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Photon and high-energy–electron-impact vibronic excitation of molecular hydrogen

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We have obtained generalized oscillator strengths, in the framework of the first Born approximation, for the electron-impact excitation of H_2 through the $X\,^1\Sigma_g^+(v=0)\rightarrow B\,^1\Sigma_u^+(v'=0-33)$, $X\,^1\Sigma_g^+(v=0)\rightarrow B'\,^1\Sigma_u^+(v'=0-8)$ and $X\,^1\Sigma_g^+(v=0)\rightarrow C\,^1\Pi_u(v'=0-12)$ vibronic transitions. The target electronic wave functions, previously used to determine electron-impact dissociation cross sections for the same transitions [Phys. Rev. A **57**, 1025 (1998)], were calculated at the configuration-interaction level for several internuclear distances. The discrete vibrational wave functions were generated by solving the vibrational Schrödinger equation in the Born-Oppenheimer scheme. The Franck-Condon approximation was not invoked. Optical oscillator strengths for the same transitions were also obtained and compared favorably with previous theoretical and experimental results. The calculated generalized oscillator strengths presented good agreement with recent measurements by Zhong *et al.* [J. Electron Spec. and Rel. Phen. **94**, 127 (1998)] for the $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$ vibronic transitions. [S1050-2947(99)11008-4]

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I. INTRODUCTION

Electron-impact cross sections of molecular hydrogen have several applications, among them laser systems, modeling of earth and space plasmas [1], gas discharges, and other weakly ionized plasmas [2]. Besides that, since the molecular hydrogen is the simplest molecule, the study of the electron-molecule collision processes may present basic insight on its fundamentals. Recently, we have studied the electron-impact dissociation cross sections of H_2 [3] via the transitions $X\,^1\Sigma_g^+(v=0)\rightarrow\{B\,^1\Sigma_u^+,B'\,^1\Sigma_u^+,C\,^1\Pi_u\}$, the same studied in the present work for discrete transitions. The three ungerade excited states correlate to the $H(1s)+H(n=2)$ dissociation limit. In particular, the Lyman ($B^1\Sigma_u^+$) and Werner ($C^1\Pi_u$) bands give rise to the strongest allowed optical transitions in the ultraviolet region of the molecular hydrogen spectra. A compilation of cross sections for various channels of electron-molecular hydrogen collisions can be found in Tawara *et al.* [4].

There are great experimental difficulties in the determination of optical and generalized oscillator strengths (the latter is directly proportional to the differential cross sections) for vibronic transitions in H_2. The reason is the extensive overlap of bands with considerable intensities in this region of the molecular hydrogen spectra [5,6], making difficult the acquisition of accurate optical and electron energy-loss vibronic spectra. This turns the theoretical calculations, besides having intrinsic interest, into a specially important asset for the interpretation of the spectra.

Glass-Maujean *et al.* [7] have measured transition probabilities, directly related to optical oscillator strengths, from the ground state to the B, B', and C states for high vibrational numbers, near the states' same dissociation limit. Experimental optical oscillator strengths for the $X\,^1\Sigma_g^+(v=0)\rightarrow\{B\,^1\Sigma_u^+,C\,^1\Pi_u\}(v')$ bands were measured and, up to 1992, reviewed by Chan *et al.* [8]. Khakoo and Trajmar [2] have obtained differential cross sections for the B and C states at electron-impact energy of 60 eV, lower than the region of validity of the first Born approximation. Chen and Msezane [9] have used these experimental data to obtain integral cross sections using a universal function. Geiger and Schmoranzer [10] have obtained optical oscillator strengths from electron-impact experiments. Recently, Zhong *et al.* [5] have measured the optical oscillator strengths and intensity distributions at 1500 eV electron-impact energy for the Lyman and Werner vibronic bands, the latter as a function of the scattering angle. Those authors also reviewed the experimental work on these transitions up to 1998. We derived experimental generalized oscillator strengths from their [5] vibrational intensity distributions as a function of the scattering angle, using one theoretical vibronic transition for each band, as it will be explained. Concerning the experimental work on the vibronic transition $X\,^1\Sigma_g^+(v=0)\rightarrow B'\,^1\Sigma_u^+(v')$, as far as we are aware, there is only Chan *et al.* [8] measurement of the optical oscillator strength for the $v=0\rightarrow v'=0$ transition, and Glass-Maujean *et al.* [7] for high v' vibrational numbers, near the dissociation limit.

On the theoretical side, there are the optical oscillator strength calculations of Allison and Dalgarno for the B and C vibronic bands [11,12], and the transition probabilities calculations for the B' vibronic band of Kwok, Dalgarno, and Posen [13], and Glass-Maujean [14]. The latter two results were converted into optical oscillator strengths. Those calculations have used the accurate transition dipole moments and potential-energy curves of Kolos and Wolniewicz [15,16]. Concerning generalized oscillator strengths, there are some purely electronic, i.e., without vibrational degrees of freedom, generalized oscillator strengths calculations for low-

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lying transitions of molecular hydrogen utilizing correlated electronic wave functions; as a representative of these Franck-Condon calculations we mention the work of Arrighini *et al.* [17] and Liu and Hagstrom [18]. With regard to the three reported transitions, we are aware only of generalized oscillator strength calculations done by Kolos, Monkhorst, and Szalewics for the B state [19], including vibrational degrees. Recently, Celiberto and Rescigno [1] reported electron-impact excitation cross sections, as a function of the impact energy (20–100 eV) and the initial and final vibrational quantum numbers, for the Lyman and Werner transitions. They have employed an impact-parameter formulation [1].

In this study we report theoretical optical and generalized oscillator strengths for the $X\,^1\Sigma_g^+(v=0)\rightarrow B\,^1\Sigma_u^+(v'=0-33)$, $X\,^1\Sigma_g^+(v=0)\rightarrow B'\,^1\Sigma_u^+(v'=0-8)$, and $X\,^1\Sigma_g^+(v=0)\rightarrow C\,^1\Pi_u(v'=0-12)$ vibronic transitions. The calculations are compared with previous optical and theoretical results, when available.

II. THEORETICAL BACKGROUND AND CALCULATION DETAILS

The calculations employed the Born-Oppenheimer approximation for the target wave functions and the first Born approximation to describe the collision process. In short, within the Born-Oppenheimer approximation, the target wave functions are written as

$$\Psi_{n\nu}(\mathbf{r}_1,\mathbf{r}_2;R)=\psi_n(\mathbf{r}_1,\mathbf{r}_2;R)\chi_{n\nu}(R), \tag{1}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the two electrons of the hydrogen molecule, R is the internuclear distance, ψ_n is the electronic wave function, and $\chi_{n\nu}(R)$ is the discrete ν vibrational function of the n electronic state. The spin functions are factored out in Eq. (1) since we do not consider spin-orbit interactions.

The generalized oscillator strength $f(K,E)_{00\rightarrow n'\nu'}$, for the excitation from the $\nu=0$ vibrational level of the ground $n=0$ electronic state to the ν' vibrational level of the n' electronic excited state is written, in atomic units, as [20]

$$f(K,E)_{00\rightarrow n\nu'}=\frac{2E}{K^2}\frac{g_n}{4\pi}\int\left|\int\chi^*_{n\nu}(R)\chi_{00}(R)\varepsilon_{0n}\right.$$
$$\left.\times(K,R,\Omega)dR\right|^2 d\Omega, \tag{2}$$

where $\mathbf{K}$ is the transferred momentum and equals $\mathbf{k}_{00}-\mathbf{k}_{n\nu}$, $\mathbf{k}_{00}$, and $\mathbf{k}_{n\nu}$ are the momenta of the incident and the scattered electron, respectively, g_n is the degeneracy of the final state (1 for Σ, 2 for Π), and E is the transferred energy, equal to the vibronic transition energy. The solid angle Ω specifies the relative orientation between $\mathbf{R}$ and $\mathbf{K}$, that is, the orientation of the molecule. The integration over Ω in Eq. (2) results from averaging over the orientation of the molecular axis with respect to $\mathbf{K}$, i.e., the classical average. The electronic scattering amplitude, ε_{0n}, is written in the first Born approximation [20,21] as

$$\varepsilon_{0n'}(K,R,\Omega)=-\int\psi^*_{n'}(\mathbf{r}_1,\mathbf{r}_2;R)$$
$$\times\left(\sum_{i=1}^{N}e^{i\mathbf{K}\cdot\mathbf{r}_i}\right)\psi_0(\mathbf{r}_1,\mathbf{r}_2;R)dr_1dr_2. \tag{3}$$

The generalized oscillator strength, a nondimensional quantity independent of the electron impact energy, is directly proportional to the differential cross section,

$$f(K,E)=\frac{E}{2}\frac{k_{00}}{k_{n\nu}}\frac{1}{K^2}\frac{d\sigma_{0n}}{d\omega}, \tag{4}$$

where ω is the scattered solid angle of the scattered electron, which is related to the transferred momentum $\mathbf{K}[d\omega=2\pi\sin\theta d\theta=2\pi KdK/(k_{00}k_{nW})]$. This property allows one to obtain differential and integral cross sections in the wide range of validity of the first Born approximation. For present purpose, we consider the range of validity of the first Born approximation for valence transitions [20] as being from 100 eV electron-impact energy upwards, as it was discussed in our previous work [3].

In the limit when the transferred momentum K goes to zero, the generalized oscillator strength goes to the optical oscillator strength $f(E)$ in the length form

$$\lim_{K\rightarrow 0}f(K,E)=f(E)=\frac{2}{3}g_nE|M_{no}|^2, \tag{5}$$

where M_{0n} is the usual dipole transition moment in the length form [20–22], including vibrational degrees of freedom and integrated over the internuclear distance R. This property of the generalized oscillator strength relates electron impact with optical experiments and calculations.

Discrete ground $(v=0)$ and excited (v') vibrational wave functions were obtained by integrating numerically the nuclear Schrödinger equation according to Le Roy's methodology [23], from the most accurate potential-energy curves available [24,25]. The Born-Oppenheimer energies are taken from Ref. [15] for the ground state (X) and from Ref. [25] for the excited states (B,B',C). We have also used a modified version of Le Roy's program [22] to perform the R integration of Eq. (2).

The electronic wave functions were previously used to calculate dissociation cross sections [3]. They were obtained within the distance interval $1.0\leqslant R\leqslant 2.4$ a.u. (steps of 0.2 a.u.) at the configuration-interaction level with single and double excitations (CI-SD) expanded on a basis set of Gaussian-type orbitals. The Gaussian basis set was a $(12s,6p,3d)/[9s,6p,3d]$, suggested by Jaszunski and Roos [26].

The ground and each of the excited electronic states were independently calculated. We performed independent self-consistent Hartree-Fock calculations for the ground and each of the excited states, allowing all of the molecular orbitals to fully relax. The corresponding molecular orbitals were used in the CI-SD calculation. In other words, we have not used the frozen core approximation.

Improved virtual orbitals (IVO) [27] for each electronic state were constructed from these molecular basis sets, re-

TABLE I. Optical oscillator strengths ($\times 10^{-3}$) for the $X\,^1\Sigma_g^+(v=0) \rightarrow C\,^1\Pi_u(v'=0-12)$ vibronic transitions (Werner band). The numbers in parentheses are reported experimental error bars.

v'	This work	[11,12]	[5]	[8]^a	[10]	[32]	[7]
0	47.55	47.60	47.1 (4.9)	45.4	34.8		
1	72.73	74.82	71.7 (7.5)	71.8	59.2	59.2	
2	69.74	69.82	68.5 (7.4)	69.5	55.5	64.2	
3	54.68	54.72	52.4 (7.8)	54.4	43.7	44.2	
4	38.71	38.74	38.5 (4.3)	38.7	33.7	31.7	
5	25.98	25.98	26.5 (3.1)	25.5	21.0	22.4	
6	17.00	17.0	16.1 (1.9)	16.5	15.3	17.0	
7	11.01	10.99					
8	7.133	7.098					
9	4.635	4.592					
10	3.016	2.976					
11	1.956	1.909					1.43 (0.60)
12	1.195	1.171					0.63 (0.09)

[a] Chan *et al.* [8] report, as uncertanties, $\pm 5\%$ for fully resolved peaks and $\pm 7-15\%$ for the partially resolved peaks.

sulting in an improved convergence of the CI calculations [28]. This methodology has been used before for several molecules and atoms [22,29–31] and presented generalized and optical oscillator strength values close to experimental values. The full CI space of 48 molecular orbitals (occupied + virtuals) was made of $10\sigma_g$, $10\sigma_u$, $12\pi_u$, $12\pi_g$, and 4δ molecular orbitals [3]. For the CI-SD wave functions all single and double excitations were allowed from the reference Hartree-Fock configuration for each state.

The resulting four different molecular basis sets for the CI calculations, one for the ground state and one for each of the excited states, incorporate in the target wave functions relaxation and correlation effects. Therefore, the molecular basis used in the CI calculations for the ground and excited states are no longer orthogonal. In order to compute the matrix elements $\varepsilon_{0n}(K,R,\Omega)$ [Eq. (3)] between these nonorthogonal basis, we used a bi-orthogonalization procedure [29]. For such purpose, unitary transformations are applied on the two sets of N nonorthogonal molecular orbitals, turning $(N-1)$ of them orthogonal.

III. RESULTS AND DISCUSSION

A. Optical oscillator strengths

Tables I, II, and III present the optical oscillator strengths from the ground $X\,^1\Sigma_g^+(v=0)$ vibronic state to the $C\,^1\Pi_u(v'=0-12)$, $B'\,^1\Sigma_u^+(v'=0-8)$, and $B\,^1\Sigma_u^+(v'=0-33)$ excited states, respectively. Table I shows very good agreement between the present results and the theoretical results of Allison and Dalgarno [11,12] for the whole range of vibrational levels of the Werner band (C), as well as with the electron-impact measurements of Chan *et al.* [8] and with the electron-impact measurements of Zhong *et al.* [5]. The optical oscillator strengths obtained by the electron-impact measurements of Geiger and Schmoranzer [10], and by the optical measurements of Fabian and Lewis [32], are lower then the present results, except for $v'=6$. Both the present theoretical results and those of Allison and Dalgarno [11,12] disagree with the experimental results of Glass-Maujean *et al.* [7] for the last two vibrational levels ($v'=11,12$).

TABLE II. Optical oscillator strengths ($\times 10^{-3}$) as function of the transferred momentum squared K^2 for the $X\,^1\Sigma_g^+(v=0) \rightarrow B'\,^1\Sigma_u^+,(v'=0-8)$ vibronic transitions. The numbers in parentheses are reported error bars.[a]

v'	This work	[13]	[14]	[7]
0	2.933	2.90	2.92	
1	5.923	5.96	5.98	
2	7.179	7.31	7.34	
3	6.782	6.96	7.00	
4	5.352	5.51	5.55	
5	3.076	3.30	3.31	2.91 (1.08)
6	0.3345	0.335	0.336	0.215 (0.54)
7	0.3250	0.320	0.326	0.279 (0.64)
8	0.2059	0.210	0.215	0.203 (0.43)

[a] Chan *et al.* [8] report 3.84×10^{-3} for the $v'=0$ band.

Table II shows good agreement between the present optical oscillator strength values for the B' transition and the theoretical values of Kwok *et al.* [13] and those of Glass-Maujean [14], for the whole range of vibrational states. Chan *et al.* [8] have measured, by electron-impact technique, a value of 3.84×10^{-3} for $v'=0$, about 25% higher than the theoretical values. The experimental results of Glass-Maujean *et al.* [7] for the range $v'=5-7$ are lower than the theoretical values, although they are within the experimental uncertainties, except for $v'=6$. The vibronic band $v'=8$ present good agreement between the theoretical values and the experimental result [7].

The present optical oscillator strengths for the B transition, the Lyman band, shown at Table III, are about 10% lower than the theoretical result of Allison and Dalgarno [11,12]. There are several experimental measurements for the optical oscillator strengths of this band, divided in two major groups, dipole (e-e) (electron impact) [5,8,10] and optical [7,32–34] experimental measurements.

For most of the $B(v')$ levels our results are within the error bars of the electron-impact values [5,8,10]. In particular, the present theoretical results are about 15% lower than those of Chan *et al.* [8] although they are, in general, within the error bars, and slightly lower than the error bars of Zhong *et al.* [5]. The agreement between the present results and those of Chan *et al.* [8] improves for the $v'=13$ level upwards, and the same trend may be observed with Zhong *et al.* [5] from the $v'=10$ level, except for the $v'=11$ and $v'=13$ levels. Our calculations are closer to the Geiger and Schmoranzer experimental results [10] than with those of Zhong *et al.* and Chan *et al.* for the first vibrational levels, and for the remaining vibrational levels the same trend of the last two groups is followed.

Some absolute optical cross-section measurements suffer from severe ‘‘line saturation’’ effects, as was extensively discussed by Chan *et al.* [8,36] and by us in a previous work on valence transitions of CO [22]. These seem to be a case for the three optical measurements of the Lyman band [32–34], which encompass only a few vibrational levels and have some inconsistency among them. The comparison between

TABLE III. Optical oscillator strengths ($\times 10^{-3}$) for the $X\,{}^1\Sigma_g^+(v=0) \rightarrow B\,{}^1\Sigma_u^+(v'=0-33)$ vibronic transitions (Lyman band). The numbers in parentheses are reported experimental error bars.

v'	This work	[11,12]	[5]	[8] [a]	[10]	[32]	[33]	[34]	[7]
0	1.462	1.689		1.54		1.75		1.9	
1	4.999	5.790	6.27 (0.75)	5.75	5.45	5.19		13	
2	10.22	11.56	12.3 (1.4)	11.4	9.94	11.5		24	
3	15.26	17.55	18.1 (2.0)	17.7	16.5	17.6		37	
4	19.84	22.50	25.5 (2.8)	22.8	21.0	24.5	30		
5	22.65	25.71	22.6 (2.5)	26.3	23.8	25.8			
6	23.80	27.04	28.8 (3.1)	27.6	26.4				
7	23.53	26.73	27.3 (3.0)	27.6	26.7				
8	22.21	25.23	23.7 (2.7	25.4	23.2				
9	20.24	22.98	23.6 (2.7)	23.6	22.2				
10	17.94	20.35	18.2 (2.4)	20.0	20.3				
11	15.57	17.64	18.4 (2.3)	17.4	18.1				
12	13.30	15.64	13.3 (2.8)	15.3	15.5				
13	11.22	12.66	15.4 (2.5)	12.2	12.8	11.4	12.0		
14	9.377	10.55	9.71 (1.53)	10.1	10.4				
15	7.782	8.730		7.94	8.25	10.1			
16	6.427	7.185	7.18 (1.35)	6.87	7.03	7.87	5.0		
17	5.291	5.891	5.18 (0.91)	5.31	6.12	5.75	4.2		
18	4.348	4.820	4.74 (1.28)	4.68	5.52				
19	3.569	3.939		3.84	4.25	3.44	2.3		
20	2.913	3.219		3.08	3.29				
21	2.408	2.632		2.67					
22	1.980	2.154		2.09					
23	1.632	1.766							
24	1.347	1.450							
25	1.115	1.193							
26	0.9228	0.9815							
27	0.7634	0.8057							
28	0.6319	0.6603							
29	0.5258	0.5432							
30	0.4405	0.4598							
31	0.3652	0.3702							
32	0.2193	0.2961								0.30 (0.16)
33	0.1314	0.1616								0.21 (0.02)

[a] Chan *et al.* [8] report as uncertanties ±5% for fully resolved peaks, and ±7−15% for the partially resolved peaks.

the present results and those of Glass-Maujean [7] ($v'=32{,}33$) shows a behavior also found for the Werner band (C); their optical oscillator strength values are higher than the present results, although they agree within their experimental error bar for $v'=32$.

B. Generalized oscillator strengths

The favorable comparison between our optical oscillator strengths and the other theoretical and experimental values for the three bands allows us to infer that our electronic wave functions should also provide accurate values for the generalized oscillator strengths.

Figures 1 and 2 show the present values for the generalized oscillator strength for the excitation from the ground $X\,{}^1\Sigma_g^+(v=0)$ vibronic state to the vibronic states $B\,{}^1\Sigma_u^+(v'=1-5)$ and $C\,{}^1\Pi_u(v'=1-6)$, compared with the other available experimental and theoretical results. Concerning the $B'\,{}^1\Sigma_u^+$ bands, shown in Fig. 3 for some transitions, there is a lack of other experimental and theoretical results involving vibronic resolution. The complete listing of generalized oscillator strengths, as a function of the squared transferred momentum K^2, up to $K^2=36$ a.u., for all of the calculated vibronic excited states $B'\,{}^1\Sigma_u^+(v'=0-8)$, $C\,{}^1\Pi_u(v'=0-12)$, and $B\,{}^1\Sigma_u^+(v'=0-33)$, together with the theoretical transition excitation energies, may be obtained in PAPS tables [35], or in Latex form via e-mail from one of the authors.

To our knowledge, the only available angle resolved, high-energy–electron-impact measurements of vibronic bands of H_2 were the ones recently performed by Zhong *et al.* [5] for the $B\,{}^1\Sigma_u^+$ and $C\,{}^1\Pi_u$ bands, and the only previous theoretical calculations for vibronic generalized oscillator strengths of H_2 were performed by Kolos, Monkhorst, and Szalewicz [19] for the $B\,{}^1\Sigma_u^+$ state.

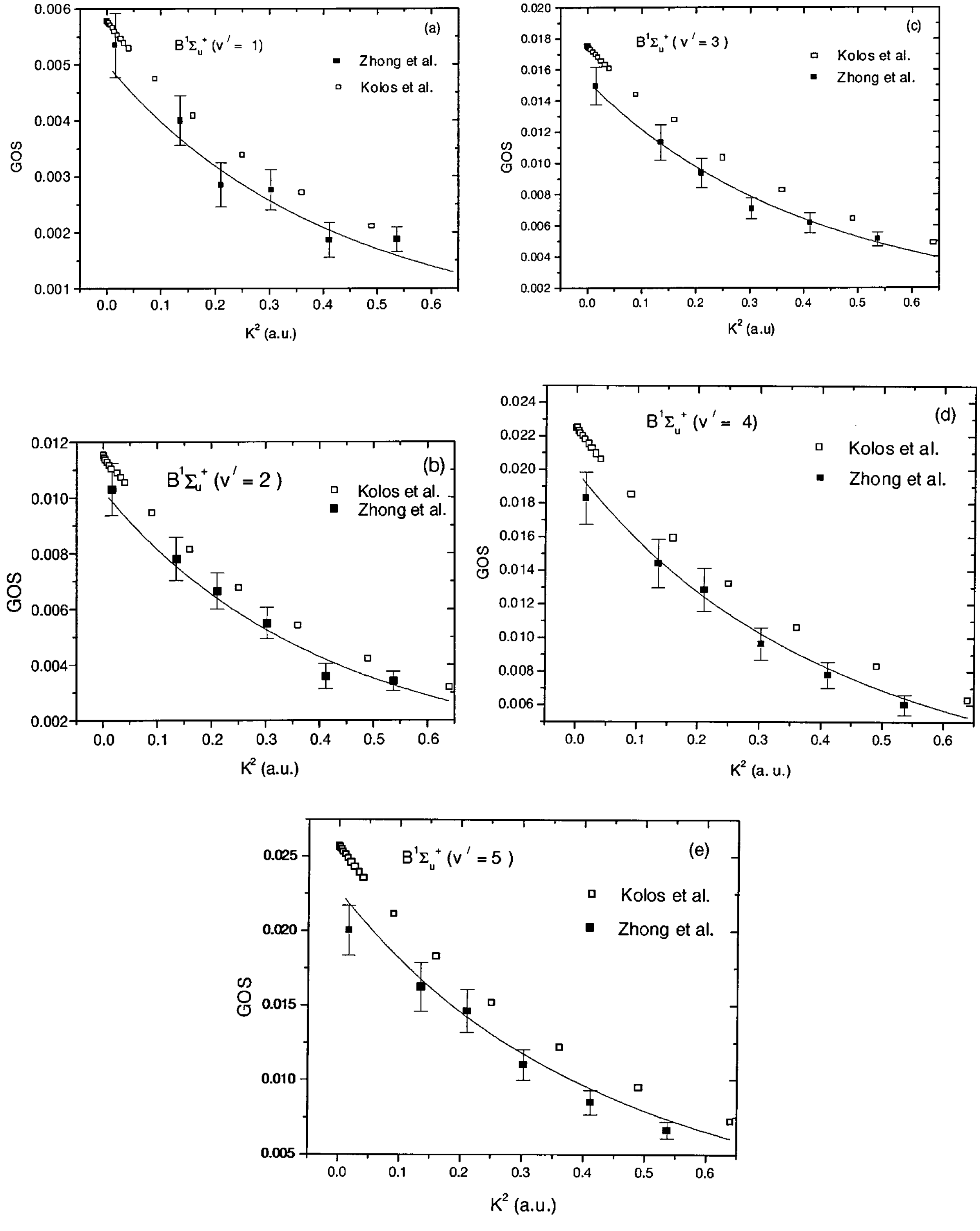

FIG. 1. Experimental results of Zhong *et al.* [5], obtained using the procedure described in the text, the theoretical ones of Kolos, Monkhorst, and Szalewicz [19], and the calculated generalized oscillator strengths for the Lyman band $X\,^1\Sigma_g^+(v=0)\rightarrow B\,^1\Sigma_u^+(v')$. See the text for the discussion.

A good overall agreement is observed in Fig. 1 between the present generalized oscillator strengths results and those of Kolos, Monkhorst, and Szalewicz [19], their results being about 10% greater than ours within the range of transferred K^2 and vibrational levels studied. As both calculations employ similar potential energy curves, the discrepancy must be attributable to the different electronic wave functions. We have shown before [3] that the present electronic functions and their type of wave functions, similar to the ones used by Kolos, Monkhorst, and Szalewicz [19], have comparable ac-

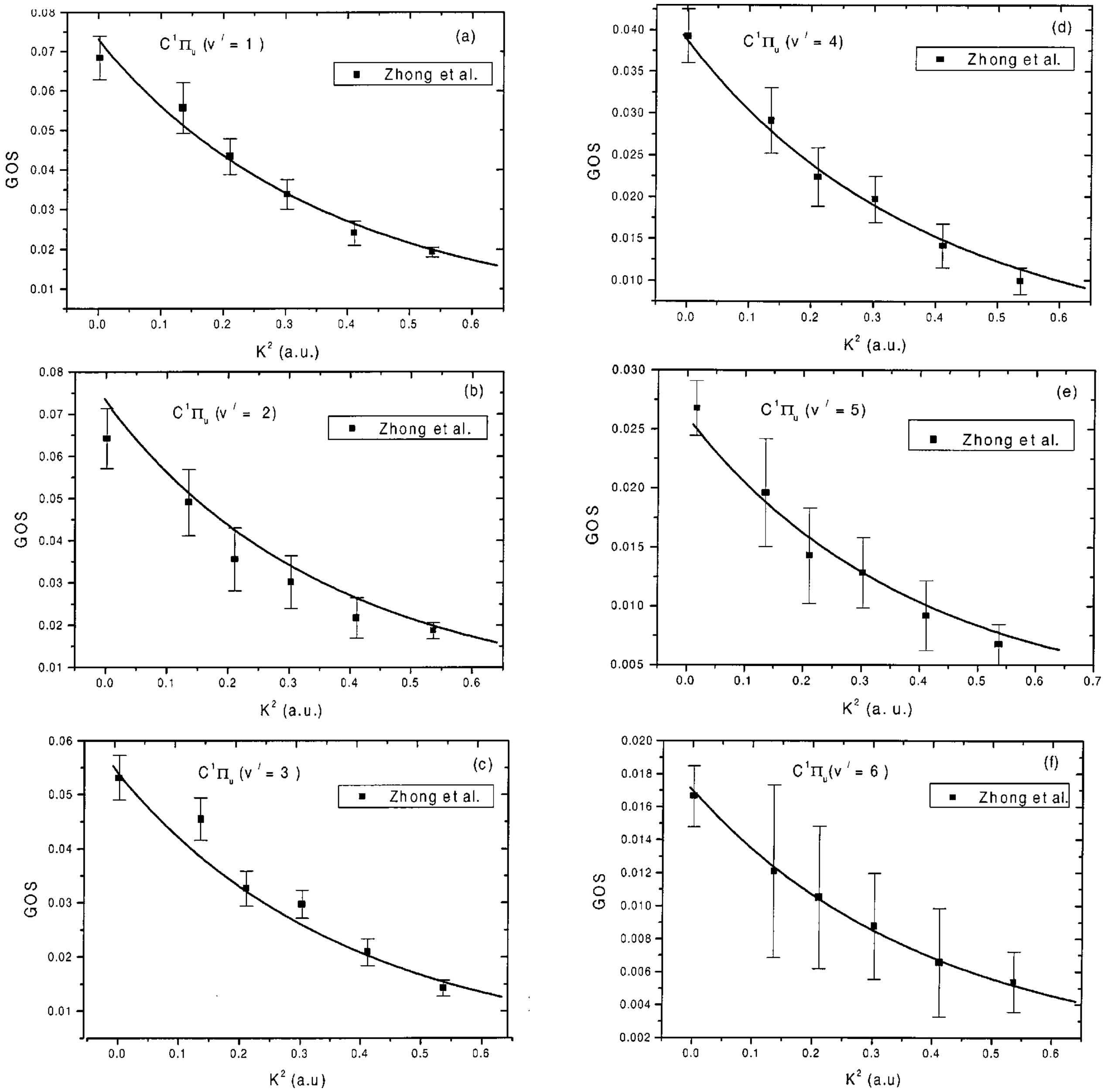

FIG. 2. Experimental results of Zhong *et al.* [5], obtained using the procedure described in the text, the theoretical ones of Kolos, Monkhorst, and Szalewicz [19], and the calculated generalized oscillator strengths for the Werner band $X\,{}^1\Sigma_g^+(v=0)\rightarrow C^1\Pi_u(v')$. See the text for the discussion.

curacy.

Zhong *et al.* [5] measured the intensity distributions as a function of the scattering angle at 1500 eV electron-impact energy for the vibronic transitions $X\,{}^1\Sigma_g^+(v=0)\rightarrow\{B\,{}^1\Sigma_u^+,C\,{}^1\Pi_u\}(v')$, the Lyman and Werner bands, respectively. Their angular range was 0.0–4.0 °, corresponding to a momentum-transferred squared K^2 range of about 0.002–0.6 atomic units. The Lyman band was obtained in the $v'=1-5$ vibrational interval while the Werner band was obtained in the $v'=1-6$ interval. Zhong *et al.* [5] measured the intensity ratio for the Lyman band (B) with respect to the $v'=6$ transition of this same band. The intensity ratios for the Werner band (C) were measured with respect to the $v'=0$ of this same band.

In order to compare our absolute generalized optical oscillator strength calculations with the Zhong *et al.* experiment [5], we have normalized their experimental intensity results, for the Lyman and Werner bands, by our calculated values of the generalized oscillator strength as a function of K^2. For the Lyman band we used the $v'=6$ transition of the same band, and for the Werner band, the $v'=0$ transition of the same band. Figures 1 and 2 show an overall agreement between the experimental results and the calculated generalized oscillator strengths for the B and C bands, the latter mostly within the error bars. Concerning the B state, the agreement is especially good for the $v'=3$ transition, except for the experimental point at $K^2\sim0.3$. The agreement is also good for $v'=3$ and 4 for the B transitions. The worst result for the B state is the $v'=1$ band. This result and the experimental points in some transitions, having error bars not crossing our curves, may be understood by bearing in mind the extremely difficult conditions to measure the present

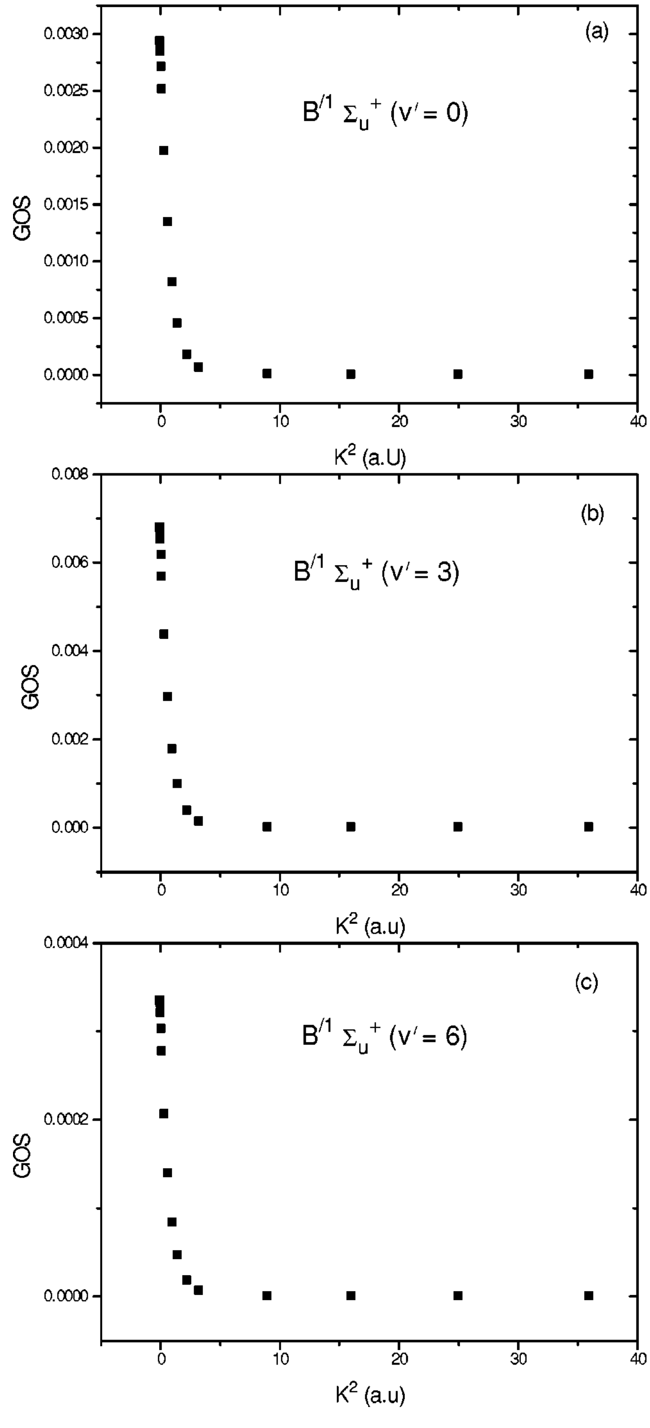

FIG. 3. Calculated generalized oscillator strengths for the Lyman band $X\,^1\Sigma_g^+(v=0)\rightarrow B'\,^1\Sigma_u^+(v')$, selected transitions.

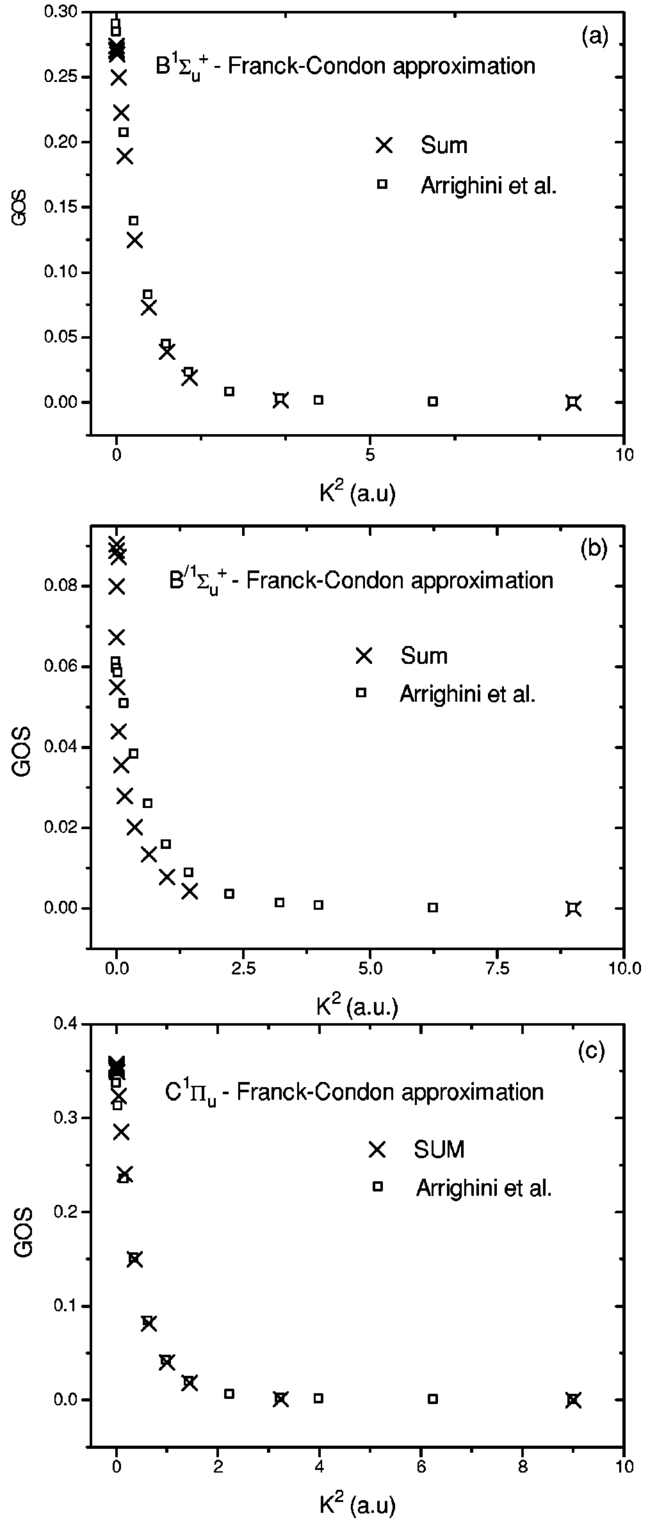

FIG. 4. This figure compares our generalized oscillator strengths results, summed over the final vibrational states, with the Franck-Condon results of Arrighini *et al.* [17] for the (a) $B\,^1\Sigma_u^+$, (b) $B'\,^1\Sigma_u^+$, and (c) $C\,^1\Pi_u$ final electronic states.

bands, especially in the region of small transferred momentum [22].

In a previous paper we discussed the use of the Franck-Condon approximation in the calculations of the electron-impact dissociation cross sections of H_2 [3] via the same transitions. We found a ratio between the Franck-Condon dissociation cross sections and the non-Franck–Condon dissociation cross sections for the transitions to the $B\,^1\Sigma_u^+$, $B'\,^1\Sigma_u^+$, and $C\,^1\Pi_u$ states, respectively, of 1.741, 1.07, and 1.236. It is interesting to investigate the same question for the discrete excitation processes. This can be achieved by comparing our results, summed over all the vibronic transitions for each final electronic state, with the Franck-Condon calculations of Arrighini *et al.* [17]. Liu and Hagstrom [18] also did a Franck-Condon calculation for the B and B' states, and their results are similar to Arrighini's. Figure 4 compares our results, summed over the final vibrational states, with the

Franck-Condon results of Arrighini *et al.* [17] for the (a) $B\ ^1\Sigma_u^+$, (b) $B'\ ^1\Sigma_u^+$, and (c) $C\ ^1\Pi_u$ electronic states.

Figures 4(a)–4(c) show that the Franck-Condon results (Arrighini *et al.* [17]) match exactly the present non-Franck–Condon results for the C transition, present a good agreement for the B transition, and show considerable differences for the B' transition, especially for the low values of the transferred momentum, a situation where the first Born approximation is expected to properly describe the collision process. These results confirm the recent experimental predictions of Zhong *et al.* [5], concerning the Franck-Condon nature of the $B\ ^1\Sigma_u^+$ and $C\ ^1\Pi_u$ discrete excitations. Experimental results on the vibronic generalized oscillator strengths for the $B'\ ^1\Sigma_u^+$ electronic state are needed in order to further investigate the non-Franck–Condon character of the $B'\ ^1\Sigma_u^+$ process.

As a final remark on the above subject, the present results do not show a correspondence, in what concerns the validity of the Franck-Condon approximation, with our previous dissociation cross sections [3]. For instance, the Franck-Condon approximation for the $C\ ^1\Pi_u$ transition seems to work in the calculation of the discrete excitation cross sections and clearly fails in the calculation of the dissociation cross sections. Further investigation on this question, involving other molecules and processes, may shed some new light on this problem.

The good agreement between the theoretical and experimental results for the B and C transitions may be attributed both to the Franck-Condon character of the vibronic excitations, as pointed out by Zhong *et al.* [5], and to the relatively low values of K^2 where the comparison was possible. This is a favorable situation in what concerns the use of the first Born approximation, keeping in mind that this approach is expected to present a better description of the collision process for smaller rather than for larger values of the transferred momentum. Since the latter corresponds to a stronger interaction between the incident electron and the target, this is a situation where higher-order terms in the Born expansion should give larger contributions [22,31].

Recently, experimental electron-impact measurements have been able to obtain generalized oscillator strength values up to very large values of the transferred momentum, for instance, the recent experimental results for inner-shell excitations of the CO_2 with generalized oscillator strength values up to $K^2=60$ a.u. [37]. As we have already pointed out, the experimental determination of the generalized oscillator strengths for the $B'\ ^1\Sigma_u^+$, $C\ ^1\Pi_u$, and $B\ ^1\Sigma_u^+$ states is particularly difficult, even for low values of K^2. Nevertheless, it would be very interesting to extend experimental results to larger K^2 values. For this reason, we have calculated generalized oscillator strength values up to $K^2=36$ a.u. [35] for excitations to the $B'\ ^1\Sigma_u^+(v'=0-8)$, $C\ ^1\Pi_u(v'=0-12)$, and $B\ ^1\Sigma_u^+(v'=0-33)$ states.

IV. CONCLUSION

We have calculated optical and generalized oscillator strengths for the electron-impact vibronic excitation of H_2 through the $X\ ^1\Sigma_g^+(v=0)\rightarrow B\ ^1\Sigma_u^+(v'=0-33)$, $X\ ^1\Sigma_g^+(v=0)\rightarrow B'\ ^1\Sigma_u^+(v'=0-8)$, and $X\ ^1\Sigma_g^+(v=0)\rightarrow C\ ^1\Pi_u(v'=0-12)$ transitions in the range of squared transferred momentum $K^2=0-36$ a.u. The electronic CI wave functions were determined independently for the ground and each of the excited states, which means that correlation and relaxation effects were explicitly considered in the present calculations.

The optical oscillator strengths presented a good agreement with the theoretical results of Dalgarno *et al.* [11,12] and with those determined by electron-impact measurements [5,8,10]. The experimental optical oscillator strengths measured by optical methods does not, in general, agree with the present theoretical results, as well as with those obtained by electron-impact techniques. Saturation effects in the optical measurements may be responsible for this discrepancy.

The generalized oscillator strength for the B transition agrees reasonably with the theoretical results of Kolos, Monkhorst, and Szalewicz [19]. Excellent agreement between the Franck-Condon and the non-Franck–Condon results was found for the B and C transitions, and considerable discrepancies for the B' transition. A comparison with the intensities, provided by the recent electron-impact experimental results of Zhong *et al.* [5] was performed for the B and C vibronic excitations up to the square transferred momentum $K^2=0.6$ a.u. We have normalized the experimental intensities by our calculated values for the generalized oscillator strength as a function of K^2 for the $v'=6$ vibronic transition of the Lyman band (B) and for the $v'=0$ vibronic transition of the Werner band (C), and compared these results with the other measured vibronic excitations. The agreement was good, as expected, once the first Born approximation adequately represented the collision process for these low values of the transferred momentum.

The complete set of values for the generalized oscillator strength are available as tables [35] and may stimulate new electron-impact measurements for larger K^2 values of such important bands of molecular hydrogen.

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