making the measurement through model calculations as discussed below. The method of measuring the cross section for reaction (R1) in past work depends on the insertion of a filter to remove most of the blended  $H_2$  transitions to obtain a  $\sigma_{CUV}$  cross section, which must then be converted into a value for  $\sigma_{R1}(2p)$ . We discuss this method (method 1) here and introduce another method (method 2) of obtaining  $\sigma_{R1}(2p)$  through calculation of the  $H_2$  Rydberg, Werner, and Lyman band cross sections.

### a) Method 1

The ratio  $\sigma_{CUV}/\sigma_{R1}(2p)$  established by the CdH experiment is the only available published result accessible for reexamination. The combination of this estimate of  $\sigma_{CUV}/\sigma_{R1}(2p)$  with the measured value of  $\sigma_{CUV}$  (Kauppila *et al.* 1971), giving  $\sigma_{R1}(2p)$ , has been used universally in the literature up to the present time. The CUV cross section ( $\sigma_{CUV}$ ) measured by Fite and Brackmann (1958) and later, more accurately, by Kauppila *et al.* (1971) depends on an estimate of the atomic hydrogen cross section at 100 eV. Kauppila *et al.* (1971) use the measured cross section ( $e + H$ ) by Long, Cox, and Smith (1968),

$$\sigma_{R2}(2p) = 6.00 \times 10^{-17} \text{ cm}^2.$$

However, the Long, Cox, and Smith (1968) cross section depends on fixing the absolute cross section at high energy with the Born approximation, so that ultimately the value at 100 eV is determined by theory. On the other hand, we now have close-coupling calculations (three-state) by Kingston, Fon, and Burke (1976) which give essentially the same value,

$$\sigma_{R2}(2p) = 5.99 \times 10^{-17} \text{ cm}^2. \quad (1)$$

Williams and Willis (1975) have obtained differential cross sections in the energy range 54–680 eV. Kingston, Fon, and Burke (1976) show that the three-state close-coupling calculations accurately reproduce the experimental (Williams and Willis 1975) differential cross sections except at high energy and high scattering angles. However, the integrated cross sections are in good agreement in any case, because the reaction has a basically forward scattering characteristic (Kingston, Fon, and Burke 1976). The experimental work of Williams and Willis (1975) does not depend on the Born approximation for calibration and is unaffected by cascade contributions. We therefore have experimental and theoretical confirmation of the  $\sigma_{R2}(2p)$  cross section above 54 eV. Using the Kauppila *et al.* (1971) ratio,

$$\sigma_{CUV}/\sigma_{R2}(2p) = 0.247 \quad (2)$$

at 100 eV, we then have

$$\sigma_{CUV} = (1.48 \pm 0.05) \times 10^{-17} \text{ cm}^2. \quad (3)$$

The quantity  $\sigma_{CUV}$  must then be converted to the dissociative excitation cross section  $\sigma_{R1}(2p)$  for the  $H\ Ly\alpha$  line. The measurement of  $\sigma_{CUV}/\sigma_{R1}(2p)$  is described by CdH, in which the Fite and Brackman (1958) experiment was repeated in a static system (see Mumma and Zipf 1971). The contribution of the  $H\ Ly\alpha$  emission to the total (CUV) transmitted through the LiF– $O_2$  filter was estimated by measuring the spectrum with a scanning spectrometer. The effective transmission window of the combined detector-filter system is 105.0–126.0 nm, with strong transmission structure between these wavelengths imposed by the absorption characteristics of  $O_2$ . It was therefore necessary for CdH to obtain a relative response for their spectrometer over the 105.0–126.0 nm range. The sensitivity function was obtained using the theoretical emission characteristics of the  $H_2$  Werner system bands dominating this part of the spectrum. We suggest that some error may be introduced here without the use of a theoretical model, because the  $H_2$  bands are heavily overlapped, and the  $H_2$  Lyman band system also makes a contribution through the 105.0–126.0 nm region. However, errors in the estimated relative sensitivity are judged to be small compared to the method applied by CdH to the estimation of the integrated  $H_2$  emission contribution to the total signal in the 105.0–126.0 nm region. The method was one of summing the transmission peaks in the spectrum to obtain the integrated contribution at six wavelengths (CdH). The ratio given in Table 1 of CdH is

$$\sigma_{CUV}/\sigma_{R1}(2p) = 1.26$$

at 100 eV. Our criticism of this method is that the peak signals cannot be given the same weights as measures of the integrated signal, because the source is complex in its emission distribution, and the  $O_2$  transmission characteristics are irregular.

In order to reexamine the accuracy of the  $\sigma_{CUV}/\sigma_{R1}(2p)$  ratio, we have repeated the experiment theoretically, using a detailed model of the  $H_2$  Rydberg systems (Ajello *et al.* 1984; Shemansky and Ajello 1983), and a model of the filter-detector system. Figure 1 shows the result of the model calculation assuming a spectrometer triangular transmission function with FWHM of 0.48 nm. The filter-detector transmission function was calculated using a standard LiF transmission curve, combined with the measured  $O_2$  cross sections (Watanabe 1958; Ogawa 1968). Zipf (1984) has pointed out the fact that the dissociative excitation of  $H\ Ly\alpha$  produces a broadened emission line that could potentially affect the transmission effi-

ciency of the cell. A rough estimate of the line width can be obtained from the Freund, Schiavone, and Brader (1976) measurements of the H Balmer series. The mean kinetic energy of 6–7 eV corresponds to 0.015 nm FWHM at 121.6 nm. Application of the high-resolution measurements of Ogawa (1968) for O<sub>2</sub> transmission near 121.6 nm shows that the transmission efficiency of a broadened line of the indicated width is effectively the same as a delta function distribution at line center. Figure 1a shows a superposition of the incident and transmitted signals, and Figure 1b displays the scaled transmitted signal, separating the H<sub>2</sub> and H I emissions in the model. In this case we obtain a true integration of the signals, rather than a summation of peaks, to obtain

$$\sigma_{\text{CUV}}/\sigma_{\text{R1}}(2p) = 1.52. \quad (4)$$

If we follow the more approximate method of CdH, we obtain

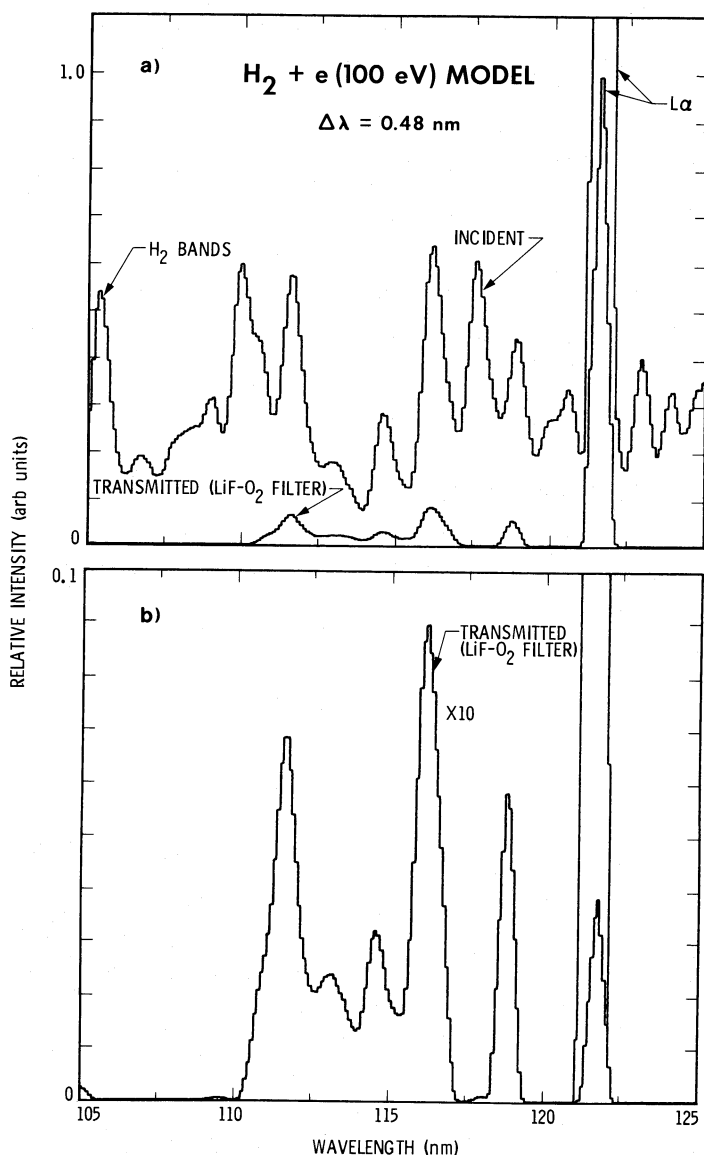


FIG. 1.—Model of the Carrière and de Heer (1972) experiment, and theoretical calculations of the  $e + \text{H}_2$  spectrum. (a) Upper curve: Theoretical incident spectrum at a resolution of 0.48 nm,  $e + \text{H}_2$  at 100 eV electron energy based on cross section measurements by Ajello *et al.* (1984). Lower curve: Theoretical calculation of emission transmitted through the LiF–O<sub>2</sub> filter in the CdH experiment (see text). (b) Transmitted spectrum scaled to show detail of spectrum structure (see Fig. 1a). The H Ly $\alpha$  is off scale. (c) Model calculation of  $e + \text{H}_2$  at 100 eV with an assumed triangular spectral resolution of 0.48 nm, showing the shape of the H<sub>2</sub> Rydberg bands blended with the H Ly $\alpha$  line.

TABLE 1  
CALCULATION OF  $\sigma_{\text{CUV}}(100)/\sigma_{\text{H}_2}(100)$   
USING THE METHOD OF CdH

$\lambda$ (nm)	Normalized Model Calculation <sup>a</sup>	CdH <sup>b</sup>
121.57 .....	43.6	43.6
121.7 .....	1.52	0.5
119.0 .....	2.31	3.59
116.7 } .....	3.58	3.44
116.1 } .....		
114.9 .....	1.28	1.71
113.0 .....	0.943	...
110.6 .....	2.74	1.85
Total <sup>c</sup> .....	55.98	...
Total <sup>d</sup> .....	55.04	54.7

<sup>a</sup> Model calculation of intensity peaks normalized to CdH data at  $\lambda = 121.57$  nm.

<sup>b</sup> CdH measured intensity peaks.

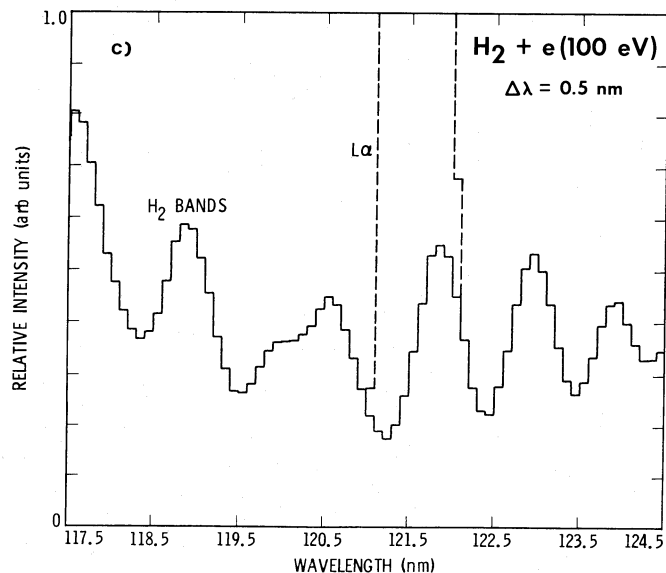
<sup>c</sup>  $\sigma_{\text{CUV}}(100)/\sigma_{\text{H}_2}(100) = 55.98/43.6 = 1.28$ : Total includes the feature at  $\lambda = 113.0$  nm.

<sup>d</sup>  $\sigma_{\text{CUV}}(100)/\sigma_{\text{H}_2}(100) = 55.04/43.6 = 1.26$ : from present model calculation. Totals exclude the feature at  $\lambda = 113.0$  nm;  $\sigma_{\text{CUV}}(100)/\sigma_{\text{H}_2}(100) = 54.7/43.6 = 1.25$ : from CdH.

the results shown in Table 1. The model calculations shown in the middle column of the table have been normalized at the H Ly $\alpha$  peak value as given by CdH. Although there are differences in individual peak values in the two data sets, the  $\sigma_{\text{CUV}}/\sigma_{\text{R1}}(2p)$  ratio obtained from the model is almost identical with the CdH value of 1.25 (Table 1). However, as we have indicated above, a true integration of the model spectrum yields the value 1.52. The estimated dissociative excitation cross section of H Ly $\alpha$  is therefore

$$\sigma_{\text{R1}}(2p) = 9.76 \times 10^{-18} \text{ cm}^2 \quad (5)$$

at 100 eV, from equations (3) and (4) above. Unfortunately the

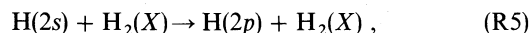




accuracy of this cross section is uncertain, because available data are not sufficient to provide accurate pressure dependence (CdH; Gaily 1969) of the  $O_2$  absorption coefficients required for the calculations. This uncertainty can, in theory, be avoided by working directly with the experimental spectra shown by CdH. We have attempted to accomplish this by working with the spectra in Figure 3 of CdH, because the original data are not available (F. J. de Heer 1984, private communication). The calculation involves establishing the relative response of the spectrometer by comparison with a model calculation of the excited  $H_2$  spectrum, and subsequently integrating the signal in the spectrum after transmission through the LiF- $O_2$  filter. We have modeled the CdH spectra on this basis, and the resulting cross section at 100 eV is

$$\sigma_{R1}(2p) = 1.07 \times 10^{-17} \text{ cm}^2. \quad (6)$$

However, equation (6) contains uncertainties that are also difficult to quantify. The published spectra on which the calculations are based are not on a uniform scale, and the reconstruction of the spectra may contain systematic errors. Moreover, the  $H_2$  density in the experiment is high enough at its lowest point ( $2 \times 10^{-3}$  torr) to allow a measurable contribution by the reaction



based on the measured rates by Comes and Wenning (1969) (see Van Zyl, Gealy, and Neumann 1985). CdH correct for the contribution of reaction (R5) in their experiment but assume that the effect is negligible at  $2 \times 10^{-3}$  torr. On the basis of these considerations we conclude that the value of  $\sigma_{R1}(2p)$  obtained from the CdH experiment must be reduced, but the magnitude of the reduction is uncertain.

In many experimental circumstances facilities are not available to provide sufficient resolution to separate the H Ly $\alpha$  line from the surrounding  $H_2$  Rydberg lines in a direct manner. In order to aid in estimating the H Ly $\alpha$  component at lower resolution, we give in Table 2 the results of model calculations of the integrated intensity at H Ly $\alpha$  over the full width of the spectrometer resolution, as a fraction of the total integrated signal. We assume in these calculations that the instrument transmission function is triangular. Figure 1c shows a model calculation at 0.5 nm spectral resolution indicating the shape of the  $H_2$  bands underlying the H Ly $\alpha$  line.

TABLE 2  
MODEL CALCULATION OF  
FRACTIONAL H Ly $\alpha$  SIGNAL<sup>a</sup>

$\Delta\lambda$ (nm) FWHM	$I_H \text{ Ly}\alpha / I_T$	
	100 eV	200 eV
0.40.....	0.887	0.884
0.50.....	0.868	0.865
0.60.....	0.850	0.846
0.70.....	0.831	0.826
1.00.....	0.769	0.764
1.50.....	0.706	0.700
2.00.....	0.627	0.620

<sup>a</sup> Calculated as a function of spectrometer resolution. Signal integrated over full width of triangular resolution function.

### b) Method 2

The experimental measurements of Ajello *et al.* (1984) establish the relative cross sections  $\sigma_{R1}(2p)/\sigma_{R4}(B)$  and  $\sigma_{R1}(2p)/\sigma_{R3}(C)$ . The  $H_2$  B-X and C-X Rydberg systems are dipole allowed transitions, and, given sufficiently accurate relative excitation functions, one can establish absolute cross sections using the first Born approximation. Thus in effect we propose to establish the  $H_2$  band cross sections by the same basic method that provided the atomic excitation cross section of reaction (R2). The methods of determining cross sections using this technique are discussed in Paper II. The Born approximation has been used extensively in suitable circumstances to establish excitation functions on an absolute scale. The cross sections estimated using the first Born approximation can be accurate provided that the Born component can be identified quantitatively in the observed excitation function. It is desirable to obtain experimental relative excitation functions for this purpose to as high an energy as possible. The method applied here fits the measured relative excitation function from threshold using a collision strength ( $\Omega_{ij}$ ) of the form

$$\Omega_{ij} = [C_0(1/X^2) + C_5](1 - 1/X) + \sum_{n=1}^4 C_n(X - 1) \exp(-\alpha n X) + C_7 \ln X, \quad (7)$$

where the  $C_n$  and  $\alpha$  are constants,

$$X = E/E_{ij}, \quad (8)$$

$E$  is electron energy, and  $E_{ij}$  is the excitation threshold energy. The cross section ( $\sigma$ ) is given by the relation

$$\sigma = \frac{\Omega_{ij}}{\omega_i} \frac{1}{E}, \quad (9)$$

where  $\omega_i$  is the lower electronic state degeneracy, with  $E$  and  $\sigma$  given in rydbergs and atomic units.

A calculation fitting the experimental excitation function using equations (7) and (9) establishes the relative values of the constants  $C_n$  in equation (1). The absolute value of the collision strength is then fixed by the first Born approximation through the relation (Paper II)

$$C_7 = \omega_i \frac{8ma_0^2}{\hbar^2} \frac{f_{ij}}{E_{ij}} = \omega_i(4.00) \frac{f_{ij}}{E_{ij}}, \quad (10)$$

where  $a_0$  is the Bohr radius,  $m$  is the electron mass, and  $f_{ij}$  is the absorption oscillator strength.

The experimental data on the excitation of the  $H_2$  B and C states for the present calculation are obtained from measurements using the experimental apparatus described in Paper II. In addition, we combine the  $H_2$  C state data of the present work with the higher energy data of de Heer and Carrière (1971). The combined data for the  $H_2$  C state extend from threshold to  $E = 3000$  eV. The  $H_2$  C state excitation function obtained in this work extends from threshold to  $E = 100$  eV, where it is merged with the de Heer and Carrière (1971) results. The present data were obtained at 94.8 nm, dominated by the  $H_2$  C(3, 0) band. Contaminating emissions were removed using model calculations (Ajello *et al.* 1984). The de Heer and Carrière (1971) data were obtained from the (3, 7) band at 123.0 nm. The excitation function for the  $H_2$  B state was obtained

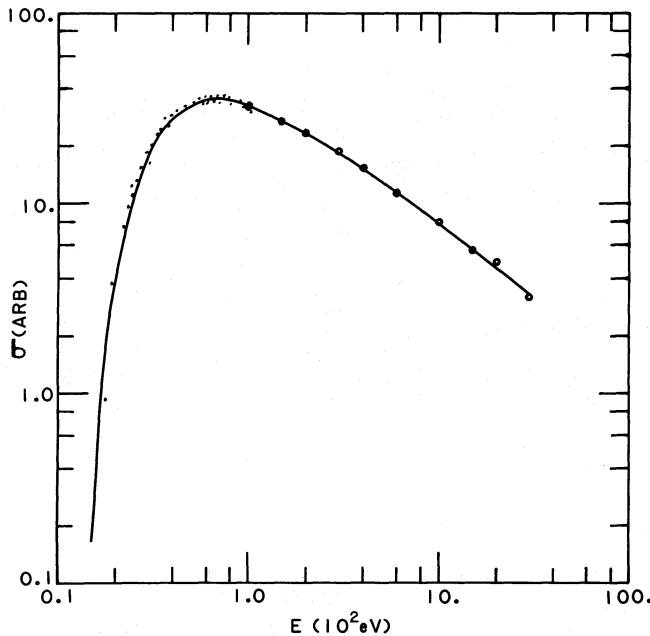


FIG. 2a

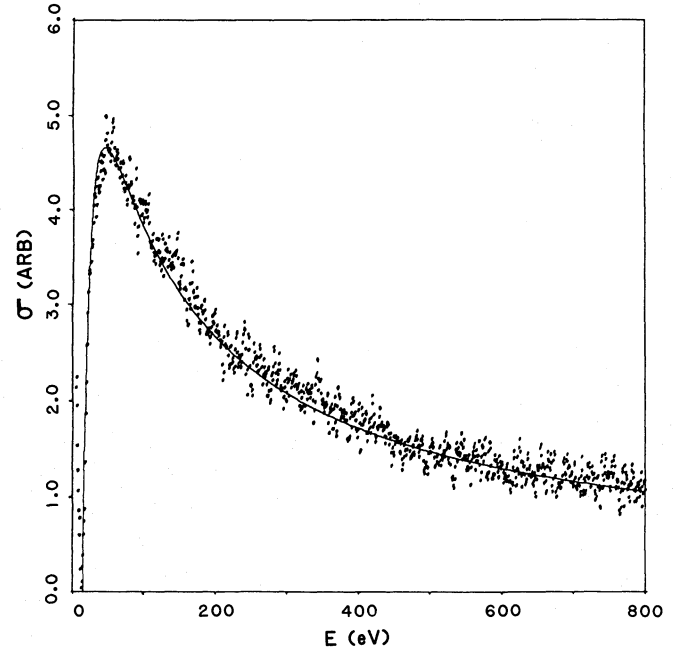


FIG. 2b

FIG. 2.—Excitation functions of the H<sub>2</sub> B  $^1\Sigma_u^+ - X^1\Sigma_g^+$  and C  $^1\Pi_u - X^1\Sigma_g^+$  transitions. The solid curves are analytic approximations to the data (see text). Coefficients are given in Table 3. (a) H<sub>2</sub> C( $v=3$ ). Circles: de Heer and Carrière (1971); dots: present work, averaged data (see text). (b) H<sub>2</sub> B(14, 11) band. Data points are present work.

from the present experimental work using the (14, 11) band transition at 137.2 nm, in order to avoid contamination from  $E, F$  state cascade. The H<sub>2</sub> B state data extend from threshold to  $E = 800$  eV. The cross sections derived from the data are plotted in Figures 2a and 2b, with the fitted analytic curves. Table 3 gives the coefficients of equation (1) derived in the fitting process. The oscillator strengths used (eq. [4]) to fix the absolute cross sections are obtained from the lifetime measurements of Schmoranzler, Imschweiler, and Noll (1984). The latter work claims a  $3\sigma$  uncertainty of 1%–2% in the measured lifetimes. These lifetimes are 8% and 15% longer than the theoretical calculation of Allison and Dalgarno (1970) for the H<sub>2</sub> B and C states. According to A. Dalgarno (1984, private communication), differences of this order are not surprising in view of the level of accuracy of the H<sub>2</sub> wave functions applied in the work of Allison and Dalgarno. We used the relative transition probabilities of Allison and Dalgarno (1970) to establish the H<sub>2</sub> B and C state cross sections. The cross sections at 100 eV for each of the H<sub>2</sub> B and C state vibrational levels are given in Table 4. The total cross sections for each state must, in general, be calculated from a sum of values for each vibrational level because of significant differences in excitation thresholds. On this basis the total cross sections are

$$\sigma_{R3}(B) = 2.67 \times 10^{-17} \text{ cm}^2 \quad (11)$$

and

$$\sigma_{R4}(C) = 2.78 \times 10^{-17} \text{ cm}^2 \quad (12)$$

at  $E = 100$  eV.

The ratios

$$\sigma_{R1}(2p)/\sigma_{R3}(B) = 0.293 \quad (13)$$

and

$$\sigma_{R1}(2p)/\sigma_{R4}(C) = 0.306 \quad (14)$$

at 100 eV are obtained by Ajello *et al.* (1984) with an estimated uncertainty of 10%. We then obtain two values of  $\sigma_{R1}(2p)$  for reaction (R1), from equations (11)–(14):

$$\sigma_{R1}(2p) = 7.84 \times 10^{-18} \text{ cm}^2$$

and

$$\sigma_{R1}(2p) = 8.51 \times 10^{-18} \text{ cm}^2,$$

with an average value

$$\sigma_{R1}(2p) = (8.18 \pm 1.2) \times 10^{-18} \text{ cm}^2. \quad (15)$$

at 100 eV.

The cross sections of the H<sub>2</sub> Rydberg states and H Ly $\alpha$  using equations (11) and (12) with the relative values of Ajello *et al.* (1984) are given in Table 5.

### III. DISCUSSION

Uncertainties in cross section estimates are generally difficult to quantify because of the diversity of factors entering the analysis, whatever the measurement method may be. Ultimately the best method of determining accuracy is to assess consistency with other independent measurements and calculations. According to the argument given above, the cross section for reaction (R1) used uniformly over the past decade must be reduced by at least 20% because of systematic factors entering the original analysis of  $\sigma_{\text{CUV}}/\sigma_{R1}(2p)$  by CdH. A much greater degree of certainty is attached to the present estimate (method 2), based on the first Born approximation applied to the H<sub>2</sub> B and C states. The quality of the excitation function data appears to be high enough so that other factors in the analysis tend to limit accuracy. Figure 3 shows a comparison of the analytic collision strength curves for the two H<sub>2</sub> states. The curves are parallel at dimensionless (threshold) energies  $X > 10$ , because the Born term  $C_7$  is dominant in this region.

TABLE 3  
ANALYTIC COEFFICIENTS<sup>a</sup> FOR THE H<sub>2</sub> RYDBERG AND E, F STATE CROSS SECTIONS

V	B <sup>1</sup> Σ <sup>+</sup> <sub>u</sub>		B' <sup>1</sup> Σ <sup>+</sup> <sub>u</sub>		B'' <sup>1</sup> Σ <sup>+</sup> <sub>u</sub>		C <sup>1</sup> Π <sub>u</sub>		D' <sup>1</sup> Π <sub>u</sub>		E, F <sup>1</sup> Σ <sup>+</sup> <sub>g</sub>	
	E <sub>ij</sub> (Ryd)	C <sub>7</sub>	E <sub>ij</sub> (Ryd)	C <sub>7</sub>	E <sub>ij</sub> (Ryd)	C <sub>7</sub>	E <sub>ij</sub> (Ryd)	C <sub>7</sub>	E <sub>ij</sub> (Ryd)	C <sub>7</sub>	E <sub>ij</sub> (Ryd)	C <sub>7</sub>
0.....	0.82211	0.7635-2 <sup>e</sup>	1.02663	0.1813-2	1.08516	0.5691-3	0.90337	0.1835+0	1.08593	0.3199-1	1.09380	0.1269-1
1.....	0.83413	0.2580-1	1.04377	0.4024-1	1.10394	0.1263-1	0.92440	0.2744+0	1.10622	0.5390-1	1.11389	0.2138-1
2.....	0.84581	0.5079-1	1.05941	0.5569-1	1.12149	0.1748-1	0.94420	0.2575+0	1.12533	0.5538-1	1.13282	0.2196-1
3.....	0.85717	0.7613-1	1.07337	0.6225-1	1.13779	0.1954-1	0.96300	0.1979+0	1.14328	0.4561-1	1.15060	0.1809-1
4.....	0.86786	0.9643-1	1.08522	0.5733-1	1.15285	0.1800-1	0.98025	0.1376+0	1.16008	0.3317-1	1.16724	0.1316-1
5.....	0.87716	0.1094+0	1.09393	0.3680-1	1.16667	0.1155-1	0.99649	0.9086-1	1.17580	0.2286-1	1.18272	0.0968-2
6.....	0.88944	0.1130+0	1.09674	0.6279-2	1.17924	0.1971-2	1.01154	0.5854-1	1.19044	0.1522-1	1.19705	0.6037-2
7.....	0.89960	0.1105+0	1.09767	0.1147-2	1.19058	0.3600-3	1.02541	0.3733-1	1.20402	0.1001-1	1.21023	0.3970-2
8.....	0.90948	0.1031+0	1.09828	0.2839-3	1.20067	0.8914-4	1.03803	0.2383-1	1.21655	0.6605-2	1.22225	0.2619-2
9.....	0.91908	0.9293-1	...	...	...	...	1.04934	0.1525-1	1.22788	0.4383-2	1.23313	0.1738-2
10.....	0.92840	0.8149-1	...	...	...	...	1.05923	0.9792-2	1.23816	0.2991-2	1.24286	0.1186-2
11.....	0.93470	0.7055-1	...	...	...	...	1.06758	0.6231-2	1.24727	0.2044-2	1.25143	0.8105-3
12.....	0.94621	0.5905-1	...	...	...	...	1.07415	0.3799-2	1.25516	0.1392-2	1.25886	0.5521-3
13.....	0.95471	0.4929-1	...	...	...	...	1.07858	0.1807-2	1.26182	0.9774-3	1.26513	0.3876-3
14.....	0.96378	0.4063-1	...	...	...	...	...	...	1.26717	0.7404-3	1.27025	0.2936-3
15.....	0.97184	0.3333-1	...	...	...	...	...	...	1.27108	0.2073-3	1.27422	0.8222-4
16.....	0.97870	0.2729-1	...	...	...	...	...	...	...	...	...	...
17.....	0.98692	0.2216-1	...	...	...	...	...	...	...	...	...	...
18.....	0.99342	0.1804-1	...	...	...	...	...	...	...	...	...	...
19.....	1.00045	0.1464-1	...	...	...	...	...	...	...	...	...	...
20.....	1.00722	0.1188-1	...	...	...	...	...	...	...	...	...	...
21.....	1.01381	0.9651-2	...	...	...	...	...	...	...	...	...	...
22.....	1.02009	0.7852-2	...	...	...	...	...	...	...	...	...	...
23.....	1.02620	0.6398-2	...	...	...	...	...	...	...	...	...	...
24.....	1.03210	0.5224-2	...	...	...	...	...	...	...	...	...	...
25.....	1.03789	0.4272-2	...	...	...	...	...	...	...	...	...	...
26.....	1.04311	0.3499-2	...	...	...	...	...	...	...	...	...	...
27.....	1.04829	0.2858-2	...	...	...	...	...	...	...	...	...	...
28.....	1.05323	0.2331-2	...	...	...	...	...	...	...	...	...	...
29.....	1.05790	0.1909-2	...	...	...	...	...	...	...	...	...	...
30.....	1.06230	0.1578-2	...	...	...	...	...	...	...	...	...	...
31.....	1.06636	0.1291-2	...	...	...	...	...	...	...	...	...	...
32.....	1.07007	0.1029-2	...	...	...	...	...	...	...	...	...	...
33.....	1.07331	0.7871-3	...	...	...	...	...	...	...	...	...	...
34.....	1.07576	0.5587-3	...	...	...	...	...	...	...	...	...	...
35.....	1.07776	0.2984-3	...	...	...	...	...	...	...	...	...	...
36.....	1.07853	0.4286-4	...	...	...	...	...	...	...	...	...	...

<sup>a</sup> See text, eq. (7).

<sup>b</sup> C<sub>0</sub>/C<sub>7</sub> = -0.6439, C<sub>5</sub>/C<sub>7</sub> = -0.3560, C<sub>n</sub> = 0.0 for n = 1-4.

<sup>c</sup> C<sub>1</sub>/C<sub>7</sub> = -2.082, C<sub>4</sub>/C<sub>7</sub> = 4.6732, C<sub>5</sub>/C<sub>7</sub> = -0.26316, α = 0.8424, C<sub>n</sub> = 0.0 for n = 0, 2, 3.

<sup>d</sup> C<sub>0</sub>/C<sub>7</sub> = 5.40, C<sub>5</sub>/C<sub>7</sub> = -0.6336, C<sub>n</sub> = 0.0 for n = 1-4.

<sup>e</sup> The notation 0.7635-2 means 0.7635 × 10<sup>-2</sup>.

TABLE 4  
CROSS SECTIONS OF H<sub>2</sub> B-X AND C-X EXCITATION  
TRANSITIONS FOR 100 eV ELECTRONS<sup>a</sup>

<i>V</i>	<i>B</i> <sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	<i>C</i> <sup>1</sup> Π <sub>u</sub>
0.....	0.1940-2 <sup>b</sup>	0.4619-1
1.....	0.6505-2	0.6815-1
2.....	0.1271-1	0.6316-1
3.....	0.1892-1	0.4797-1
4.....	0.2380-1	0.3300-1
5.....	0.2686-1	0.2156-1
6.....	0.2753-1	0.1376-1
7.....	0.2675-1	0.8698-2
8.....	0.2481-1	0.5507-2
9.....	0.2224-1	0.3499-2
10.....	0.1939-1	0.2233-2
11.....	0.1672-1	0.1413-2
12.....	0.1390-1	0.8581-3
13.....	0.1155-1	0.4069-3
14.....	0.9466-2	...
15.....	0.7730-2	...
16.....	0.6303-2	...
17.....	0.5093-2	...
18.....	0.4130-2	...
19.....	0.3338-2	...
20.....	0.2699-2	...
21.....	0.2184-2	...
22.....	0.1771-2	...
23.....	0.1438-2	...
24.....	0.1170-2	...
25.....	0.9535-3	...
26.....	0.6676-3	...
27.....	0.6343-3	...
28.....	0.5158-3	...
29.....	0.4214-3	...
30.....	0.3473-3	...
31.....	0.2835-3	...
32.....	0.2255-3	...
33.....	0.1722-3	...
34.....	0.1221-3	...
35.....	0.6513-4	...
36.....	0.9351-5	...
Total cross section.....	0.3034 au	0.3164 au
	2.67-17 cm <sup>2</sup>	2.78-17 cm <sup>2</sup>

<sup>a</sup> Atomic units.

<sup>b</sup> The notation 0.1940-2 means  $0.1940 \times 10^{-2}$ .

Both sets of data appear to follow closely the Born shape functions ( $X > 10$ ), leaving little doubt that results were obtained to sufficiently high energy. The H<sub>2</sub> *B* and *C* state cross sections are given equal weight, because the lower energy range of the H<sub>2</sub> *B* data tends to be compensated by the much simpler shape function relative to that of the H<sub>2</sub> *C* state. The H<sub>2</sub> *C* state for  $X < 10$  shows a complex shape, requiring more coefficients in the fitting process (Table 3). Most of the uncertainty in the  $\sigma_{R1}(2p)$  cross section (eq. [15]) is thus associated with the magnitude of the cross section ratios in equations (13) and 14. A recent estimate of

$$\sigma_{R1}(2p) = (7.22 \pm 1.28) \times 10^{-18} \text{ cm}^2 \quad (16)$$

at 100 eV has been obtained by Van Zyl, Gealy, and Neumann (1985) using an entirely independent absolute calibration.

Zipf (1984), in a recent review, has suggested that  $\sigma_{R1}(2p)$  may be as large as  $1.44 \times 10^{-17} \text{ cm}^2$ , a factor of  $\sim 2$  larger than the values recommended in this paper. The basis of Zipf's argument is that the value of  $\sigma_{R2}(2p)$ , the atomic hydrogen excitation cross section as determined initially by Long, Cox, and Smith (1968), may be too low by a factor of 1.2. This

TABLE 5  
CROSS SECTIONS OF H Ly $\alpha$ , H<sub>2</sub> RYDBERG,  
AND H<sub>2</sub> E, F SYSTEMS<sup>a</sup>

	$\sigma(100 \text{ eV})$	$\sigma(200 \text{ eV})$	$\Sigma f_{ij}^b$
H(2p).....	0.818	0.578	...
<i>B</i> <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> .....	2.67	1.85	0.289
<i>B'</i> <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> .....	0.505	0.358	0.0702
<i>B''</i> <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> .....	0.153	0.110	0.0234
<i>C</i> <sup>1</sup> Π <sub>u</sub> .....	2.78	1.93	0.310
<i>D</i> <sup>1</sup> Π <sub>u</sub> .....	0.547	0.398	0.0821
<i>D'</i> <sup>1</sup> Π <sub>u</sub> .....	0.216	0.157	0.0327
<i>E, F</i> <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> .....	0.286	0.197	0.0357 <sup>c</sup>

<sup>a</sup> Units of  $10^{-17} \text{ cm}^2$ .

<sup>b</sup> System oscillator strength  $\Sigma f_{ij} = [\Sigma(C_i)E_{ij}]/4$ .

<sup>c</sup> Generalized oscillator strength.

adjustment of the previously accepted value,  $\sigma_{R1}(2p) = 1.2 \times 10^{-17} \text{ cm}^2$ , then produced the suggested  $1.44 \times 10^{-17} \text{ cm}^2$  estimate. The basis for the suggestion by Zipf (1984) that the  $\sigma_{R2}(2p)$  value at 100 eV, as quoted here in equation (1), is 20% too low is not entirely clear. The references cited by Zipf (1984) as source information (Williams and Willis 1974; Morgan, McDowell, and Callaway 1977) refer only to the near-threshold region. However, as noted above, Kingston, Fon, and Burke (1976), using three-state close-coupling calculations, show good agreement with the later experimental work by Williams and Willis (1975) at energies above 55 eV, and near exact agreement with the shape function measured by Long, Cox, and Smith (1968) above 60 eV. Of course, all of the theoretical calculations converge to the same cross section at high energy, corresponding to the first Born approximation. The question then is one of excitation shape function above  $\sim 55$  eV, and this appears to be well established by both theory and experiment. Difficulties with the reaction (R2) cross section in the near-threshold region are a separate question in our view.

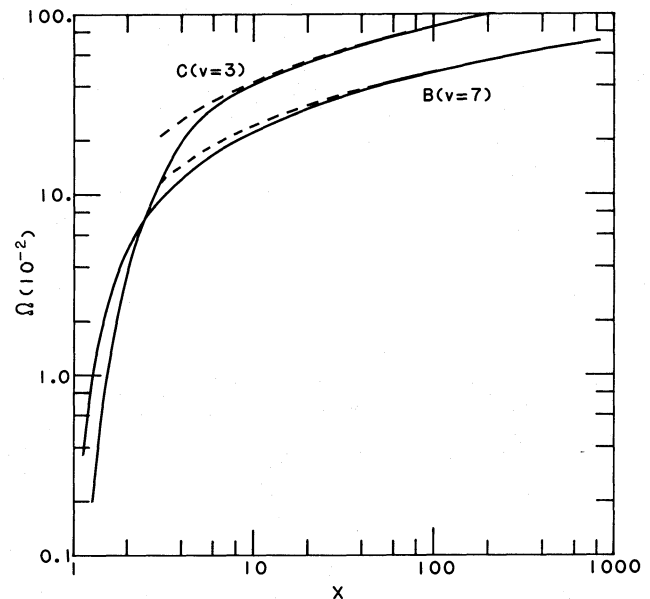


FIG. 3.—Collision strengths of the H<sub>2</sub> *B*(*v* = 7) and *C*(*v* = 3) states, as a function of dimensionless (threshold) energy, *X*. The curves show conformity to the first Born approximation for  $X > 10$  between the *B* and *C* states. The dashed curves show the first Born approximation component of the total strength.



The cross sections for the  $H_2$  Rydberg states at 100 eV as determined here (Table 5) are now generally lower than theoretical calculations such as those of Arrighini *et al.* (1980) (see Ajello *et al.* 1984). However, the apparent agreement based on the earlier values of  $\sigma_{R1}(2p)$  (Ajello *et al.* 1984) appears to be fortuitous. All of the theoretical calculations obtain the same Born cross section at high energy, if adjusted to a common oscillator strength. The divergence of the present result from the earlier theoretical calculations is therefore one of different excitation function shapes, causing differing cross sections at 100 eV. The differences in shape function are shown in Figure 4, where the present total cross sections of the  $H_2$  Lyman and Werner bands are compared with those of Arrighini *et al.* (1980) normalized to the same oscillator strengths. The Arrighini *et al.* (1980) excitation functions show a slightly higher slope toward lower energies below 400–500 eV. The divergence is 17% and 13% for the  $H_2$  B and C states, respectively, at 100 eV, and factors of 2 and 10 at 20 eV (Fig. 4). The differences in shape between the present  $H_2$  B and C state cross sections below 60 eV are quite evident in Figure 4, resulting from basic differences in collision-strength shape (Fig. 3) and in threshold energies. This difference in cross section shape in the low-energy region is of significance to model calculations in astrophysics, but appears to have been unrecognized heretofore. The analytic equations (eqs. [7] and [9]) applied in this paper provide cross section estimates from threshold to arbitrary high energy. Thermally averaged collision strengths are thus easily obtained; formulae for the direct calculation of rate coefficients for Maxwellian electrons are given in equations (14) and (15) of Paper II.

A substantial number of experimental cross sections for electron impact on various species with emission transitions in the EUV and FUV regions have been determined through measurements relative to the H Ly $\alpha$  line [ $\sigma_{R1}(2p)$ ] from dissociative excitation of  $H_2$ . Many of the measurements using this method

have been made since the time of the careful work of Mumma and Zipf (1971) in establishing the H Ly $\alpha$  excitation function for dissociative excitation. If the new value given by equation (15) above is accepted, it will then be necessary to correct all cross sections that depend on the H Ly $\alpha$  dissociative excitation rate as a benchmark quantity. In particular, the very recent measurements of the  $H_2$  Rydberg system cross sections by Ajello *et al.* (1984) must be reduced by a mean multiplicative factor 0.693, as shown in Tables 4 and 5. The He 584 Å cross sections measured by an optical calibration method based on  $\sigma_{R1}(2p)$  (Paper II) shows excellent agreement with the modified Born value, showing consistency of calibration with Born cross sections. Other examples in which experimental measurements obtained by different methods show better agreement with a reduced dissociative H Ly $\alpha$  cross section are discussed by Ajello and Franklin (1985). We clearly require a comprehensive compilation of experimental cross sections, particularly those measured over the last 15 years, to make a better assessment of the effect of the reduced H Ly $\alpha$  standard. The Joint Institute of Laboratory Astrophysics reviews cover the period prior to 1980 (Gallager and Beaty 1981). A recent review by McConkey (1984) references electron impact experiments in the last 5 years. One significant example of convergence of measured cross sections obtained using the corrected H Ly $\alpha$  standard is the case of the dissociative excitation of the N I 1200 Å multiplet. Ajello and Shemansky (1985) obtain  $4.48 \times 10^{-18} \text{ cm}^2$  at 100 eV. The corrected value of Mumma and Zipf (1971) becomes  $4.64 \times 10^{-18} \text{ cm}^2$ . These values can be compared with the Aarts and de Heer (1971) measurement of  $4.72 \times 10^{-18} \text{ cm}^2$ . This latter value remains unchanged, since it is based on a generalized oscillator strength, independent of the H Ly $\alpha$  standard. The three experimental values agree within 6%, a significant improvement over the previous 35% separation.

The most significant direct result of the present cross section estimates lies in the estimated energy deposition rates derived from  $H_2$  band system observations (Smith *et al.* 1983). These rates must increase by a factor of approximately 1.45. Estimates of  $H_2$  neutral dissociation rates must also increase on this basis by a factor which varies with electron energy distribution.

#### IV. SUMMARY

We have reexamined the cross section  $\sigma_{R1}(2p)$  for excitation of H Ly $\alpha$  emission produced by electron impact on  $H_2$ . A more accurate estimate of  $\sigma_{R1}(2p)$  is obtained, based on Born approximation estimates of the  $H_2$  Rydberg system cross sections using measured relative excitation functions. This method reduces the value of  $\sigma_{R1}(2p)$  to

$$(8.18 \pm 1.2) \times 10^{-18} \text{ cm}^2$$

at 100 eV, a factor of 0.69 below the value universally applied to cross section measurements over the past decade. Because of the fact that this cross section has been used as an absolute reference for cross sections of other species in the EUV and FUV, many published results, especially after the time of the Mumma and Zipf (1971) work, must also be revised downward by a similar factor. In many cases this appears to improve agreement with measurements made by other methods. Recent work (Van Zyl, Gealy, and Neumann 1985) is in good agreement with the present results, but the importance of the H Ly $\alpha$  cross section in our view requires further independent corroboration.

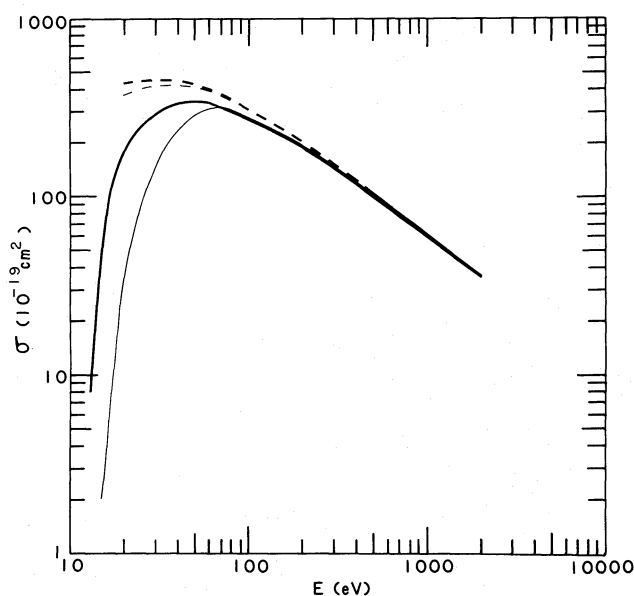


FIG. 4.—Total direct excitation cross sections of the  $H_2$  B and C states. The heavy curve is the  $H_2$  B state cross section based on the present work. The light line is the corresponding  $H_2$  C state cross section. The dashed curves are the theoretical cross sections calculated by Arrighini *et al.* (1980) normalized to the oscillator strengths applied in the present work (see text).



We have obtained cross sections for the H<sub>2</sub> Rydberg systems fixed in magnitude by the Born approximation, using experimentally determined excitation functions. Accurate analytic expressions for these cross sections allow the direct calculation of rate coefficients. Disagreement with earlier theoretical calculations is caused mainly by differences in cross section shape function, because all of the theoretical calculations, given the same oscillator strengths, are in agreement at high energy.

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