

Studies of vibronic excitations of H₂ by electron impact

Lee Mu-Tao†, L E Machado‡, L M Brescansin§ and G D Meneses§

† Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13560 São Carlos, São Paulo, Brazil

‡ Departamento de Física, Universidade Federal de São Carlos, Caixa Postal 676, 13560 São Carlos, São Paulo, Brazil

§ Instituto de Física Gleb Wataghin, Unicamp, Caixa Postal 6165, 13081 Campinas, São Paulo, Brazil

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Abstract. We report rotationally unresolved vibro-electronic cross sections and branching ratios associated with the $X\ ^1\Sigma_g^+ \rightarrow d\ ^3\Pi_u$ electronic transition in H₂, using the distorted-wave approximation within the adiabatic-nuclei framework. The present study shows that the Franck-Condon approximation (FCA) can provide reliable cross sections. The calculated branching ratios associated with the vibro-electronic transitions exhibit some oscillations at low energies; however, their magnitudes agree well with the FCA predictions.

1. Introduction

The study of molecular excitation by electron impact is of interest to several areas of research, such as the physics of low-temperature plasmas, plasma chemistry, lasers, gas-discharge light sources and astrophysics, among others. This study is very wide in scope, ranging from pure rotational excitations to more complex processes, such as electronic vibro-rotational transitions, etc. Direct measurement of the cross sections for these processes is a difficult problem. Therefore, reliable calculations for these cross sections can provide a valuable step towards the understanding of the molecular excitation dynamics.

In this work we are interested in the vibro-electronic (vibronic) excitations in diatomic molecules by electron impact. Although similar transitions have been widely studied for the processes of photoionization (Leal *et al* 1984, Lucchese *et al* 1981) and resonant enhanced multiphoton ionization (REMPI) (Stephens *et al* 1990) only a few similar studies are reported in the literature for transitions to discrete states (Teillet-Billy *et al* 1988). Here, we will particularly study the vibronic transition $X\ ^1\Sigma_g^+ (v=0) \rightarrow d\ ^3\Pi_u (v')$ in H₂, for the energy range from 15–40 eV. For the electronic transition $X\ ^1\Sigma_g^+ \rightarrow d\ ^3\Pi_u$, experimental integral cross sections (ICS) have been reported by Baltayan and Nedelec (1975, 1976), Mohlmann and de Heer (1976) and Lavrov *et al* (1979). These cross sections were derived from measured relative intensities of some emission lines occurring in the vibro-rotational decay $d\ ^3\Pi_u \rightarrow a\ ^3\Sigma_g^+$, by making use of the Franck-Condon approximation (FCA). Nevertheless, the use of this approximation to derive experimental total cross sections without a careful check of its validity can eventually lead to erroneous results. A calculation by Chung *et al* (1975), based on the Born-Ochkur-Rudge (BOR) and FCA approximations, showed very good agreement with the experimental data of Mohlmann and de Heer (1976). Specifically aiming to

take account of a possible violation of the FCA for this transition, Lavrov *et al* (1981a, b) made a semi-empirical treatment of their previous experimental data (Lavrov *et al* 1979), as well as of those from Mohlmann and de Heer (1976). In their work, the adiabatic-nuclei scattering amplitude $a_{LM-\Lambda}(k, k', R)$ was expanded in a power series of the internuclear distance R . Only the first two terms were kept in this expansion and the expansion coefficients were found from the fitting to the experimental data. Their procedure is actually formally equivalent to the well known r -centroid method (Kuznetsova *et al* 1980). In fact, the calculation by Lavrov *et al* (1981b) has shown a surprisingly strong non-Franck-Condon effect: that treatment resulted in a multiplicative factor of 2–3 in the cross sections. These new sets of cross sections also exceeded those of Chung *et al* (1975). This situation is somewhat unusual, since the BOR approximation in most cases overestimates the cross sections by a factor of 1.5–2 (Lavrov *et al* 1981b). Thus, the applicability of the FCA to the $X^1\Sigma_g^+ \rightarrow d^3\Pi_u$ transition is still not very firmly established, and further investigation on this subject is certainly very interesting.

In the present work we study the applicability of FCA to the vibronic $X^1\Sigma_g^+ (v=0) \rightarrow d^3\Pi_u (v'=0, 1, 2, 3)$ transitions of H_2 , using the distorted wave approximation (DWA; Fliflet and McKoy 1980). The initial and final continuum wavefunctions of the scattering electron, required for the computation of the DWA T -matrix, are calculated using the Schwinger variational iterative method (SVIM; Lucchese *et al* 1982). These continuum functions were obtained in a ground-state molecular potential field, at the static-exchange level, which is generated using the Hartree-Fock (HF) molecular wavefunctions. This procedure allows us to perform accurate, totally *ab-initio* calculations for both integral cross sections and differential cross sections (DCS). The numerical treatment, although computationally much simpler than other available methods such as the close-coupling (CC, Schneider and Collins 1985), the R -matrix (Baluja *et al* 1985) and the Schwinger multichannel (SMC, Lima *et al* 1985), is highly reliable and was successfully applied to low-energy inelastic electron scattering by linear molecules (Lee *et al* 1990). Particularly for the electronic excitation from the ground state to the $b^3\Sigma_u^+$, $a^3\Sigma_g^+$ and $c^3\Pi_u$ levels of H_2 , the results obtained by the DWA (Lee *et al* 1990) and SMC (Lima *et al* 1988) methods are in good agreement for both cases in which the calculations do ($b^3\Sigma_u^+$ and $a^3\Sigma_g^+$ excitations) or do not ($c^3\Pi_u$ excitation) reproduce the available experimental results.

Although vibro-rotational cross sections can lead to a more detailed understanding of the physics involved in the excitation process, the rotational structure associated to each vibrational level of the molecule is not considered in the present calculation. However, our group is interested in calculations for those cross sections and the present paper can also be seen as a first effort in that direction.

A very brief description of our theory is presented in section 2, along with references where more details can be found. In the same section we also present some numerical details of the calculations. In section 3 we present our results, in comparison with the available data in the literature. The discussion about the importance of the non-Franck-Condon effects is also in section 3. In section 4 we summarize our conclusions.

2. Theory and calculation

According to the adiabatic-nuclei (AN) approximation (Chase 1956), the electronic and nuclear parts of the molecular wavefunction can be treated separately. Thus, the rotationally unresolved laboratory frame (LF) DWA differential cross section for the

vibronic excitation can be expressed as:

$$\left(\frac{d\sigma}{d\Omega}\right)_{v,v'} = \frac{1}{8\pi^2} \frac{k'}{k} \int d\hat{R}' |f_{vv'}(\mathbf{k}, \mathbf{k}', \hat{R}')|^2 \quad (1)$$

where \mathbf{k} (\mathbf{k}') is the momentum of the incident (scattered) electron; $f_{v,v'}(\mathbf{k}, \mathbf{k}', \hat{R}')$ is the LF-DWA scattering amplitude for the transition between the vibrational levels v (of the ground electronic state) and v' (of the excited electronic state) of the target, which is related to the LF-DWA adiabatic scattering amplitude $f(\mathbf{k}, \mathbf{k}', \mathbf{R}')$ by:

$$f_{v,v'}(\mathbf{k}, \mathbf{k}', \hat{R}') = \int_0^\infty \varphi_v^*(R) f(\mathbf{k}, \mathbf{k}', \mathbf{R}') \varphi_{v'}(R) R^2 dR. \quad (2)$$

In (2), $\varphi_v(R)$ [$\varphi_{v'}(R)$] is the vibrational wavefunction for the ground (excited) state, $f(\mathbf{k}, \mathbf{k}', \mathbf{R}')$ can be obtained from the calculated body-fixed T -matrix as follows (Fliflet and McKoy 1980):

$$f(\mathbf{k}, \mathbf{k}', \mathbf{R}') = -\frac{1}{2}\pi \sum_{l'l'm'm''} [4\pi(2l'+1)]^{1/2} i^{l'-l} \quad (3)$$

$$D_{lm}^{l*}(\hat{R}') D_{0m}^{l'}(\hat{R}') Y_{lm}(\hat{r}) \langle k'l'm' | T | klm \rangle.$$

Finally, the ICS' are calculated by the usual relation:

$$\sigma_{vv'} = \int d\Omega \left(\frac{d\sigma}{d\Omega}\right). \quad (4)$$

In order to ensure the accuracy of the integral in (2), the adiabatic scattering amplitudes $f(\mathbf{k}, \mathbf{k}', \mathbf{R}')$, as well as all functions required for their construction (3) should be calculated over a sufficiently dense grid of internuclear distances R . The first step in this calculation is the construction of SCF (Hartree-Fock) molecular electronic ground-state wavefunctions at several internuclear distances, namely $R = 1.0, 1.2, 1.4006, 1.5, 1.6, 1.8, 2.1$ au. In all these calculations the Cartesian-Gaussian basis set of Lima *et al* (1988) was used. At the equilibrium geometry, $R_e = 1.4006$ au, the SCF energy was $-1.133\,30$ au, that compares well with the HF limit value of $-1.133\,63$ au (Kolos and Roothaan 1960). Then, the electronic wavefunctions for the $d^3\Pi_u$ state were determined, at the same distances R , as improved virtual orbitals (IVO) in the V^{N-1} potential of the $1\sigma_g$ SCF orbital (Lee *et al* 1990). The basis set used for these IVOs is the same as for the ground state. The calculated vertical excitation energy, at R_e , was 14.5619 eV, to be compared with the experimental value of 14.3893 eV for the $v = 0 \rightarrow v' = 2$ transition (Dieke 1958).

In the computation of the R -dependent electronic T -matrix elements, six symmetries ($\sigma_g, \sigma_u, \pi_g, \pi_u, \delta_g, \delta_u$) were considered in both incident and scattered wavefunctions, for each internuclear distance. In order to ensure convergence of all angular momentum expansions, terms up to $l_{\max} = 7$ were included for each symmetry. Higher-order partial waves were found to contribute with less than 5% to the differential cross sections (Lee *et al* 1982). The initial basis sets of Cartesian-Gaussians used in the iterative procedure are listed in table 1. Only one iteration was needed to yield converged solutions.

Finally the vibrational wavefunctions $\varphi_v(R)$ and $\varphi_{v'}(R)$ were calculated (Cooley 1961) from the experimental potential curves in a 301-point grid covering the $1.0 \leq R \leq 2.1$ au range. For the ground state and for the excited state we have used the data from Spindler (1969) and Dieke (1958), respectively. After interpolating the R -dependent T -matrix over the same grid, Simpson's rule was used to evaluate the integral in (2).

Table 1. Initial basis sets used in the SVIM.

Continuum symmetry	Type of Cartesian-Gaussian function ^a	Exponents (α)
σ_g	s	4.0, 2.0, 1.0, 0.5
	z	2.0, 1.0, 0.3
σ_u	s	4.0, 2.0, 1.0, 0.5
	z	2.0, 1.0, 0.3
π_g	x	2.0, 1.0, 0.3
π_u	x	2.0, 1.0, 0.3
δ_g	xy	1.0, 0.3, 0.1
δ_u	xy	1.0, 0.3, 0.1

^a Defined as $\phi^{\alpha,l,m,n,A}(\mathbf{r}) = N(x - A_x)^l(y - A_y)^m(z - A_z)^n \exp(-\alpha|\mathbf{r} - \mathbf{A}|^2)$.

3. Results and discussion

In this section we present our results for the DCS and ICS for the $X^1\Sigma_g^+ \rightarrow d^3\Pi_u$ electronic transition (vibrationally and rotationally unresolved) as well as those for the $v = 0 \rightarrow v' = 0, 1, 2, 3$ associated vibronic transitions. We also show our results for the branching ratio $r_v(E)$, defined as:

$$r_v(E) = \frac{\sigma_{v=0,v'}(E)}{\sigma_{v=0,v'=1}(E)} \quad (5)$$

where $\sigma_{v,v'}(E)$ is the ICS for the $(v \rightarrow v')$ vibronic transition for the electron impact energy E . Due to its higher intensity, the transition $(0 \rightarrow 1)$ was chosen as reference.

In figure 1 we show our calculated ICS as a function of the impact energy, along with the experimental results of Baltayan and Nedelec (1976) and Mohlmann and

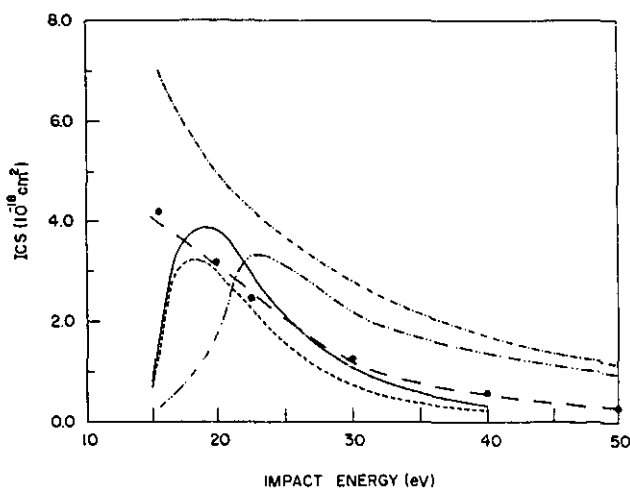


Figure 1. Integral cross sections for the transition $X^1\Sigma_g^+ \rightarrow d^3\Pi_u$ of H_2 by electron impact as a function of energy. Full curve, present vibrationaly unresolved results; short-broken curve, present vibrationaly resolved results added up to $v' = 3$; long-broken curve, theoretical results of Chung *et al* (1975); Chain curve, non-Franck-Condon results of Lavrov *et al* (1981b); double chain curve, data from Baltayan and Nedelec (1976); ●, experimental results of Mohlmann and de Heer (1976).

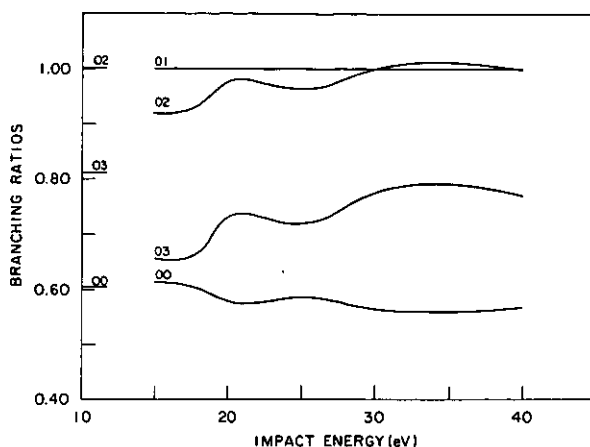


Figure 2. Branching ratios (relative to the $v=0 \rightarrow v'=1$ vibrational transition) for the vibronic transitions $X^1\Sigma_g^+(v=0) \rightarrow d^3\Pi_u(v'=0, 1, 2, 3)$ as a function of energy. Labelling numbers in the curves denote the $(v=0 \rightarrow v')$ transition. The horizontal bars at the LHS are the calculated Franck-Condon factors.

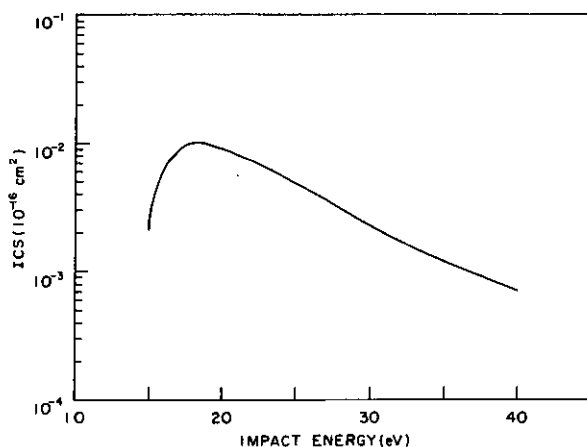


Figure 3. Vibrationally resolved integral cross sections for the $(v=0 \rightarrow v'=1)$ transition as a function of energy.

de Heer (1976), the semi-empirical results of Lavrov *et al* (1981b) and the *BO* theoretical results of Chung *et al* (1975). The present vibrationally unresolved ICS compare quite well with the experimental data of Mohlmann and de Heer (1976), as well as with the theoretical results of Chung *et al* (1975). The results of Baltayan and Nedelec (1976) agree quite well with ours, both in shape and magnitude; however, their results are shifted about 4 eV to higher energies. On the other hand, although the semi-empirical results of Lavrov *et al* (1981b) agree fairly well with those of Baltayan and Nedelec (1976) at higher energies, they differ significantly from ours, as well as from the previous data, in the entire energy range. These large differences were attributed to non-Franck-Condon semi-empirical corrections by Lavrov *et al* (1981b). The same corrections have also been applied to Mohlmann and de Heer's original data (Mohlmann and de Heer, 1976), resulting in an enhancement of the ICS by a

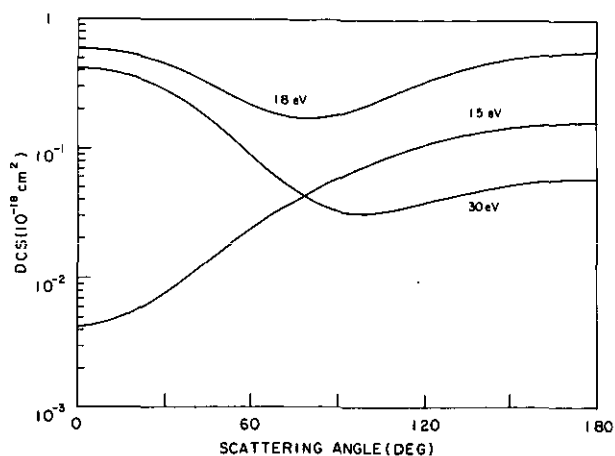


Figure 4. Unresolved differential cross sections for impact energies of 15, 18 and 30 eV.

Table 2. Differential and integral cross sections (in 10^{-16} cm^2) for the $X^1\Sigma_g^+(v=0) \rightarrow d^3\Pi_u(v'=0)$ vibronic transition of H_2 .

Angle	Energy					
	15 eV	18 eV	20 eV	25 eV	30 eV	40 eV
0.0	0.123 (-4) ^a	0.107 (-2)	0.122 (-2)	0.891 (-3)	0.533 (-3)	0.233 (-3)
10.0	0.125 (-4)	0.104 (-2)	0.118 (-2)	0.857 (-3)	0.529 (-3)	0.222 (-3)
20.0	0.135 (-4)	0.953 (-3)	0.107 (-2)	0.764 (-3)	0.460 (-3)	0.187 (-3)
30.0	0.156 (-4)	0.823 (-3)	0.909 (-3)	0.630 (-3)	0.361 (-3)	0.137 (-3)
40.0	0.195 (-4)	0.674 (-3)	0.728 (-3)	0.482 (-3)	0.256 (-3)	0.861 (-4)
50.0	0.261 (-4)	0.530 (-3)	0.552 (-3)	0.346 (-3)	0.167 (-3)	0.490 (-4)
60.0	0.361 (-4)	0.410 (-3)	0.405 (-3)	0.238 (-3)	0.104 (-3)	0.271 (-4)
70.0	0.501 (-4)	0.326 (-3)	0.297 (-3)	0.162 (-3)	0.653 (-4)	0.159 (-4)
80.0	0.681 (-4)	0.283 (-3)	0.234 (-3)	0.118 (-3)	0.442 (-4)	0.106 (-4)
90.0	0.897 (-4)	0.282 (-3)	0.211 (-3)	0.978 (-4)	0.350 (-4)	0.849 (-5)
100.0	0.114 (-3)	0.316 (-3)	0.222 (-3)	0.965 (-4)	0.328 (-4)	0.764 (-5)
110.0	0.140 (-3)	0.378 (-3)	0.259 (-3)	0.107 (-3)	0.339 (-4)	0.713 (-5)
120.0	0.167 (-3)	0.459 (-3)	0.313 (-3)	0.126 (-3)	0.370 (-4)	0.691 (-5)
130.0	0.192 (-3)	0.547 (-3)	0.376 (-3)	0.148 (-3)	0.415 (-4)	0.724 (-5)
140.0	0.215 (-3)	0.635 (-3)	0.438 (-3)	0.171 (-3)	0.466 (-4)	0.807 (-5)
150.0	0.234 (-3)	0.713 (-3)	0.495 (-3)	0.192 (-3)	0.516 (-4)	0.903 (-5)
160.0	0.248 (-3)	0.775 (-3)	0.540 (-3)	0.209 (-3)	0.553 (-4)	0.978 (-5)
170.0	0.257 (-3)	0.814 (-3)	0.568 (-3)	0.219 (-3)	0.575 (-4)	0.102 (-4)
180.0	0.259 (-3)	0.827 (-3)	0.578 (-3)	0.226 (-3)	0.582 (-4)	0.104 (-4)
ICS	0.1300 (-2)	0.610 (-2)	0.523 (-2)	0.283 (-2)	0.126 (-2)	0.393 (-3)

^a 0.123 (-4) means 0.123×10^{-4} , ext.

factor from 1.5–3 as well. In contrast, our adiabatic total ICS obtained by adding up all of our calculated vibronic transitions (from $(v=0 \rightarrow v'=0)$ to $(v=0 \rightarrow v'=3)$) differ from our vibrationally unresolved results by less than 30%. This difference can mainly be attributed to transitions to higher vibrational levels in the $d^3\Pi_u$ state, not considered here. The observed large discrepancies between our and Lavrov's results can probably be attributed to their truncation in the expansion of the scattering amplitude as a

Table 3. Same as table 2, for the $X\ ^1\Sigma_g^+ (v=0) \rightarrow d\ ^3\Pi_u (v'=1)$ vibronic transition.

Angle	Energy					
	15 eV	18 eV	20 eV	25 eV	30 eV	40 eV
0.0	0.164 (-4) ^a	0.173 (-2)	0.206 (-2)	0.153 (-2)	0.954 (-3)	0.400 (-3)
10.0	0.170 (-4)	0.168 (-2)	0.199 (-2)	0.147 (-2)	0.913 (-3)	0.381 (-3)
20.0	0.190 (-4)	0.153 (-2)	0.181 (-2)	0.131 (-2)	0.797 (-3)	0.323 (-3)
30.0	0.231 (-4)	0.132 (-2)	0.154 (-2)	0.108 (-2)	0.628 (-3)	0.238 (-3)
40.0	0.302 (-4)	0.108 (-2)	0.123 (-2)	0.827 (-3)	0.448 (-3)	0.151 (-3)
50.0	0.416 (-4)	0.847 (-3)	0.934 (-3)	0.591 (-3)	0.295 (-3)	0.871 (-4)
60.0	0.587 (-4)	0.654 (-3)	0.684 (-3)	0.405 (-3)	0.185 (-3)	0.488 (-4)
70.0	0.820 (-4)	0.523 (-3)	0.504 (-3)	0.275 (-3)	0.117 (-3)	0.289 (-4)
80.0	0.112 (-3)	0.462 (-3)	0.400 (-3)	0.198 (-3)	0.795 (-4)	0.194 (-4)
90.0	0.147 (-3)	0.470 (-3)	0.367 (-3)	0.165 (-3)	0.634 (-4)	0.154 (-4)
100.0	0.188 (-3)	0.536 (-3)	0.393 (-3)	0.164 (-3)	0.596 (-4)	0.139 (-4)
110.0	0.231 (-3)	0.647 (-3)	0.463 (-3)	0.183 (-3)	0.622 (-4)	0.130 (-4)
120.0	0.274 (-3)	0.788 (-3)	0.561 (-3)	0.215 (-3)	0.683 (-4)	0.127 (-4)
130.0	0.315 (-3)	0.942 (-3)	0.673 (-3)	0.253 (-3)	0.766 (-4)	0.133 (-4)
140.0	0.351 (-3)	0.109 (-2)	0.785 (-3)	0.292 (-3)	0.861 (-4)	0.148 (-4)
150.0	0.381 (-3)	0.122 (-2)	0.886 (-3)	0.328 (-3)	0.950 (-4)	0.164 (-4)
160.0	0.403 (-3)	0.133 (-2)	0.965 (-3)	0.356 (-3)	0.102 (-3)	0.177 (-4)
170.0	0.417 (-3)	0.139 (-2)	0.101 (-2)	0.373 (-3)	0.106 (-3)	0.185 (-4)
180.0	0.421 (-3)	0.142 (-2)	0.103 (-2)	0.379 (-3)	0.107 (-3)	0.188 (-4)
ICS	0.212 (-2)	0.101 (-1)	0.904 (-2)	0.483 (-2)	0.224 (-2)	0.692 (-3)

^a 0.164 (-4) means 0.164×10^{-4} , ext.

power series of the internuclear distance R . By choosing $j_{\max} = 1$, Lavrov *et al* (1981b) implicitly assumed a linear dependence of $a_{LM-\Lambda}(k, k', R)$ with R . In our partial-wave analysis we found that most of the T -matrix leading elements are strongly non-linear on R . Thus, it can be concluded that the non-Franck-Condon effect does not modify significantly the magnitude of the ICS in this case.

In figure 2 we show our results for the vibrational branching ratios, as given by (5). Although one can find in the literature some vibro-rotational branching ratios for the transition $X\ ^1\Sigma_g^+ \rightarrow d\ ^3\Pi_u$ of H_2 (Spindler 1969, Baltayan and Nedelec 1975, Lavrov *et al* 1981b), they are not directly comparable to ours, since our results are rotationally unresolved. Although our calculated branching ratios exhibit some oscillations at lower impact energies (15–27 eV) their magnitudes agree with the FCA predictions within 10%, except for the $0 \rightarrow 3$ transition. In this case the disagreement is around 30%. Again, these oscillations could be attributed to the non-linear dependence of $f(k, k', R')$ on R . For energies from 30–40 eV, the branching ratios reproduce quite well the Franck-Condon factors shown as horizontal bars at the LHS scale of figure 2. Further support for the approximate validity of the FCA for higher energies can also be extracted from figure 1. There, we observe, in that energy range, an approximate constant relation between our Franck-Condon and non-Franck-Condon results.

Figure 3 shows our results for the vibrationally resolved ICS for the $(0 \rightarrow 1)$ transition, as a function of the electron impact energy. Along with the data from figure 2, they can also be used to reproduce all other vibrational ICS we have calculated. Unfortunately, there is neither experimental nor theoretical results in the literature to compare with.

Table 4. Same as table 2, for the $X^1\Sigma_g^+ (v=0) \rightarrow d^3\Pi_u (v'=2)$ vibronic transition.

Angle	Energy					
	15 eV	18 eV	20 eV	25 eV	30 eV	40 eV
0.0	0.120 (-4) ^a	0.155 (-2)	0.195 (-2)	0.148 (-2)	0.927 (-3)	0.387 (-3)
10.0	0.127 (-4)	0.150 (-2)	0.189 (-2)	0.143 (-2)	0.888 (-3)	0.369 (-3)
20.0	0.151 (-4)	0.137 (-2)	0.171 (-2)	0.127 (-2)	0.778 (-3)	0.315 (-3)
30.0	0.195 (-4)	0.118 (-2)	0.146 (-2)	0.105 (-2)	0.616 (-3)	0.233 (-3)
40.0	0.267 (-4)	0.962 (-3)	0.117 (-2)	0.800 (-3)	0.443 (-3)	0.150 (-3)
50.0	0.378 (-4)	0.753 (-3)	0.884 (-3)	0.570 (-3)	0.293 (-3)	0.876 (-4)
60.0	0.539 (-4)	0.583 (-3)	0.649 (-3)	0.387 (-3)	0.186 (-3)	0.498 (-4)
70.0	0.758 (-4)	0.471 (-3)	0.481 (-3)	0.262 (-3)	0.118 (-3)	0.297 (-4)
80.0	0.103 (-3)	0.424 (-3)	0.387 (-3)	0.188 (-3)	0.810 (-4)	0.201 (-4)
90.0	0.137 (-3)	0.441 (-3)	0.361 (-3)	0.157 (-3)	0.651 (-4)	0.159 (-4)
100.0	0.174 (-3)	0.512 (-3)	0.393 (-3)	0.157 (-3)	0.618 (-4)	0.143 (-4)
110.0	0.213 (-3)	0.625 (-3)	0.467 (-3)	0.177 (-3)	0.651 (-4)	0.135 (-4)
120.0	0.252 (-3)	0.763 (-3)	0.569 (-3)	0.208 (-3)	0.718 (-4)	0.133 (-4)
130.0	0.290 (-3)	0.911 (-3)	0.682 (-3)	0.245 (-3)	0.807 (-4)	0.139 (-4)
140.0	0.322 (-3)	0.105 (-2)	0.795 (-3)	0.282 (-3)	0.906 (-4)	0.154 (-4)
150.0	0.349 (-3)	0.118 (-2)	0.895 (-3)	0.316 (-3)	0.997 (-4)	0.171 (-4)
160.0	0.368 (-3)	0.128 (-2)	0.974 (-4)	0.342 (-3)	0.107 (-3)	0.184 (-4)
170.0	0.379 (-3)	0.134 (-2)	0.102 (-2)	0.358 (-3)	0.111 (-3)	0.191 (-4)
180.0	0.383 (-3)	0.136 (-2)	0.104 (-2)	0.364 (-3)	0.112 (-3)	0.193 (-4)
ICS	0.195 (-2)	0.943 (-2)	0.882 (-2)	0.465 (-2)	0.224 (-2)	0.691 (-3)

^a 0.120 (-4) means 0.120×10^{-4} , ext.

Figure 4 shows our calculated vibrationally unresolved DCS for selected energies. A substantial change in the shape of the curves for different energies is observed. At $E = 15$ eV the DCS shows a strong backward behaviour. At $E = 18$ eV, however, the DCS is closely isotropic and shows a minimum around $\theta = 70^\circ$. Finally, for $E = 30$ eV the curve shows a maximum at the forward direction, as one should expect for higher energies.

In tables 2-5 we list our vibrationally resolved DCS for the transitions we are interested in. Once again, the lack of other results to compare with seriously limits the discussion. However, it is worth noting the very close similarity of the DCS of the various transitions for a given energy.

4. Conclusions

In this paper, we report the calculated ICS, DCS and branching ratios for the vibrational transitions $v = 0 \rightarrow v'$ ($v' = 0, 1, 2, 3$) associated with the $X^1\Sigma_g^+ \rightarrow d^3\Pi_u$ electronic transition of H_2 . Special attention was paid to the discussion about the validity of the FCA in this study. It was shown that even for low impact energy, the FCA yields reliable cross sections. This conclusion seems to contradict that of a previous publication (Lavrov *et al* 1981b). It is also shown that FCA is suitable in this region, since the calculated branching ratios for the $0 \rightarrow 0$ and $0 \rightarrow 2$ transitions lie within 10% of FCA results and for the $0 \rightarrow 3$ one the disagreement is around 30%. Above $E \approx 30$ eV, the FCA is apparently valid. A more conclusive judgment on this question could be extracted

Table 5. Same as table 2, for the $X^1\Sigma_g^+ (v=0) \rightarrow d^3\Pi_u (v'=3)$ vibronic transition.

Angle	Energy					
	15 eV	18 eV	20 eV	25 eV	30 eV	40 eV
0.0	0.689 (-5)	0.106 (-2)	0.142 (-2)	0.111 (-2)	0.696 (-3)	0.289 (-3)
10.0	0.759 (-5)	0.103 (-2)	0.137 (-2)	0.107 (-2)	0.667 (-3)	0.276 (-3)
20.0	0.968 (-5)	0.939 (-3)	0.124 (-2)	0.952 (-3)	0.586 (-3)	0.237 (-3)
30.0	0.133 (-4)	0.806 (-3)	0.106 (-2)	0.784 (-3)	0.467 (-3)	0.177 (-3)
40.0	0.188 (-4)	0.656 (-3)	0.847 (-3)	0.597 (-3)	0.338 (-3)	0.115 (-3)
50.0	0.270 (-4)	0.513 (-3)	0.642 (-3)	0.424 (-3)	0.226 (-3)	0.681 (-4)
60.0	0.387 (-4)	0.399 (-3)	0.473 (-3)	0.287 (-3)	0.144 (-3)	0.392 (-4)
70.0	0.545 (-4)	0.326 (-3)	0.353 (-3)	0.193 (-3)	0.922 (-4)	0.237 (-4)
80.0	0.744 (-4)	0.301 (-3)	0.289 (-3)	0.139 (-3)	0.639 (-4)	0.161 (-4)
90.0	0.981 (-4)	0.320 (-3)	0.275 (-3)	0.116 (-3)	0.519 (-4)	0.128 (-4)
100.0	0.125 (-3)	0.378 (-3)	0.305 (-3)	0.117 (-3)	0.498 (-4)	0.115 (-4)
110.0	0.153 (-3)	0.464 (-3)	0.365 (-3)	0.133 (-3)	0.529 (-4)	0.109 (-4)
120.0	0.181 (-3)	0.568 (-3)	0.445 (-3)	0.156 (-3)	0.586 (-4)	0.108 (-4)
130.0	0.207 (-3)	0.677 (-3)	0.533 (-3)	0.184 (-3)	0.660 (-4)	0.114 (-4)
140.0	0.229 (-3)	0.782 (-3)	0.620 (-3)	0.211 (-3)	0.740 (-4)	0.125 (-4)
150.0	0.247 (-3)	0.874 (-3)	0.696 (-3)	0.236 (-3)	0.813 (-4)	0.138 (-4)
160.0	0.259 (-3)	0.945 (-3)	0.756 (-3)	0.255 (-3)	0.868 (-4)	0.148 (-4)
170.0	0.266 (-3)	0.990 (-3)	0.794 (-3)	0.266 (-3)	0.900 (-4)	0.154 (-4)
180.0	0.268 (-3)	0.100 (-2)	0.806 (-3)	0.270 (-3)	0.910 (-4)	0.155 (-4)
ICS	0.139 (-2)	0.675 (-2)	0.662 (-2)	0.347 (-2)	0.174 (-2)	0.533 (-3)

^a 0.689 (-5) means 0.689×10^{-5} , ext.

from the comparison of more sensitive quantities, as the DCS, with experimental or other theoretical results. The lack of such results severely limits the discussion.

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