IONIZATION OF MOLECULAR HYDROGEN

XIANMING LIU AND DONALD E. SHEMANSKY

Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089;
xianming@usc.edu, dons@hippolyta.usc.edu

ABSTRACT

A general model, based on a theoretically calculated ionization oscillator strength and an experimentally determined excitation shape function, has been obtained for calculating the molecular hydrogen electron-impact ionization cross section of a transition between any discrete vibrational levels of the neutral $X\,^1\Sigma_g^+$ state and ionic $X\,^2\Sigma_g^+$ state. Specifically, the excitation shape function and ionization oscillator strength for transitions from the $v_i = 0$ level of the $X\,^1\Sigma_g^+$ neutral state to the discrete levels of the $X\,^2\Sigma_g^+$ ionic state are derived from analyzing several experimental measurements. The derived oscillator strength is found to be consistent with the 1994 photoabsorption measurements of Samson & Haddad and the 1977 theoretical cross sections of Flannery and coworkers. The derived excitation function, along with the oscillator strengths for transitions involving the $v_i > 0$ level calculated from the data of Flannery and coworkers, permits an accurate calculation of the nondissociative cross sections of H_2 between any discrete vibrational levels over a wide energy range.

Subject heading: molecular data

1. INTRODUCTION

The $X\,^2\Sigma_g^+$ state of H_2^+ can be viewed as the convergence limit of the singly excited $1s\sigma_g np\sigma_u\,^1\Sigma_u^+$ and $1s\sigma_g np\pi_u\,^1\Pi_u$ Rydberg series of H_2. The excited electronic states of H_2^+ can similarly be considered as appropriate limits for the doubly excited Rydberg series of the neutral molecule. In the absence of significant electron correlation and configuration interaction (Hesse & Baye 2003), excitation from the $X\,^1\Sigma_g^+$ neutral state to all but the $X\,^2\Sigma_g^+$ ionic states requires a simultaneous change in two electron configurations and is therefore forbidden by dipole selection rules. In addition, the $X\,^2\Sigma_g^+$ state is the only chemically bonded state of H_2^+. While electronic transitions between the $v_k = 0$–2 levels of $2p\sigma_u\,^2\Sigma_u^+$ and the high $v_j = 18$ and 19 levels of the $X\,^2\Sigma_g^+$ state have been observed in the microwave region by Carrington & McNab (1989), Carrington et al. (1993a, 1993b), and Critchley et al. (2001), these v_k levels are supported by a shallow long-range van der Waals potential (Carrington et al. 1995; Carbonell et al. 2003).

Because of the simplicity of H_2^+, it has been the subject of many theoretical and experimental investigations. The term values for all 423 discrete rovibrational levels of the $X\,^2\Sigma_g^+$ state for H_2^+ have been accurately calculated by a number of authors (Moss 1993; Taylor et al. 1999; Hilico et al. 2000; Hesse & Baye 2003). The calculated term values are in very good agreement with the experimental data of Carrington et al. (1993b). Hesse & Baye (2003) also examined the configuration interaction between the ground $X\,^2\Sigma_g^+$ state and excited $^2\Pi_g$ and $^2\Delta_g$ states and found that the contribution of the $^2\Pi_g$ and $^2\Delta_g$ states is extremely small ($<7\times10^{-6}$ and 1×10^{-10}, respectively). The photoionization cross section of H_2 from the ground vibrational level has been calculated in a number of studies, including those of Ford et al. (1975), Tai & Flannery (1977), Raseev & Le Rouzo (1983), Itikawa et al. (1983), Cacelli et al. (1993), and Yan et al. (1998). Tai & Flannery (1977) and Flannery et al. (1977) also calculated the nondissociative photoionization cross section from excited vibrational levels of the $X\,^1\Sigma_g^+$ state. Experimental measurements of the cross section have been performed by Cook & Metzger

(1964), Fryar & Browning (1973), Lee et al. (1976), Marr et al. (1980), and Samson & Haddad (1994). The rotationally resolved photoelectron spectrum of H_2^+ has been recently reported by Stimson et al. (1998) and Öhrwall et al. (1999).

There have also been many experimental measurements of the electron-impact ionization cross sections of H_2. Early experimental studies with electrons primarily focused on the threshold region, because of disagreement and controversy about the threshold behavior (Kieffer & Dunn 1966). Subsequent experimental work by Marmet & Kerwin (1960), Briglia & Rapp (1965), McGowan et al. (1968), and Schowengerdt & Golden (1975) indicate that direct ionization and resonance excitation followed by two-electron autoionization, as well as autoionization of the Rydberg states of H_2, can all contribute to the formation of H_2^+. Rapp & Englander-Golden (1965) measured the total ionization cross section of H_2. Rapp et al. (1965) also reported the total dissociative ionization cross section, subsequently shown to be almost 41% too small by Van Zyl & Stephen (1994). Crowe & McConkey (1973) obtained the absolute cross sections of H^+ for the first two ionic states and reported the H^+/H_2^+ ratio from the $X\,^2\Sigma_g^+$ states. Backx et al. (1976) measured oscillator strength distribution over the 10–70 eV range for H_2 and its isotope counterparts. More accurate cross section measurements have been recently reported by Edwards et al. (1988), Kossman et al. (1990), Krishnakumar & Srivastava (1994), Jacobsen et al. (1995), and Straub et al. (1996). The initial cross sections of Straub et al. (1996) have subsequently been refined and updated by Stebbings & Lindsay (2001) and Lindsay & Mangan (2003). The updated cross sections of Straub et al. (1996) are perhaps the most accurate measurements in the 25–1000 eV region and are the currently recommended values (Lindsay & Mangan 2003). Dissociative ionization involving excited states of H_2^+ has been studied by Van Zyl & Stephen (1994), Mangan et al. (1999), Edwards et al. (1999), and Edwards & Zheng (2001).

The ionization threshold for the lowest level of H_2 is 15.426 eV (803.7 Å). Therefore, the ionization of ground vibronic level H_2 in molecular clouds by an interstellar radiation field or in the outer planetary atmospheres by solar radiation is

TABLE 1
COMPARISON OF THE IONIZATION CROSS SECTIONS OF H_2

E (eV)	Straub et al.[a]	K & S[b]	Kossmann et al.[c]	KSS Scaled[d]	Edwards et al.[e]	Model[f]
16	0.182	0.20	...	...	...	0.10
17	0.691	0.76	...	...	...	0.59
18	1.46	1.60	...	...	...	1.22
19	1.89	2.08	...	...	...	1.81
20	2.41	2.65	...	...	...	2.35
22.5	3.59	3.95	...	...	...	3.55
25	4.58	5.03	...	...	...	4.57
27.5	...	5.85	...	...	...	5.44
30	6.42	6.70	...	...	...	6.17
32.5	...	7.35	...	...	...	6.76
35	7.42	7.78	...	...	...	7.28
40	8.12	8.55	...	...	...	8.01
45	8.39	9.02	...	...	...	8.46
50	8.59	9.45	...	...	...	8.71
55	8.74	9.66	...	...	...	8.83
60	8.82	9.71	...	...	...	8.86
65	8.8	9.70	...	...	...	8.84
70	8.79	9.66	...	...	...	8.77
75	8.71	9.58	...	...	...	8.69
80	8.63	9.50	...	...	...	8.59
85	8.53	9.40	...	...	...	8.49
90	8.43	9.31	...	...	...	8.38
95	8.35	9.21	...	...	...	8.27
100	8.24	9.11	7.03	7.11	...	8.16
105	...	9.00	...	...	...	8.05
110	7.97	8.90	...	...	...	7.94
115	...	8.79	...	...	...	7.84
120	7.8	8.68	...	...	...	7.73
125	...	8.55	...	...	...	7.63
130	...	8.43	...	...	...	7.52
135	...	8.32	...	...	...	7.42
140	7.39	8.21	...	...	...	7.32
145	...	8.10	...	...	...	7.22
150	...	8.00	6.75	6.82	...	7.13
155	...	7.89	...	...	...	7.03
160	6.99	7.78	...	...	...	6.94
165	...	7.67	...	...	...	6.84
170	...	7.57	...	...	...	6.75
175	...	7.45	6.53	6.60	...	6.66
180	6.55	7.35	...	...	...	6.57
190	...	7.14	...	...	...	6.40
200	6.22	6.92	6.32	6.39	...	6.23
225	5.85	...	5.93	6.00	...	5.84
250	5.51	6.09	5.57	5.63	...	5.49
275	5.15	...	...	...	...	5.17
300	4.9	5.50	4.73	4.78	...	4.89
350	4.43	5.07	4.31	4.36	...	4.40
400	4.07	4.66	3.95	3.99	...	4.00
408	...	...	...	...	4.05 ± 0.21	3.95
450	3.72	4.37	...	...	...	3.67
500	3.49	4.04	3.38	3.42	...	3.40
545	...	...	...	...	3.07 ± 0.11	3.19
550	3.17	3.78	...	...	...	3.16
600	2.98	3.54	2.92	2.95	...	2.96
650	2.84	3.32	...	...	...	2.79
700	2.66	3.13	2.66	2.69	...	2.63
750	2.56	2.99	...	...	...	2.50
800	2.42	2.86	2.39	2.42	...	2.38
817	...	...	...	...	2.26 ± 0.10	2.34
850	2.34	2.73	...	...	...	2.27
900	2.22	2.61	2.18	2.20	...	2.17
950	2.1	2.54	...	...	...	2.08
1000	1.99	2.48	2.00	2.02	...	2.00
1089	...	...	...	...	1.84 ± 0.07	1.87

TABLE 1—*Continued*

E (eV)	Straub et al.[a]	K & S[b]	Kossmann et al.[c]	KSS Scaled[d]	Edwards et al.[e]	Model[f]
1200	...	...	1.73	1.75	...	1.73
1362	...	...			1.63 ± 0.06	1.56
1400	...	...	1.53	1.55	...	1.53
1500	...	...	1.44	1.46	...	1.44
1600	...	...	1.37	1.39	...	1.37
1638	...	...	...	...	1.40 ± 0.07	1.35
1800	...	...	1.24	1.25	...	1.25
1906	...	...	...	...	1.19 ± 0.06	1.19
2000	...	...	1.14	1.15	...	1.14
2200	...	...	1.05	1.06	...	1.06
2400	...	...	0.98	0.99	...	0.986
2500	...	...	0.94	0.95	...	0.953
2600	...	...	0.912	0.922	...	0.923
3000	...	...	0.809	0.818	...	0.820

NOTE.—Units for the cross sections are 10^{-17} cm^2.

[a] Straub et al. (1996), as updated by Stebbings & Lindsay (2001) and Lindsay & Mangan (2003). Absolute error is $\pm 5\%$ for $E > 25$ eV and $\pm 15\%$ for $E \leq 25$ eV.

[b] Krishnakumar & Srivastava (1994) with an estimated experimental error of $\pm 15\%$.

[c] Kossman et al. (1990); the reported absolute error is 13%.

[d] Original cross sections of Kossman et al. (1990) scaled up by 1.109%, which is the averaged difference between those of Lindsay & Mangan (2003) and Kossman et al. (1990) between 200 and 1000 eV.

[e] Edwards et al. (1988) with indicated experimental error.

[f] Present work, see text.

normally expected to be unimportant. Nevertheless, as the dissociation energy of the $X\,^1\Sigma_g^+$ is quite large (4.478 eV), the energy requirement for ionization decreases for the vibrationally excited H$_2$. Under certain conditions, the ionization of H$_2$ can be an important process for the excited vibrational levels of the $X\,^1\Sigma_g^+$ state. The ionization becomes very significant in the presence of low-energy electrons, which can either ionize H$_2$ directly or excite it to the vibrationally excited levels, which is then ionized by photons, electrons, or other charged particles. Ionization from the vibrationally excited level can be very significant, as vibrational excitation of the $X\,^1\Sigma_g^+$ state molecular hydrogen by low-energy electrons is very efficient (Ehrhardt et al. 1968; Robicheaux 1991; Čížek et al. 1998; Houfek et al. 2002). For example, Bacal et al. (2002) have recently demonstrated the importance of vibrationally excited H$_2$ for the production of H$^-$ in a hydrogen plasma source with tantalum-covered walls. However, to our knowledge, the investigation of the ionization of vibrationally excited H$_2$ by electrons has been limited. The goal of the present study is to provide a general model for the electron-impact ionization cross section for the transitions between any pair of vibrational levels of the $X\,^1\Sigma_g^+$ and $X\,^2\Sigma_g^+$ states.

The present study utilizes the modified Born model (Shemansky et al. 1985a, 1985b) to determine the ionization excitation function and oscillator strength from the experimental cross sections of Kossman et al. (1990), Krishnakumar & Srivastava (1994), and Straub et al. (1996). The derived oscillator strength agrees very well with that obtained from the absorption work of Samson & Haddad (1994) and that calculated from the data given by Flannery et al. (1977). For a dipole-allowed transition, the excitation function is a product of a shape function, which represents the energy dependence of the cross section, and an absolute scale factor determined from the oscillator strength. The shape function is analytically represented with a set of collision strength parameters. The vibrational band oscillator strength calculated from the data of Flannery et al. (1977), along with the analytical shape function,

yields accurate cross sections for any vibrational band of the $X\,^1\Sigma_g^+ \rightarrow X\,^2\Sigma_g^+$ system from the threshold to the Born region.

2. DATA AND ANALYSIS

In this section, we review recent experimental cross sections of electron-impact ionization of H$_2$ and then develop a modified Born approximation model excitation function of the ionization cross section. We also outline the method for calculating photoionization oscillator strengths from the theoretical data of Flannery et al. (1977).

2.1. Experimental Data

As indicated in § 1, recent investigations that have measured H$_2^+$ cross sections over a wide energy range include those by Edwards et al. (1988), Kossman et al. (1990), Krishnakumar & Srivastava (1994), Jacobsen et al. (1995), and Straub et al. (1996). Some of the results are summarized in Table 1. The cross section of Edwards et al. (1988) was measured from 408 to 1906 eV and reported to have errors less than $\pm 5.2\%$. The data of Kossman et al. (1990) were obtained from 100 to 3000 eV, with an absolute error of 13%. The nondissociative ionization cross sections of both Krishnakumar & Srivastava (1994) and Straub et al. (1996) were measured from the threshold to 1000 eV. The experimental error of Krishnakumar & Srivastava (1994) was estimated to be $\pm 15\%$. The original cross section of Straub et al. (1996) has been revised and updated by Stebbings & Lindsay (2001) and Lindsay & Mangan (2003). The absolute error for the updated cross section is $\pm 15\%$ at an energy below or equal to 25 eV and $\pm 5\%$ at an energy above 25 eV (Lindsay & Mangan 2003).

The agreement between Kossman et al. (1990) and the updated results of Straub et al. (1996) is very good. Excluding the 100 and 150 eV values, which differ by $\sim 17\%$ and $\sim 6.5\%$, respectively, the difference between the two sets of data is always less than 4%. Between 200 and 1000 eV, the cross section of Kossman et al. (1990) is, on average, just $\sim 1.1\%$ smaller than that recommended by Lindsay & Mangan (2003). However,

the differences between the cross sections of Krishnakumar & Srivastava (1994) and the updated results of Straub et al. (1996) are significant. In general, the former cross section is 5%–20% greater than the latter, with larger differences tending to occur at higher energy. On average, the Krishnakumar & Srivastava (1994) cross section is ~11% larger than the updated value of Straub et al. (1996). Since the differences in the two sets of data are not uniform, it is clear that the shapes of the excitation functions are also different. The fifth column of Table 1 lists the Kossman et al. (1990) cross section scaled up by 1.1%. The cross sections measured by Edwards et al. (1988) occur at unusual excitation energies. A direct comparison with other measurements is not possible without using interpolation. Kossman et al. (1990) have pointed out that their cross sections are consistent with those of Edwards et al. (1988). The sixth column of Table 1 displays the cross sections of Edwards et al. (1988) along with reported experimental errors.

Dissociative ionization measurement also started with the work of Rapp et al. (1965). Subsequently, Van Zyl & Stephen (1994) reexamined the experimental setup of Rapp et al. (1965) and found that the original dissociative cross section needed to increase by a factor of 1.86 because of an overestimation of the ion collection efficiency. Crowe & McConkey (1973) reported the H$^+$/H$_2^+$ ratio from the $X\,^2\Sigma_g^+$ state from the threshold to 25 eV. Backx et al. (1976) also measured the H$^+$/H$_2^+$ ratio from the threshold to 70 eV. Krishnakumar & Srivastava (1994) and Straub et al. (1996) both reported the dissociative ionization cross section up to 1000 eV. In general, the value reported by Krishnakumar & Srivastava (1994) is significantly (up to 33%) larger than that by Straub et al. (1996). In addition, while the cross section of Straub et al. (1996) shows the expected dipole-forbidden asymptotic behavior at electron energies higher than 200 eV, the asymptotic limit is not apparent in the data of Krishnakumar & Srivastava (1994), even at 1000 eV. We therefore use the updated cross section of Straub et al. (1996; see Lindsay & Mangan 2003) for the analysis of dissociative ionization.

2.2. Excitation Function

The present approach for modeling electron-impact ionization of H$_2$ is based on the modified Born approximation proposed by Shemansky et al. (1985a, 1985b). For a dipole-allowed rovibrational excitation from electronic state i to state j, its cross section σ is given by[1]

$$\frac{\sigma(v_i,\ v_j;\ J_i,\ J_j)}{\pi a_0^2} = 4f(v_i,\ v_j;\ J_i,\ J_j)\frac{\mathrm{Ry}}{E_{ij}}\frac{\mathrm{Ry}}{E}\left[\frac{C_0}{C_7}\left(\frac{1}{X^2}-\frac{1}{X^3}\right)\right.$$
$$+\sum_{m=1}^{4}\frac{C_m}{C_7}(X-1)\exp(-mC_8X)$$
$$\left.+\frac{C_5}{C_7}\left(1-\frac{1}{X}\right)+\ln(X)\right], \tag{1}$$

$$C_7 = \frac{4\pi a_0^2(2J_i+1)\mathrm{Ry}}{E_{ij}}f(v_i,\ v_j;\ J_i,\ J_j), \tag{2}$$

where a_0 and Ry are the Bohr radius and Rydberg constant, respectively, $f(v_i,\ v_j;\ J_i,\ J_j)$ is the (integrated) absorption oscillator strength, E_{ij} is the transition energy from $(v_i,\ J_i)$ to $(v_j,\ J_j)$, E is the impact energy, and $X = E/E_{ij}$. The collision strength coefficients C_m/C_7 ($m = 0$–5) and C_8 are determined by fitting the experimentally measured relative excitation function.

Since all experimental data measure the total cross section for the production of H$_2^+$ and do not distinguish the rovibrational level of H$_2^+$, equation (1) needs to be summed over v_j and J_j, which can be performed by

$$f(v_i,\ v_j) = \sum_{J_j}f(v_i,\ v_j;\ J_i,\ J_j), \tag{3}$$

$$f(v_i,\ v_j) = \frac{f_{\mathrm{ds}}(v_i,\ j)q(v_i,\ v_j)}{\sum_{v_j}q(v_i,\ v_j)}, \tag{4}$$

where $q(v_i,\ v_j)$ is the Franck-Condon factor obtained from Table I of Flannery et al. (1977).[2] Note that $f_{\mathrm{ds}}(v_i,\ j)$ refers to the oscillator strength for transitions from v_i to all discrete vibrational levels of the $X\,^2\Sigma_g^+$ state, which are the only levels that lead to production of H$_2^+$. Since excitation into the continuum levels of the $X\,^2\Sigma_g^+$ state is not completely negligible, a summation of $q(v_i,\ v_j)$ over the discrete level v_j is not unity. A normalization in equation (4) is therefore required.

For nonlinear least-squares analysis, we have selected the ionization cross section of Straub et al. (1996) as updated by Lindsay & Mangan (2003), which is listed in the second column of Table 1. The updated data cover from 16 to 1000 eV. Following the suggestion of Lindsay & Mangan (2003), the scaled cross section of Krishnakumar & Srivastava (1994) is used for $E \leq 25$ eV. Beyond 1000 eV, we have used the cross section reported by Kossman et al. (1990), adjusted upward by 1.1%, which is the average difference between the data of Kossman et al. (1990) and Lindsay & Mangan (2003) in the 200–1000 eV region. Furthermore, we have also considered the slight difference in the threshold energy of different rovibrational excitations ($\Delta J = 0$ only). The normalized population for $J_i = 0$–4 levels at 300 K is utilized as a rotational weighing factor. The rovibrational energy levels of Dabrowski (1984) and Moss (1993) and the ionization potential of de Lange et al. (2002) are used to calculate the required E_{ij}. Finally, the reported experimental data do not distribute uniformly over the excitation energy range. They concentrate in the low-energy region (≤ 200 eV) and become very sparse in the high-energy region (≥ 1000 eV). If each selected data point were given the same statistical weight, it would have resulted in a significant overweight and underweight in the low- and high-energy regions, respectively. The statistical weights for the high-energy cross section are adjusted upward slightly to compensate for the nonuniformity of the data distribution. The determined collision strength parameters, C_k/C_7 ($k = 0$–5) and C_8, along with the total discrete ionization oscillator strength, $f_{\mathrm{ds}}(v_i = 0,\ j)$, are displayed in first two columns of Table 2. Model calculated cross sections at selected excitation energies are shown in the last column of Table 1. Figure 1 compares the model cross section with various experimental cross sections.

The dissociative ionization of H$_2$ consists of dipole-allowed and dipole-forbidden components. The former arises from

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[1] Strictly speaking, instead of the total rotational angular momentum quantum (J), the difference of J and the electron spin (S), which is usually denoted by N, should be used. Since Hund's case b provides a good description for both neutral $X\,^1\Sigma_g^+$ and ionic $X\,^2\Sigma_g^+$ states, we neglect the electron spin and use J as if it were identical to N.

[2] The highest discrete vibrational level (for $J_j = 0$ and 1 only) is $v_j = 19$ (Carrington et al. 1993a; Moss 1993). The calculation of Flannery et al. (1977) is limited to $v_j = 0$–18. Neglect of $v_j = 19$ is insignificant, as $q(0, 19)$ is extremely small, $< q(0, 18) = 2.5\times10^{-4}$. In the present study, we treat $X\,^2\Sigma_g^+$ as if it had only 19 discrete vibrational levels.

TABLE 2

Collision Strength Parameters for Nondissociative and Dissociative Ionization of H_2

Parameter	Value[a]	Parameter	Value[b]
C_0/C_7.....................................	0.055976742	C_0/C_5.....................................	0.00599632
C_1/C_7.....................................	−0.46360835	C_1/C_5.....................................	0.26340560
C_2/C_7.....................................	−0.50327054	C_2/C_5.....................................	−0.35943630
C_3/C_7.....................................	2.0717210	C_3/C_5.....................................	0.49221094
C_4/C_7.....................................	−4.8031018	C_4/C_5.....................................	1.6814641
C_5/C_7.....................................	0.63887415	C_5.....................................	0.14815805[c]
C_8.....................................	0.30067297	C_8.....................................	0.06143081
$f_{ds}(v_i = 0, j)$[d].....................................	1.0464865[e]		

Note.—See eqs. (1)–(5) for definitions of the parameters. Parameters are intentionally listed in eight digits to ensure an accurate reproduction of the experimental cross section.
[a] For nondissociative ionization (see eqs. [1]–[4]).
[b] For the dipole-forbidden portion of dissociative ionization (see eq. [5] and the text for definitions of parameters).
[c] Denotes the sum of all dipole-forbidden components of dissociative ionization from the $v_i = 0$ level of the $X\,^1\Sigma_g^+$ state.
[d] Represents the total value from $v_i = 0$ of the $X\,^1\Sigma_g^+$ neutral state to all possible discrete vibrational levels of the ionic $X\,^2\Sigma_g^+$ states.
[e] The standard error (σ) for f_{ds} is 0.020745.

excitation to the continuum levels of the $X\,^2\Sigma_g^+$ state, while the latter arises from excitation into the dissociative excited states. The contribution of the dipole-allowed component can be readily obtained from the collision strength parameters of the second column in Table 2 and the calculated Franck-Condon factor for the continuum transition. The threshold energy for the continuum excitation is taken to be 18.10 eV.

For the dipole-forbidden portion of the dissociative ionization, the C_7 term of equation (1) vanishes. The asymptotic limit of the cross section is controlled by the C_5 term. We can rewrite the dipole-forbidden portion of the ionization cross section as (Liu et al. 2003)

$$\frac{\sigma}{\pi a_0^2} = \frac{Ry}{E} C_5 \left[\frac{C_0}{C_5}\left(\frac{1}{X^2} - \frac{1}{X^3}\right) \right.$$
$$\left. + \sum_{m=1}^{4} \frac{C_m}{C_5}(X-1)\exp(-mC_8 X) + \left(1 - \frac{1}{X}\right) \right]. \quad (5)$$
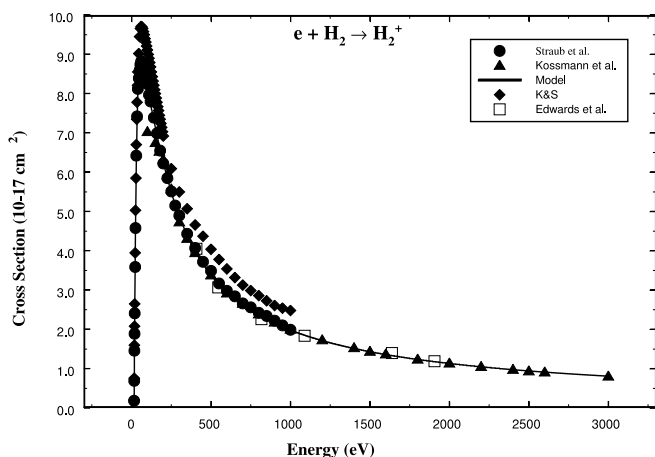

Fig. 1.—Comparison of nondissociative ionization cross sections of H_2 by electron impact. The circles refer to the experimental cross section of Straub et al. (1996), as subsequently updated by Lindsay & Mangan (2003). The triangles represent the cross section of Kossman et al. (1990), while the diamonds denote the original data of Krishnakumar & Srivastava (1994). The squares refer to the data of Edwards et al. (1988). The solid line denotes the model cross section.

It is generally believed that four processes contribute to the dipole-forbidden portion of dissociative ionization (Van Zyl & Stephen 1994). The first is autoionization of doubly excited states, $^1\Sigma_g^+$, $^1\Sigma_u^+$, and $^1\Pi_g$, as suggested by Edwards et al. (1990) and Edwards & Zheng (2001). Potential energy curves calculated by Guberman (1983) permit a crude estimate of weighted threshold energies of 28, 30, and 30 eV for these three states, respectively. Based on the result of Van Zyl & Stephen (1994), we assume that each of the three doubly excited states contributes ∼6.2% to the dipole-forbidden portion of the ionization cross section. The second process refers to excitation to the repulsive $2p\sigma_u\,^2\Sigma_u^+$ state, while the third process refers to excitation to the $2p\pi\,^1\Pi_u$ and $2s\sigma_g\,^2\Sigma_g^+$ states. The weighted E_{ij} for these three states is estimated as 33.5, 38, and 39.5 eV, respectively. Edwards et al. (1990) have measured the relative contribution of these three ionic states from 191 to 1906 eV. We assign their contribution to the total as 36.4%, 13%, and 18.2%, respectively. The fourth process refers to excitation that results in double ionization. The threshold for double ionization is ∼51 eV. Kossman et al. (1990) have measured the double ionization cross section in the 150–1000 eV region and shown that it contributes 9%–14% of the total dissociative ionization. We assume the double ionization contributes 13.8% to the nondipole portion of dissociative ionization. In absence of additional information, we further assume that all four processes have the same shape function (in terms of X). With these assumptions, the collision strength parameters for the nondipole dissociative ionization can be determined with similar nonlinear least-squares analysis. The results are shown in the third and fourth columns of Table 2. The value of C_5 listed in Table 2 represents the sum of all four processes. It is obvious that the estimates for relative contributions and threshold energies for the four dipole-forbidden processes are very crude. For this reason, the collision strength parameters in the fourth column of Table 2 are by no means unique and should be viewed as one of many possible representations of the overall dipole-forbidden component of dissociative ionization.

Figure 2 shows the collision strength plots for various dissociative ionization processes by electron impact. The circles show the experimental data of Straub et al. (1996), as updated
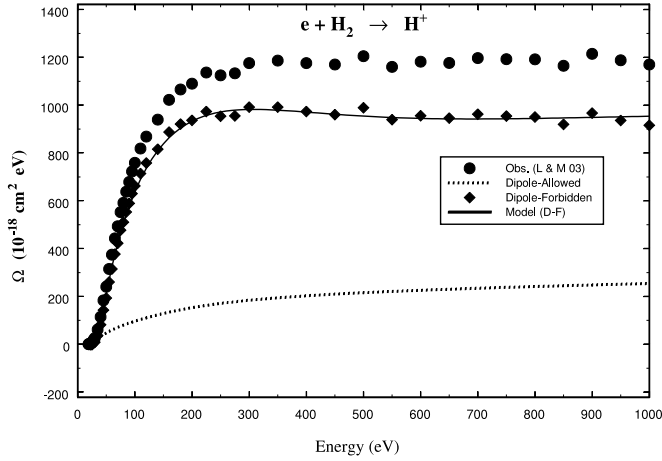
FIG. 2.—Dissociative ionization collision strength of H$_2$ by electron impact. The circles are obtained from the experimental data of Straub et al. (1996), as subsequently updated by Lindsay & Mangan (2003). The dotted line denotes the excitation into the continuum levels of the $X\,^2\Sigma_g^+$ state, which is dipole-allowed. The diamonds show the difference between the circles and the dotted line and represent the dipole-forbidden portion of the dissociative ionization. The solid line denotes the model output of the dipole-forbidden component of the dissociative ionization.

by Lindsay & Mangan (2003), and represent total dissociative ionization. The dipole-allowed portion is shown as a dotted line. The diamonds (the difference between the circles and the dotted line) denote the dipole-forbidden portion of the dissociative ionization. Finally, the solid line represents the model output for the dipole-forbidden component of the dissociative ionization.

2.3. *Photoionization Oscillator Strength and Cross Section*

The photoionization cross section $\sigma_{\rm ph}(v_i,\ v_j)$ from the v_i to the v_j level, as given by Flannery et al. (1977), is

$$\sigma_{\rm ph}(v_i,\ v_j) = \frac{2}{3}\pi^2\alpha\,\frac{E_{\rm ph}}{\rm Ry}\left[4\big|\langle v_i \mid M_x \mid v_j\rangle\big|^2 + \big|\langle v_i \mid M_z \mid v_j\rangle\big|^2\right], \quad (6)$$

where $E_{\rm ph}$ is the energy of incident photons and α is the fine-structure constant. The squares of the two matrix elements inside the brackets denote the average of the x- and z-components of the electronic dipole matrix elements (i.e., M_z and M_x) over the initial and final vibrational wave functions. The units for $\sigma_{\rm ph}$ are a_0^2, and M_z and M_x are in a_0. Rotational motion in Flannery et al. (1977) has been neglected, and the cross section in equation (6) actually refers to the $J_i = 0$ to $J_j = 0$ transition.

The terms M_x and M_z depend on the internuclear distance R and the kinetic energy of the photoelectron ϵ. The R-dependence was represented by a second-degree polynomial over three internuclear distance regions. The energy (ϵ) dependence, from 0 to 41 eV, has been listed in tabular form (see Table II of Flannery et al. 1977). Flannery et al. (1977) also tabulated values of the vibrational overlap integral and R-centroids over the entire R region. However, because the coefficients of the polynomial have different values in different internuclear distance regions, the data listed by Flannery et al. (1977) are insufficient to reproduce their photoionization cross section. We thus utilized the fixed nuclei approximation of Tai &

Flannery (1977) with a small modification. First, the internuclear distance was fixed at $\bar{R} = \langle v_i \mid R \mid v_i\rangle$, and M_x and M_z for all ϵ entries listed in Table II of Flannery et al. (1977) were calculated. The kinetic energy ϵ was calculated from $E_{\rm ph}$, the energy levels of Dabrowski (1984) and Moss (1993), and the ionization potential of de Lange et al. (2002), and the values of M_x and M_z at the exact ϵ were obtained with a cubic spline interpolation. For the strong transitions, the differences between the photoionization cross section obtained with the fixed nuclei approximation and those tabulated by Flannery et al. (1977) are less than 15%. To improve the accuracy, we have slightly modified the fixed nuclei approximation of Tai & Flannery (1977) by adding one more step: when $\bar{R}$ is close to the region boundaries, two sets of M_x and M_z, using polynomials of the two adjacent regions, are calculated, and the averaged values of M_x and M_z are utilized. The cross section for a strong transition obtained in this way generally differs by less than 3% from that given by Flannery et al. (1977). For the $v_i = $ 6–9 levels, the difference tends to be slightly larger and is 4%–6%. For the $v_i = 0$ level, it is less than 0.4%.

The integrated photoionization oscillator strength $f(v_i,\ v_j)$ of equation (3) is related to the photoionization cross section $\sigma_{\rm ph}(v_i,\ v_j)$ by (Fano & Cooper 1968)

$$f(v_i, v_j) = 9.1137\times10^{15}\int_0^\infty \sigma_{\rm ph}(v_i,\ v_j)\,d\epsilon, \quad (7)$$

where the units for the cross section $\sigma_{\rm ph}$ are cm^2 and the kinetic energy of the photoelectron ϵ is in eV. As indicated, the integration requires the photoionization cross section for ϵ up to ∞. We have therefore assumed that the squares of M_x and M_z above 41 eV asymptotically fall according to $\epsilon^{-4.5}$, as required by the high-energy asymptotic limit (Fano & Cooper 1968). The calculated oscillator strengths are listed in Table 3.

3. DISCUSSION

3.1. *Electron-Impact Cross Section*

The differences between the model-predicted and experimentally observed cross sections are generally well within the stated experimental errors. Three exceptions are at 16, 17, and 18 eV, where the model-predicted values are significantly smaller than their experimental counterparts. As noted earlier, both the auto-ionization of the neutral high Rydberg states (Dehmer & Chupka 1976; Xu et al. 1989) and resonance excitation, followed by two-electron autoionization (Schowengerdt & Golden 1975), can significantly contribute to the observed cross section in the threshold energy regions. While these additional excitation mechanisms are important in the threshold region, the contribution becomes negligible beyond the threshold region. Since the model does not consider the contribution of autoionization and the data are heavily weighted by the direct ionization, the difference can be attributed to the presence of autoionization. Furthermore, the absolute value of the excitation energy could be in error. For instance, Lindsay & Mangan (2003) have suggested that the uncertainty in the energy of Straub et al. (1996) can be as large as ±0.5 eV when the excitation energy is below 25 eV. Indeed, an upward adjustment of excitation energy by merely 0.1–0.2 eV is sufficient to bring the model cross section into very good agreement with the observed value.

The collision strength parameters C_k/C_7 ($k = 0$–5) and C_8, listed in Table 2, are derived from the excitation cross section from the $v_i = 0$ level. However, since the parameters

TABLE 3

Oscillator Strength of Nondissociative Ionization of H_2

v_j/v_i	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	$\Sigma_i f_{ij}$	$\Sigma_i q_{ij}$
0..........	8.65E−02	2.40E−01	2.56E−01	1.37E−01	3.90E−02	5.82E−03	3.88E−04	7.86E−06	6.75E−08	2.91E−11	1.60E−10	3.95E−12	4.64E−13	1.66E−13	3.92E−14	7.65E−01	9.99E−01
1..........	1.58E−01	1.60E−01	2.86E−03	9.45E−02	1.76E−01	9.43E−02	2.04E−02	1.74E−03	3.06E−05	8.16E−07	1.31E−08	3.07E−09	3.26E−10	3.23E−11	1.52E−11	7.08E−01	1.00E+00
2..........	1.76E−01	3.69E−02	5.90E−02	9.29E−02	8.53E−04	1.13E−01	1.30E−01	4.28E−02	4.04E−03	5.67E−05	4.62E−06	9.10E−08	1.21E−08	4.33E−09	9.52E−10	6.55E−01	1.00E+00
3..........	1.59E−01	2.05E−05	1.00E−01	3.72E−03	7.81E−02	2.94E−02	3.85E−02	1.38E−01	6.98E−02	6.45E−03	3.09E−05	1.52E−05	1.29E−06	1.22E−07	1.75E−08	6.24E−01	1.00E+00
4..........	1.26E−01	1.63E−02	6.44E−02	2.04E−02	5.50E−02	1.50E−02	6.51E−02	3.85E−03	1.29E−01	8.93E−02	7.61E−03	2.03E−04	1.57E−05	7.44E−06	1.66E−06	5.92E−01	1.00E+00
5..........	9.44E−02	4.19E−02	2.13E−02	5.60E−02	5.60E−03	5.70E−02	1.90E−03	6.11E−02	2.43E−03	1.08E−01	1.04E−01	5.16E−03	1.00E−03	5.97E−05	6.64E−06	5.59E−01	1.00E+00
6..........	6.77E−02	5.83E−02	1.65E−03	5.70E−02	5.22E−03	3.93E−02	1.90E−02	2.31E−02	3.48E−02	1.28E−02	9.75E−02	1.08E−01	1.21E−03	1.59E−03	4.01E−04	5.28E−01	9.98E−01
7..........	4.77E−02	6.31E−02	1.88E−02	3.71E−02	2.64E−02	8.53E−03	4.06E−02	1.83E−04	3.75E−02	1.26E−02	1.82E−02	1.05E−01	9.16E−02	6.71E−03	1.98E−03	4.99E−01	9.93E−01
8..........	3.35E−02	5.98E−02	1.05E−02	1.67E−02	3.82E−02	1.87E−04	3.09E−02	1.62E−02	7.48E−03	3.34E−02	2.86E−03	1.47E−02	1.35E−01	3.62E−02	1.59E−02	4.52E−01	9.45E−01
9..........	2.35E−02	5.21E−02	1.93E−02	4.55E−03	3.58E−02	8.19E−03	1.19E−02	2.85E−02	7.68E−04	1.90E−02	2.18E−02	1.71E−04	6.22E−03	1.64E−01	4.25E−03	4.00E−01	8.49E−01
10........	1.64E−02	4.34E−02	2.52E−02	2.23E−04	2.64E−02	1.83E−02	1.39E−03	2.48E−02	1.06E−02	2.93E−03	2.14E−02	1.17E−02	2.38E−04	1.74E−02	6.39E−02	2.84E−01	5.36E−01
11........	1.15E−02	3.52E−02	2.75E−02	6.45E−04	1.61E−02	2.26E−02	5.04E−04	1.42E−02	1.79E−02	4.80E−04	9.70E−03	1.67E−02	6.27E−03	5.83E−03	5.09E−02	2.36E−01	4.53E−01
12........	8.21E−03	2.78E−02	2.68E−02	2.83E−03	8.44E−03	2.19E−02	3.99E−03	5.60E−03	1.80E−02	5.07E−03	1.65E−03	1.18E−02	1.04E−02	6.54E−03	4.17E−02	2.01E−01	3.83E−01
13........	5.79E−03	2.14E−02	2.44E−02	4.94E−03	3.74E−03	1.81E−02	7.50E−03	1.22E−03	1.36E−02	8.97E−03	4.58E−05	5.29E−03	9.27E−03	5.43E−03	3.75E−02	1.67E−01	3.19E−01
14........	4.07E−03	1.61E−02	2.04E−02	6.15E−03	1.35E−03	1.36E−02	9.10E−03	2.32E−05	8.55E−03	9.89E−03	1.36E−03	1.45E−03	5.86E−03	5.34E−03	9.55E−03	1.13E−01	1.49E−01
15........	2.80E−03	1.16E−02	1.63E−02	6.16E−03	3.59E−04	9.28E−03	8.66E−03	2.29E−04	4.70E−03	8.55E−03	2.66E−03	1.46E−04	2.94E−03	3.84E−03	7.46E−03	8.57E−02	1.25E−01
16........	1.81E−03	7.79E−03	1.17E−02	5.13E−03	5.53E−05	5.81E−03	6.82E−03	5.90E−04	2.32E−03	6.08E−03	2.87E−03	1.52E−05	1.24E−03	2.21E−03	1.66E−03	5.61E−02	5.85E−02
17........	9.91E−04	4.39E−03	6.73E−03	3.28E−03	2.37E−06	3.05E−03	4.19E−03	5.83E−04	9.90E−04	3.44E−03	2.03E−03	9.11E−05	4.46E−04	1.07E−03	9.32E−04	3.22E−02	3.58E−02
18........	2.94E−04	1.32E−03	2.07E−03	1.05E−03	3.12E−07	8.94E−04	1.31E−03	2.19E−04	2.58E−04	1.04E−03	6.78E−04	4.90E−05	1.02E−04	2.96E−04	2.27E−04	9.81E−03	1.04E−02
$\Sigma_j f_{ij}$......	1.02E+00	8.98E−01	6.98E−01	5.50E−01	5.17E−01	4.84E−01	4.02E−01	3.63E−01	3.63E−01	3.28E−01	2.94E−01	2.80E−01	2.72E−01	2.57E−01	2.37E−01	. . .	. . .
$\Sigma_j q_{ij}$.....	9.85E−01	9.12E−01	7.84E−01	6.99E−01	7.16E−01	7.34E−01	6.99E−01	6.97E−01	7.31E−01	7.37E−01	7.39E−01	7.73E−01	8.24E−01	8.78E−01	9.43E−01	. . .	. . .

reflect the properties of a particular electronic transition, they are equally applicable to the excitation from the other v_i levels of the $X\,^1\Sigma_g^+$ state. The calculated oscillator strength in Table 3, the energy levels of Dabrowski (1984) for H$_2$ and of Moss (1993) for H$_2^+$, and the ionization potential of de Lange et al. (2002) can be utilized to calculate the required cross sections.

The advantage of the present modified Born approximation is obvious. Equation (1) yields both the correct asymptotic value and the form in the Born limit and accurately reproduces the experimental cross section from the threshold region up to 3000 eV. Moreover, the oscillator strength for the transition from the $v_i = 0$ level derived from experimental cross sections agrees with values derived from the calculation of Flannery et al. (1977) and the absorption measurements of Samson & Haddad (1994; see § 3.2). Finally, the absolute value of C_7 (i.e., the oscillator strength) provides a direct linkage for transitions between the vibrational levels of the band system.

Younger & Märk (1985) have discussed many empirical and semiclassical formulae for the ionization cross section by electron impact. Bell et al. (1983) and Lennon et al. (1988) have proposed a formula for ionization cross sections that, like the present formulation, has the correct limits for both the near-threshold and high-energy regions. They have applied their formulation for a large number of neutral atoms and have provided extensive tabulation of the collision strength parameters. While some of their parameters, such as A and B_1, are equivalent to ours (C_7 and C_5), most are different. Kim & Rudd (1994) and Hwang et al. (1996) have developed a slightly different formula for the total ionization cross section from binary-encounter-Bethe (BEB) theory, which yields the proper behavior for the threshold and high-energy regions. They have also successfully applied their BEB model to a large number of molecules. It should be noted that formulations of both BEB and Bell et al. (1983) are primarily developed for the total ionization cross section from the ground level. As a result, the oscillator strength in both formulations is embedded in the collision strength parameters, which makes them less straightforward to apply to vibrational or rovibrational transitions and to transitions started with the excited levels. More recently, Dose et al. (2000), using Bayesian probability theory and the experimental data of Rapp et al. (1965), Crowe & McConkey (1973), and Krishnakumar & Srivastava (1994), have derived a cross section formula for the ionization of H$_2$.

One of the deficiencies of the present modified Born formulation is that equation (1) does not have the correct threshold behavior as predicted by Wannier (1953) and observed by Fiegele et al. (2000) and Hanel et al. (2002). Nevertheless, the deficiency is generally inconsequential, especially when a sufficient number of experimental data points are available in the threshold region. Indeed, equation (1) has successfully been applied to both dipole-allowed (James et al. 1997; Liu et al. 1998) and dipole-forbidden (Liu et al. 2003) excitations of H$_2$ and H from the threshold to a few keV.

It is important to note that the present study deals with ionization at the vibrational structure level and does not address the role of rotational motion in the ionization process of H$_2$. For a $X\,^1\Sigma_g^+$–$X\,^2\Sigma_g^+$ transition, the symmetry-allowed ΔJ values are even integers. Like the photoionization calculation of Flannery et al. (1977), the present study has implicitly assumed that $\Delta J = 0$ is the only allowed excitation and that the variation of oscillator strength with rotational quantum number is negligible. The presence of the $\Delta J = \pm 2$ transition in photoionization has been inferred from the study of the angular distribution of photoelectrons with synchrotron experiments (Marr et al. 1980). Xie & Zare (1990, 1992) have presented the rotational line strength for the photoionization of diatomic molecules and estimated the importance of $\Delta J = \pm 2$ relative to that of $\Delta J = 0$. More recently, Öhrwall et al. (1999) have obtained the rotationally resolved $\Delta J = 0$ and 2 photoelectron spectrum and measured the relative intensity of the S- and Q-branch at several photon energies. They found that the intensity of the S-branch relative to that of the Q-branch decreases with the v_j quantum number of H$_2^+$. Although the relative intensity depends on the excitation wavelength, the Q-branch transition is always several (>5) times stronger than that of the S-branch. In all electron-impact experimental investigations performed so far, the total number density of H$_2^+$ is measured, and the internal states (i.e., v_j and J_j) of H$_2^+$ are not resolved. The importance of transitions such as $\Delta J = \pm 2$ relative to that of $\Delta J = 0$ in electron-impact ionization is not known. If consideration of $\Delta J = \pm 2$ is required for the ionization of H$_2$ by electrons, rotational factors developed for the H$_2$ $EF\,^1\Sigma_g^+$–$X\,^1\Sigma_g^+$ transition of Liu et al. (2002) can be used. Finally, because of the light mass and short internuclear distance, the centrifugal potential of H$_2$ and H$_2^+$ can be quite significant. The assumption that variation of oscillator strength with rotational quantum number is negligible may break down for some rovibronic excitations. The breakdown of this assumption has been well documented for some Lyman-band transitions of H$_2$ and D$_2$ by both calculation and experimental observation (Abgrall et al. 1993a, 1993b, 1999; Liu et al. 1995).

The Born asymptote for the nondissociative ionization of H$_2$ by electrons starts around the 1000–1400 eV region. The corresponding asymptotic limit for the dissociative ionization, based on the experimental data of Straub et al. (1996) and Lindsay & Mangan (2003), begins around the 300–400 eV region. As noted elsewhere (Liu et al. 2003), the Born limits of H$_2$ and H tend to occur at a much higher energy than those of other species. For instance, the Born asymptotic limit for the $B\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ and $C\,^1\Pi_u$–$X\,^1\Sigma_g^+$ transitions is thought to start at 3–4 keV (Liu et al. 1998). Similarly, the starting point of the Born limit at $\sim$1000 eV has been observed for atomic hydrogen $1s\,^2S$–$2p\,^2P$ excitation (James et al. 1997). For the dipole-forbidden $EF\,^1\Sigma_g^+$–$X\,^1\Sigma_g^+$ transition, the Born asymptotic limit starts at $\sim$400 eV (Liu et al. 2003). In the case of both dipole- and spin-forbidden $a\,^3\Sigma_g^+$–$X\,^1\Sigma_g^+$ excitation of H$_2$, the asymptotic limit, where σ falls according to E^{-3}, is found to begin at slightly higher than 50 eV (Ajello & Shemansky 1993). In contrast, Born asymptotic limits for dipole-allowed $1\,^1S \rightarrow 2\,^1P$, $3\,^1P$, and $4\,^1P$ excitations of helium all start at an energy lower than 240 eV (Shemansky et al. 1985b).

While the dipole-allowed portion of the dissociative ionization from excited vibrational levels can be obtained from the collision strength parameters of Table 2 and the oscillator strengths and Franck-Condon factors of Table 3, the dipole-forbidden portion cannot be similarly calculated. This is because the value of C_5 listed in the last column of Table 2 is applicable only to the latter process starting from the $v_i = 0$ level. The value of C_5 from other vibrational levels is not known without additional calculations or experimental measurements. While the calculation of C_5 for other levels is beyond the scope of the present work, we note that it can be obtained from numerical integrations of theoretical electronic form factors (Liu et al. 2003). Celiberto et al. (1997) also

presented a scaling law for $X\,^1\Sigma_g^+ \rightarrow 2p\sigma_u\,^2\Sigma_u^+$ dissociative ionization by electrons from various v_i levels of H_2.[3]

3.2. *Oscillator Strength*

The total nondissociative ionization oscillator strength of H_2 from the $v_j = 0$ level determined from the experimental cross sections of Kossman et al. (1990) and Lindsay & Mangan (2003) is 1.046 ± 0.041 ($\pm 2\,\sigma$). It agrees with the value 1.023 calculated from the data of Flannery et al. (1977) within 1.5 σ. As indicated in § 2.1, the Kossman et al. (1990) cross section between 200 and 1000 eV is, on average, ~1.1% smaller than that recommended by Lindsay & Mangan (2003). The oscillator strength was obtained after the experimental data between 1000 and 3000 eV from Kossman et al. (1990) were scaled up by 1.1%. A slightly lower nondissociative ionization oscillator strength, 1.014 ± 0.044, along with a slightly different set of collision strength parameters in Table 2, would have been obtained if no scale-up had been made. The scaled data yield a better set of parameters in the sense that both the sum of the squares of the residuals for the fit and the standard errors for many derived parameters are smaller than their counterparts in the nonscaled data.

The total ionization oscillator strength can be obtained from the absorption cross sections. In § 3.3, the total ionization oscillator strength of 1.062 is obtained from the experimental absorption cross section of Samson & Haddad (1994), supplemented by the calculated near-threshold cross section. The ionization oscillator strength for the $X\,^1\Sigma_g^+$–$X\,^2\Sigma_g^+$ band system can be obtained from the discrete Franck-Condon factor listed in Table 3 as $(1.046 \pm 0.041)/0.9849$, or 1.063 ± 0.042. The calculation of Ford et al. (1975) shows that the dissociative and nondissociative ionization ratio has a slight energy dependence and ranges from 2.0% to 2.6% between 19 and 29 eV. The experimental measurement of Backx et al. (1976) has yielded a H^+/H_2^+ ratio of 1.52%–3.22% between 19 and 28 eV, in good agreement with the calculations of Ford et al. (1975). However, the same ratio in the 19–30 eV range obtained in the more recent electron-impact measurements of Krishnakumar & Srivastava (1994) and Straub et al. (1996) is only 0.2%–1.6%. If the ratios of Ford et al. (1975) and Backx et al. (1976) are used, the implied total ionization oscillator strength obtained from electron-impact measurement is slightly larger than 1.063. In either case, the oscillator strength derived from photoabsorption data agrees very well with that from electron-impact data. Furthermore, the fact that the ionization oscillator strength for the $X\,^1\Sigma_g^+$–$X\,^2\Sigma_g^+$ band system is very close to the total ionization oscillator strength indicates that contributions from ionic states higher than $X\,^2\Sigma_g^+$ are negligible within experimental error. The good agreement also clearly demonstrates the accuracy of the electron-impact cross section of Kossman et al. (1990), Straub et al. (1996), and Lindsay & Mangan (2003).

We note that Yan et al. (1998, 2001) have also derived the oscillator strength of H_2 based on their calculation at high energies and the experimental data of Samson & Haddad (1994). While the total ionization oscillator strength of Yan

et al. (1998), 1.010, is slightly smaller than the present value of 1.063 derived from the electron-impact cross section, the difference is within 3 σ. Similarly, their number is also smaller than the oscillator strength of 1.062 derived here from the experimental data of Samson & Haddad (1994) and from the theoretical data of Flannery et al. (1977).

It is possible to discuss the distribution of oscillator strength over the electronic states for transitions from the $v_i = 0$ level of the $X\,^1\Sigma_g^+$ state. The oscillator strength for the $X\,^1\Sigma_g^+$–$X\,^2\Sigma_g^+$ transition is 1.063. If the configuration interaction between the $X\,^2\Sigma_g^+$ and other ionic states is negligible, the value represents the total ionization oscillator strength. The total oscillator strength for the neutral transitions from the $X\,^1\Sigma_g^+$ state to the $1s\sigma_g np\sigma_u\,^1\Sigma_u^+$ and $1s\sigma_g np\pi_u\,^1\Pi_u$ Rydberg states is thus $2 - 1.063$ or 0.937, which is slightly smaller than the value (0.943) estimated by Yan et al. (1998) for all discrete neutral transitions. The electron energy loss measurement performed at 8 keV by Backx et al. (1976) has obtained an integrated oscillator strength of 0.832 over the 10.0–15.5 eV region. Since some neutral transitions extend well beyond 15.5 eV (Herzberg & Jungen 1972; Glass-Maujean et al. 1987; Liu et al. 2000), 0.832 is a lower limit for the neutral Rydberg series.[4] The transition probabilities for the first six lowest Rydberg states have been calculated by Abgrall et al. (1993a, 1993b, 1994, 2000; H. Abgrall et al. 2004, in preparation), and their relative accuracies have been verified by the electron-impact studies of Abgrall et al. (1997; H. Abgrall et al. 2004, in preparation), Liu et al. (1995), and Jonin et al. (2000). The sum of the band oscillator strengths to the first six excited electronic states ($B\,^1\Sigma_u^+$, $C\,^1\Pi_u$, $B'\,^1\Sigma_u^+$, $D\,^1\Pi_u$, $B''\,^1\Sigma_u^+$, and $D'\,^1\Pi_u$) are determined to be 0.861–0.866 from the calculated transition probabilities.[5] This means that the total oscillator strength for transitions from the $v_i = 0$ level of the $X\,^1\Sigma_g^+$ state to the $n = 5-\infty$ neutral Rydberg states is only 0.071–0.076, ~8% of the total oscillator strength for the neutral transitions.

It should be pointed out that the sum of the nondissociative ionization oscillator strength over v_j, as listed in Table 3, monotonically declines with the initial vibrational quantum number v_i. Indeed, the total ionization oscillator strength, as calculated from the ratio of the nondissociative ionization oscillator strength to the discrete Franck-Condon factors, also decreases with v_i. The corresponding oscillator strengths for the $X\,^1\Sigma_g^+$–$np\sigma_u\,^1\Sigma_u^+$ and $X\,^1\Sigma_g^+$–$np\pi_u\,^1\Pi_u$ transitions should thus generally increase with v_i.

3.3. *Near-Threshold Photoionization Cross Section*

Because of the presence of autoionization in the threshold region, experimental measurement of the direct ionization cross

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[3] Celiberto et al. (1997) appear to have treated the $X\,^1\Sigma_g^+ \rightarrow 2p\sigma_u\,^2\Sigma_u^+$ transition as if it were dipole-allowed. They also mistakenly designated the $2p\sigma_u\,^2\Sigma_u^+$ state as $X\,^2\Sigma_u^+$, instead of the conventional $A\,^2\Sigma_u^+$ state. Separately, Van Zyl & Stephen (1994) mistakenly indicated that the $X\,^1\Sigma_g^+ \rightarrow 2p\sigma_u\,^2\Sigma_u^+$ transition is dipole-allowed, even though they noted that the excitation function is consistent with a dipole-forbidden transition. As mentioned in § 1, the electronic dipole transition moments for transitions from the $X\,^1\Sigma_g^+$ state to all but the $X\,^2\Sigma_g^+$ ionic states, in a single-configuration representation, vanish because they require a simultaneous change of two electron configurations.
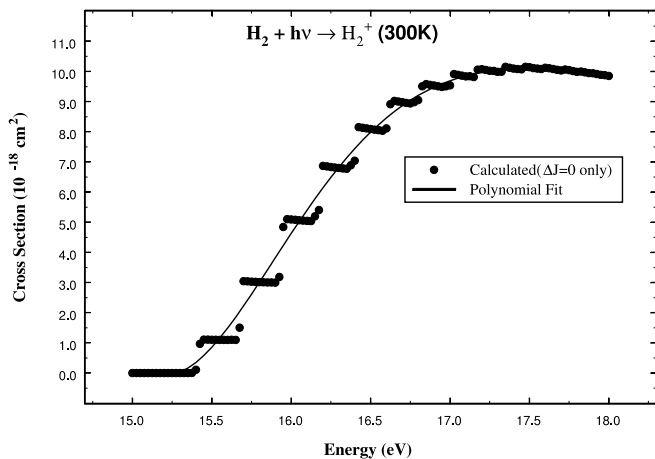
[4] Based on the experimental data of Backx et al. (1976), § 3.3 provides an estimate of 0.096 as the contribution to the oscillator strength by the neutral levels above 15.5 eV.

[5] Because of coupling among the Rydberg states, the calculated oscillator strength for each band system varies slightly, depending on the selected rotational quantum number. The band oscillator strengths for $B\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ and $C\,^1\Pi_u$–$X\,^1\Sigma_g^+$, calculated from the $R(0)$ transition, are 0.3243 and 0.3442, respectively. The corresponding values, calculated from the $P(1)$, $Q(1)$, and $R(1)$ transitions, are 0.3411 and 0.3280, respectively. A significant portion of $B'\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ excitation involves the continuum levels. The sum of discrete oscillator strength from the $R(0)$ transition is 0.0293. The Franck-Condon factor for the discrete transition is ~0.55 (Jonin et al. 2000). The band oscillator strength for the $B'\,^1\Sigma_u^+$ state is thus 0.0533. The corresponding number, based on the $P(1)$ and $R(1)$ transitions, is 0.0628. The oscillator strengths for the $D\,^1\Pi_u$–$X\,^1\Sigma_g^+$ and $D'\,^1\Pi_u$–$X\,^1\Sigma_g^+$ band systems can be calculated as twice that of the $Q(1)$ transitions and are 0.0828 and 0.0329, respectively. Finally, the oscillator strength for the $B''\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ band system is 0.0235 or 0.0185, depending on whether $R(0)$ or $P(1) + R(1)$ is used.

Fig. 3.—Near-threshold photoionization cross section of H$_2$ at 300 K. The circles are obtained by considering the $\Delta J = 0$ transition only. At room temperature, only the first five rotational levels need to be considered. The relative contribution for these five levels is assumed to be proportional to their relative population. The solid line shows a polynomial representation of the circles via eq. (8).

section of H$_2$ is presumably difficult. A model near the threshold cross section is very useful. An accurate near-threshold ionization cross section permits evaluation of the ionization oscillator strength. However, many experimental measurements of the photoionization cross section of H$_2$, instead of starting at the threshold, begin a few eV above the threshold (Gallagher et al. 1988). The recent cross section measurement of Samson & Haddad (1994), for example, starts at 18 eV.

A good near-threshold ionization cross section invariably requires consideration of rotational motion. Many calculations were performed using the $J_i = 0$ to $J_j = 0$ excitation. A partial consideration of the effect of rotational motion is to account for the threshold energy difference in various $\Delta J = 0$ transitions. At room temperature, only the first four J_i levels are significantly populated. One can assume that the dipole matrix elements for the $J_i = 0$ to $J_j = 0$ transition in equation (6) are equally applicable for other $\Delta J = 0$ transitions. The relative contribution for each J_i level is then proportional to its fractional population. Obviously, this approach will only slightly alter the cross section near the rovibrational threshold and will not change the value of the integrated oscillator strength.

A different and more realistic approach is to use the experimentally measured intensity ratios of the $\Delta J = 0$ to $\Delta J = \pm 2$ transitions. As mentioned, Xie & Zare (1992) have formulated rotational line strengths for diatomic molecules. For the $X\,^1\Sigma_g^+ – X\,^2\Sigma_g^+$ transition of H$_2$, it is sufficient to consider the $\Delta J = 0$ and ± 2 transitions. The relative intensities of the probabilities of these transitions are characterized by a generalized line strength and two parameters, $|\bar{\mu}(0, 0)|^2$ and $|\bar{\mu}(2, 0)|^2$. Theoretical studies by Itikawa (1978a, 1978b, 1979), Chandra (1986), and Hara & Ogata (1985) have shown that the ratio of $|\bar{\mu}(2, 0)|^2$ to $|\bar{\mu}(0, 0)|^2$ changes significantly, depending on whether the f-wave of the photoelectron is considered. Stimson et al. (1998) recently obtained the rotationally resolved photoelectron spectrum of H$_2^+$ and noted that the observed relative intensities for various rotational branches of the low-v_j levels are strongly affected by autoionization. Experimental work by Öhrwall et al. (1999) has also obtained the ratio of $|\bar{\mu}(2, 0)|^2$ to $|\bar{\mu}(0, 0)|^2$ for several v_j levels at a few

excitation energies. Their results show that the ratio of $|\bar{\mu}(2, 0)|^2$ to $|\bar{\mu}(0, 0)|^2$ increases with excitation energy but decreases with v_j. One approach is to use their ratios at 16.85 eV for the threshold region. If the contribution of f- and higher odd-order partial waves can be neglected, the $\Delta J = \pm 2$ transition arises purely from the p-wave via the x- and y-components of the dipole matrix elements. One can partition the x- and y-component of the dipole matrix element M_x (which equals M_y) of equation (6) to the $|\bar{\mu}(0, 0)|^2$ and $|\bar{\mu}(2, 0)|^2$ components according to the results of Öhrwall et al. (1999) and assume that the partition does not change with energy. When compared with the cross section obtained with the first method, the calculated cross section is slightly higher near the threshold but slightly lower at higher energy. The difference, however, is entirely negligible. The circles in Figure 3 show the calculated cross sections for $\Delta J = 0$ only in the 15–18 eV region.

Samson & Haddad (1994) have pointed out that the ionization cross section of Flannery et al. (1977) agrees with their experimental cross section within 2%–3% in the 18–28 eV range. The present cross section calculated from the data of Flannery et al. (1977) actually differs less than ± 1.8% from that of Samson & Haddad (1994) over the 18–30 eV region. In deriving the experimental oscillator strength from the cross section of Samson & Haddad (1994), we have used the calculated cross section between 15.4 and 18 eV to supplement the experimental data. In the energy regions of 15.4–18, 18–115, 115–300, and 300 eV–∞, the integrated ionization oscillator strengths are 0.174, 0.872, 0.013, and 0.002, respectively. These numbers are slightly different from the oscillator strengths of Yan et al. (1998, 2001), who listed 0.121, 0.873, 0.014, and 0.002 for the same regions. We also find a large difference between the present cross section and their analytical cross section at 15.4–18 eV.[6] A polynomial approximation of our near-threshold photoionization cross section at $T = 300$ K can be obtained as

$$\sigma = 0.350329 + 64.3332(X-1) + 2233.84(X-1)^2$$
$$- 33619.7(X-1)^3 + 172063(X-1)^4 - 313928(X-1)^5,$$

$$(8)$$

where $X = E/15.40$ and the applicable range for E is from 15.30 to 18.0 eV, with the units of the cross section σ being 10^{-18} cm^2. Figure 3 compares the near-threshold cross section with its polynomial fit.

The total oscillator strength between 15.5 and 18 eV has been experimentally determined to be 0.269 by Backx et al. (1976). The calculated oscillator strength of the direct ionization in the same energy range is 0.173. Thus, the contribution of neutral Rydberg states in this region is 0.096.

In conclusion, excitation functions for both nondissociative and dissociative ionization of H$_2$ have been derived from the electron-impact measurements of Kossman et al. (1990), Krishnakumar & Srivastava (1994), Straub et al. (1996), and Lindsay & Mangan (2003). The derived oscillator strength is in

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[6] The significant difference between the two sets of cross sections remains, even with the revised analytical equation of Yan et al. (2001). In particular, the revised equation for E between 15.4 and 18 eV results in a negative cross section for $E \leq 15.6$ eV ($x \leq 1.013$), which perhaps is primarily responsible for the lower value of the integrated oscillator strength in the 15.4–18 eV region.

good agreement with the experimental measurements of Samson & Haddad (1994) and the theoretical calculation of Flannery et al. (1977). The derived excitation function, together with oscillator strengths obtained from the data of Flannery et al. (1977), enables an accurate evaluation of the $X\,^1\Sigma_g^+ - X\,^2\Sigma_g^+$ ionization cross section between any vibrational levels over a wide energy range.

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