

Rotationally inelastic scattering of H_2 ($1\Sigma_g$, $v = 0$) molecule due to He atom

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Abstract : The He- H_2 interaction potential surface as obtained by Lesar [1] has been used to describe the inelastic collision between the two at the thermal (0.05–0.5 eV) energies. The centrifugally decoupled exponential distorted wave (CDEDW) method has been used to calculate total and partial cross sections for excitation and de-excitation of a large number of rotational transitions in ortho and para hydrogen molecule. The results have been analysed in the light of accurate cross sections reported earlier. Also, R-T energy transfer mechanism has been discussed in detail on the basis of the calculated partial excitation cross sections.

Keywords : CDEDW approximation, close-coupling method, total/partial cross sections

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1. Introduction

The collisional study of the He- H_2 system have been done extensively using different methods as well as interaction potentials. Zarur and Rabitz [2] derived an approximate close-coupling equations for scattering starting with an effective interaction potential between two atomic molecules (Roberts [3]). They calculated the scattering cross sections with the program developed by Gordon [4] at the incident energies ≤ 0.86 eV. While results of integral cross section for $j = 1$ to 3 transition were in quite good agreement with the previously calculated close-coupling results (Johnson and Secrest [5]), those for $j = 0$ to 2 were somewhat in error. McGuire and Kouri [6] have derived coupled scattering equations and calculated the cross sections for only those transitions for which the initial rotational state

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quantum number is zero. They have also employed Robert's interaction potential in their calculation. Cross [7] have used Krauss and Mies [8] potential surface averaged over the vibrational coordinates (McGuire and Micha [9]) whereas, Jolicard and Bonamy [10] have done their calculation using Gordon and Secrest's [11] potential in which the vibrational degrees of freedom are ignored.

Within the framework of the limited basis set and for simple systems the close-coupling (CC) method of course, is the most reliable dynamical procedure to calculate the scattering cross sections [12]. The problem with close-coupling method however, is that it is expensive even for simple systems and prohibitively cumbersome for moderately large ones. Therefore, approximation methods will continue to find relevance in the context of atom-molecule collisions. In the present work, CDEDW method has been used to calculate the partial and total integral cross sections for several $j-j'$ transitions in He-H₂ collision in the energy range of 0.05 to 0.5 eV. The interaction potential given by Lesar [1] has been used. The calculated results are compared with the close-coupling results of Zarur and Rabitz [2] as well as those of McGuire and Kouri [6]. The R-T energy transfer behaviour in He-H₂ collisions have also been studied.

2. Interaction potential

The interaction potential used in the present work is the modified from of the Lennard Jones [12, 6] potential surface and is given as ;

$$V(R, \theta) = V_0(R) + V_2(R)/P_2(\cos \theta)$$

$$\text{with } V_0(R) = \epsilon [R_m / R]^{12} - 2(R_m / R)^6,$$

$$\text{and } V_2(R) = \epsilon' [(R'_m / R)^{12} - 2(R'_m / R)^6],$$

as the isotropic and the angle dependent part of the interaction potential. The terms and symbols in the above equation have their usual meaning. Their values are given as follows [1] :

$$\epsilon = 0.488 \times 10^{-4} \text{ a.u.} \quad R_m = 6.50 \text{ a. u.}$$

$$\epsilon' = 0.039 \times 10^{-4} \text{ a.u.} \quad R'_m = 6.95 \text{ a. u.}$$

$V_2(R)$ is sensitive to the anisotropy parameters relating to the dispersion energy of Tang and Toennies [13]. The isotropic part $V_0(R)$ agrees much better with experimental results of Shafer and Gordon [14] and Gengenbach and Ch Hahn [15] whereas, angle dependent part $V_2(R)$ agrees with the theoretical calculations of Meyer *et al* [16]. This interaction potential is claimed to be quite accurate and is better in many aspects than the other model potentials given so far.

3. Theory and computation

In the body fixed coordinate system the basic set of coupled differential equations for the scattering of a structureless atom by a diatomic molecule in its electronic (Σ) and vibrational ($v = 0$) ground state takes the form [17-19] :

$$\begin{aligned}
 & \left[(d^2/dR^2) + k_{j'}^2 - (C_{\Omega\Omega'}^{Jj'}/R^2) - U_{j',j'}^{\Omega'}(R) \right] \psi_{j'\Omega}^{Jj\Omega}(R) \\
 & = \left(C_{\Omega,\Omega'-1}^{Jj'}/R^2 \right) \psi_{j',\Omega'-1}^{Jj\Omega}(R) + \left(C_{\Omega',\Omega'+1}^{Jj'}/R^2 \right) \psi_{j',\Omega'+1}^{Jj\Omega}(R) \\
 & + \sum_{j'' \neq j'} U_{j',j''}^{\Omega'}(R) \psi_{j''\Omega}^{Jj\Omega}(R), \quad (1)
 \end{aligned}$$

where the helicity quantum numbers Ω correspond to the projection of the total angular momentum onto the body-fixed z axis, J the total and j, j' are the rotational angular momentum quantum numbers. The CDEDW approximation involves neglecting the off-diagonal matrix elements of the orbital angular momentum operator, *i.e.* the coupling terms involving $C_{\Omega,\Omega'-1}^{Jj'}$ and $C_{\Omega',\Omega'+1}^{Jj'}$ on the right hand side of the eq. (1). This approximation is also used in the popular coupled state [6] p-helicity decoupling [17] method. After neglecting these coupling terms, there still remains the coupling terms arising from the interaction potential (*i.e.* the $U_{j',j'}^{\Omega'}(R)$ terms). This residual coupling is treated using the distorted wave or exponential distorted wave approximation.

The distorted waves are obtained by solving the uncoupled differential equation viz;

$$\left[(d^2/dR^2) + k_j^2 - (C_{\Omega\Omega}^J/R^2) - U_{jj}^{\Omega}(R) \right] \phi_{j\Omega}(R) = 0 \quad (2)$$

with the boundary conditions.

$$R\phi_{j\Omega}(R) \underset{R \rightarrow 0}{\sim} 0,$$

and

$$\phi_{j\Omega}(R) \underset{R \rightarrow \infty}{\sim} \sin(k_j R - 1\pi/2 + \eta_{j\Omega}), \quad (3)$$

where the number l is determined in such a way that :

$$l(l+1) = C_{\Omega\Omega}^J = J(J+1) + j(j+1) - 2\Omega^2. \quad (4)$$

Using the distorted waves the action matrix is then calculated as,

$$A_{jj}^{J\Omega} = 0,$$

$$A_{j'j}^{J\Omega} = -2/(k_j k_{j'})^{1/2} \int_0^\infty \phi_{j'\Omega}(R) U_{j'j}^{\Omega}(R) \phi_{j\Omega}(R) dR, \quad (5)$$

for $j' \neq j$.

The S -matrix may then be evaluated using exponential distorted wave (CDEDW) approximation as,

$$S_{j'j}^{J\Omega} = e^{i\eta_{j'\Omega}} \left[e^{iA_{j'j}^{J\Omega}} \right]_{j'j} e^{i\eta_{j\Omega}}. \quad (6)$$

The equations and S matrices for positive and negative Ω are equal within the centrifugally decoupled approximation and need therefore only be calculated for $\Omega \geq 0$. The cross section is then given within this centrifugally decoupled formalism by the formula [17] :

$$\sigma_{j' \leftarrow j} = \pi/k_j^2(2j+1) \sum (2J+1) \sum_{\Omega} \left| \delta_{j'j} - S_{j'j}^{J\Omega} \right|^2 \quad (7)$$

and the dimensionless partial cross section is given by :

$$P_{j' \leftarrow j}^J = (2J+1)/(2j+1) \sum \delta_{j'j} - S_{j'j}^{J\Omega} \quad (8)$$

The calculations have been carried out using the computer program developed by Balint Kurti *et al* [20] after a slight modification and its adoption for the MIGHTY FRAME-II computer. The value of R_{\min} and R_{\max} (lower and upper limits of integration in eq.(5)) has been set at 3.0 Å and 80.0 Å after a large number of trial and errors keeping the convergence in cross sections within 1% . The value of Ω has been taken to be two. With the proper adjustment of the control parameters (*viz*; EPS = 0.002 and CWKBJ = 0.01 (see Balint Kurti *et al* [20])) the partial cross sections are obtained with a numerical accuracy of better than 2%.

4. Results and discussion

The calculated total and partial cross sections for the 0-2, 0-4, 0-6, 2-4, 4-6, 1-3, 1-5 and 3-5 rotational transitions of H₂ molecule due to He atom in the energy range of 0.05 to 0.5 eV are shown in Figures 1, 2(a), 2(b), 3(a) and 3(b). The corresponding close-coupling results of the total cross sections due to others [2,6] are also plotted for the sake of comparison. The excitation cross sections for all the transitions increase steeply with incident energy near the threshold and gradually acquire plateaus of different shapes for different transitions. This nature of the cross sections curve for 0-2 and 1-3 transitions resembles quite well the earlier reported CC cross sections. In both of them the agreement with the CC cross sections is excellent particularly, in the very low energy region near the threshold. As expected, it deviates slightly with an increase of the energy. Excitation cross sections for the 0-2 transition are in better agreement with McGuire and Kouri as compared to Zarur and Rabitz's CC results.

On the basis of the above mentioned agreements found between the CC and CDEDW cross sections regarding the 0-2 and 1-3 rotational transitions the accuracy of other cross sections reported in this paper can safely be claimed. The ratios of the excitation to de-excitation cross section *viz*; $\sigma(j-j')/\sigma(j'-j)$ at different energies are given in Table 1. The detailed balance condition is very poor at the lower energies which of course, improves as the incident energy increases.

The partial cross sections *viz*; $\sigma^E(j)$ regarding the 0-2 and 1-3 transitions at the incident energies of 0.125, 0.199, 0.312 and 0.499 eV are plotted in Figures 2(a) and 3(a). The partial cross sections *viz*; $\sigma^J(E)$ at $J = 0, 5, 10, 20$ and 50 are shown in Figures 2(b) and 3(b) for para and ortho hydrogen, respectively. Total cross sections can be understood in terms of

these partial cross sections. These results would be discussed in detail while analysing the $R-T$ energy transfer processes.

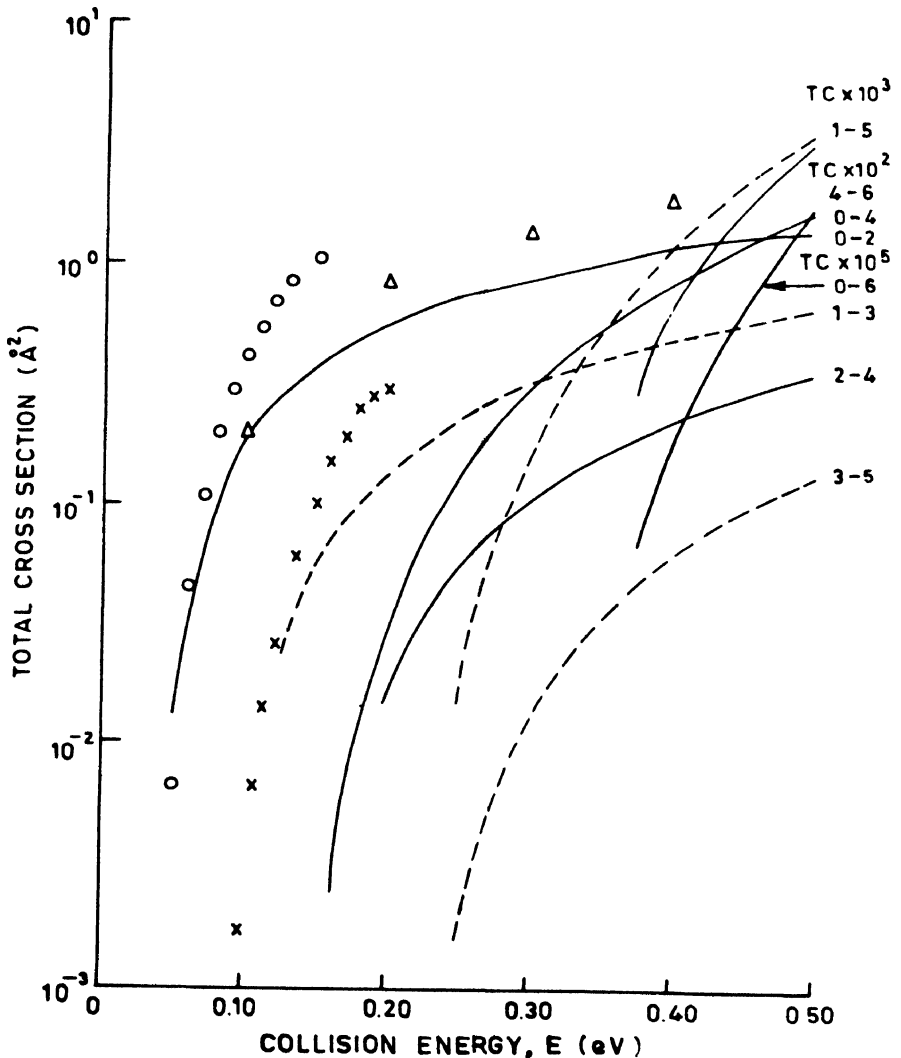


Figure 1. Logarithmic plots of rotational cross sections (in \AA^2) vs. collision energy (in eV)
 — present work.
 O, x Zarur and Rabitz [2].
 Δ McGuire and Kouri [6]

It is invariably noticed in Figures 2(a) and 3(a) that the partial cross sections show a significant peak at a certain value of J (say J_{\max}^1) followed by a second comparatively much reduced peak at a higher value of J (say J_{\max}^2) (see inset of the Figures 2a and 3a). This smaller peak (J_{\max}^2) is caused due to the long range anisotropic part of the interaction potential. The value of J_{\max} increases with the increase of the incident energy *i.e.* larger the translational incident energy, larger will be the value of J_{\max} at which the transfer takes place

most efficiently. Also, the relative magnitude of the excitation cross sections at J_{\max} increases with energy. There is smooth variation of the partial cross section with energy at a fixed J (see Figures 2b and 3b).

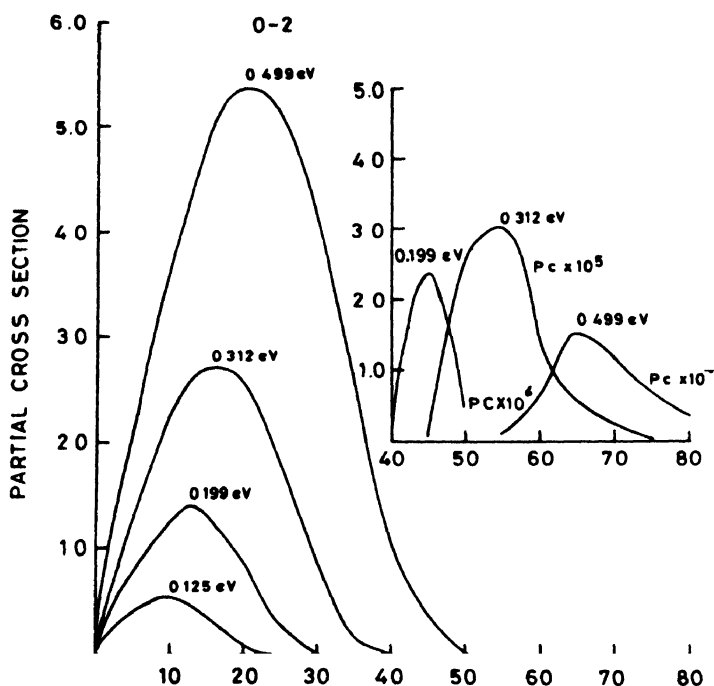


Figure 2. (a) Partial cross sections vs J [$\sigma^E(J)$] for para hydrogen.

Partial cross sections are found to increase with different slopes after the threshold. The slope increases with increase of the J value. It is seen that as energy increases, the main peak (J_{\max}^1) slightly shifts to a higher J value for para as well as ortho hydrogen. This is in accordance with a simple model proposed by Shapiro and Tamir [17], in which a transition is most likely to occur for a J value which corresponds to a minimal radial kinetic energy. Rotational transition is expected to be more effective if the radial forces acting on the rotating particles are minimal, causing particles to remain at a fixed distance from each other for a reasonably long duration. The results of our calculation for the He-H₂ like He-N₂, Ne-N₂ [21,22] systems conform with this model.

An expression for estimating J_{\max}^1 approximately has been determined by Shapiro and Tamir [17] on the basis of the long range effective interaction potential containing the attractive short range anisotropy and the repulsive centrifugal component in it, which is given as,

$$\left[\left\{ E - B j_m (j_m + 1) \right\} (3\mu) (6\mu b j_m)^{1/2} \right]^{1/3}, \quad (9)$$

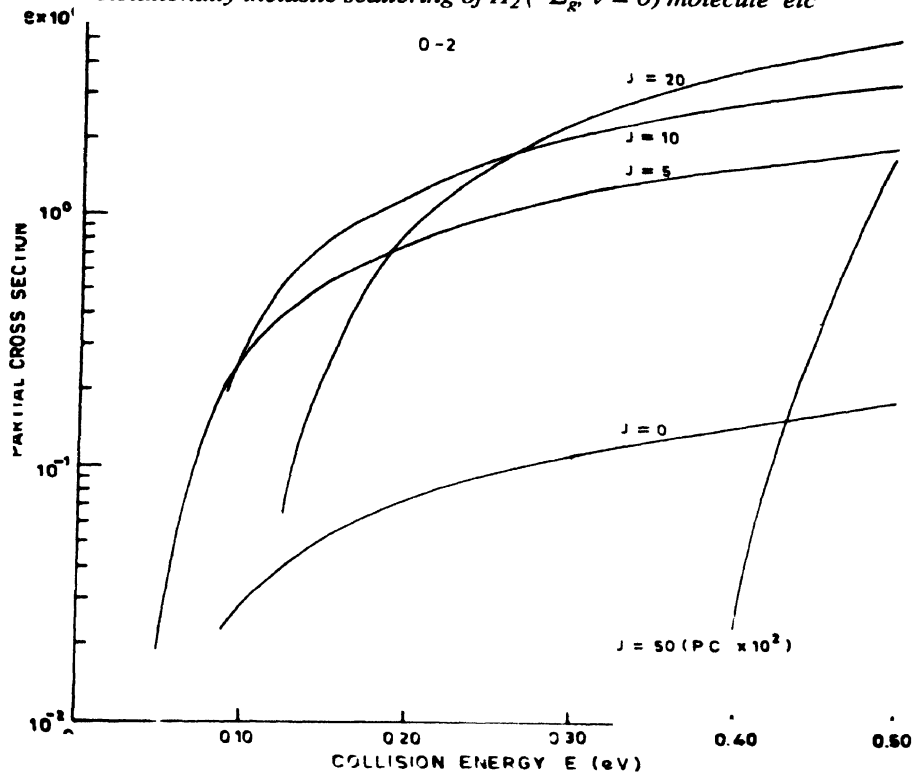


Figure 2. (b) Partial cross sections vs $E [\sigma^E(E)]$ for para hydrogen.

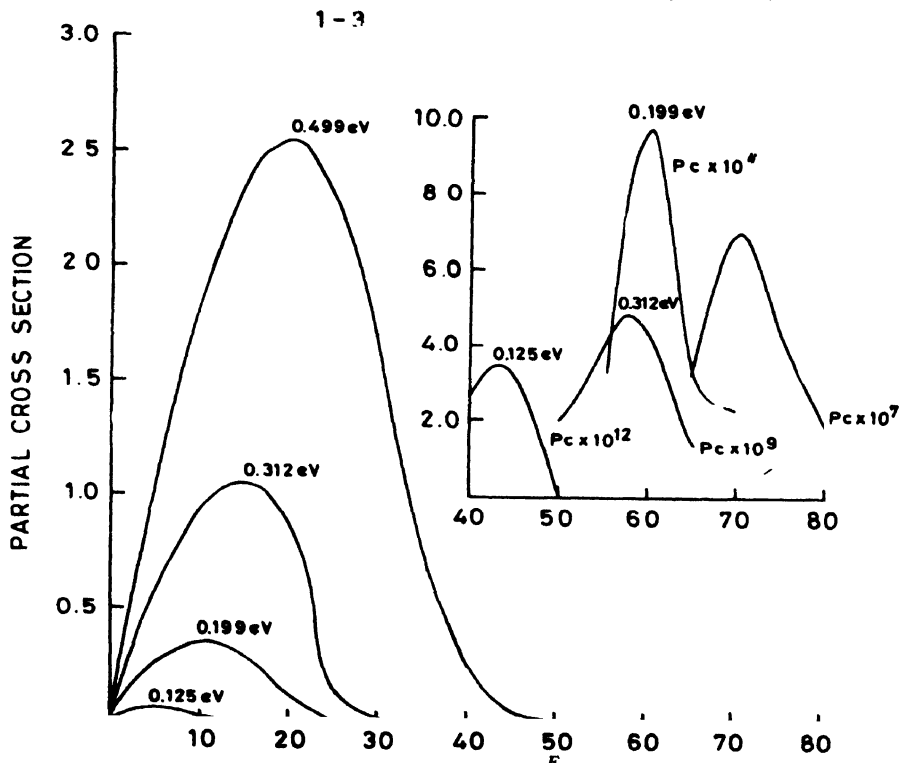


Figure 3. (a) Partial cross sections vs $J [\sigma^E(J)]$ for ortho hydrogen.

where E is the incident energy, j_m is maximum of j and j' , μ is the reduced mass and b_j the coefficient of the short-range attractive potential. The values of the J_{max}^I as obtained on the

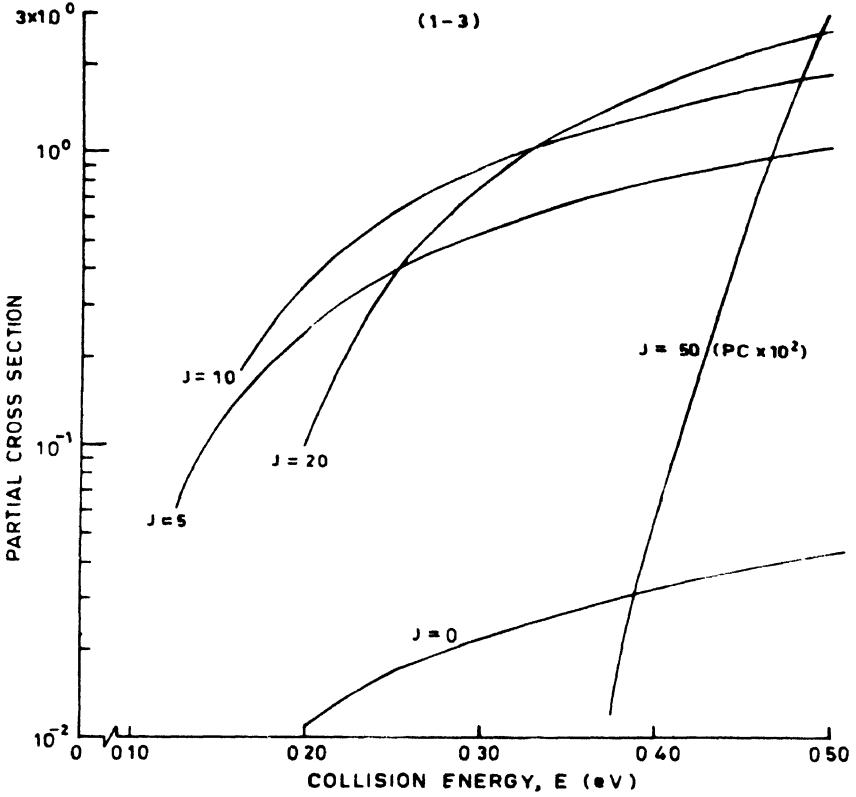


Figure 3. (b) Partial cross sections vs $E [\sigma^I(E)]$ for ortho hydrogen.

basis of the above expression at various energies are tabulated in Table 2 along with the corresponding values obtained from the partial cross section curves [see Figures 2(a) and 3(a)]

Table 1. Ratio of excitation to de-excitation cross sections for He-H₂.

| Energy in eV | $\sigma(0-2)/$ $\sigma(2-0)$ | $\sigma(0-4)/$ $\sigma(4-0)$ | $\sigma(2-4)/$ $\sigma(4-2)$ | $\sigma(1-3)/$ $\sigma(3-1)$ | $\sigma(1-5)/$ $\sigma(5-1)$ | $\sigma(3-5)/$ $\sigma(5-3)$ |
|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.049 | 0.637 | — | — | — | — | — |
| 0.125 | 3.255 | — | — | 0.798 | — | — |
| 0.199 | 3.910 | 2.456 | 0.628 | 1.418 | — | — |
| 0.312 | 4.302 | 4.812 | 1.118 | 1.763 | 1.161 | 0.658 |
| 0.409 | 4.454 | 5.728 | 1.893 | 1.893 | 1.731 | 0.914 |
| 0.499 | 4.562 | 6.383 | 1.985 | 1.985 | 2.129 | 1.073 |

The J_{\max}^1 at 0.499 eV is the same for para and ortho hydrogen whereas at the energies below it, J_{\max}^1 is higher for para than that for ortho hydrogen (see Table 2).

Table 2. Position of J_{\max}^1 and J_{\max}^2 at different energies.

| Energy in eV | J_{\max}^1 | | J_{\max}^2 | | J_{\max}^1 / J_{\max}^2 | | J_{\max}^1 | | J_{\max}^2 | | J_{\max}^1 / J_{\max}^2 | | | | | |
|-----------------|--------------|----------|--------------|----------|---------------------------|----------|--------------|----------|--------------|----------|---------------------------|----------|----|-------|----|-------|
| | 0-2 + | 0-4 * | 2-4 + | 0-2 + | 0-2 + | 1-3 + | 1-5 * | 3-5 + | 1-3 + | 1-3 + | 1-3 + | 1-3 + | | | | |
| 0.125 | 10 | 10 | | 7 | 60 | 0.167 | 5 | 9 | | | 43 | 0.111 | | | | |
| 0.199 | 13 | 13 | 5 | 9 | 5 | 11 | 45 | 0.289 | 10 | 12 | | 10 | 60 | 0.167 | | |
| 0.312 | 17 | 16 | 10 | 13 | 10 | 14 | 55 | 0.309 | 15 | 15 | 10 | 12 | 15 | 14 | 58 | 0.259 |
| 0.499 | 20 | 19 | 15 | 17 | 15 | 18 | 65 | 0.308 | 20 | 18 | 10 | 16 | 15 | 18 | 70 | 0.286 |

+ as obtained from present calculation.

* as obtained using eq. (9) [17].

The peak cross sections corresponding to J_{\max}^1 for para $\sigma(0-2)$ and ortho $\sigma(1-3)$ hydrogen molecule are given in Table 3 at four energies. The excitation cross sections for 0-2 transition are larger than that of the 1-3 transition. The ratio of $\sigma(0-2)$ to $\sigma(1-3)$ decreases from 9.82 at 0.125 eV to 2.09 at 0.499 eV. The two cross sections tend to be the same towards higher energy. It shows that the initial rotor state angular momentum affects its excitation probability particularly, at low collision energies for a given angular momentum transfer ($\Delta j = 2$ in this case).

The energy transfer behaviour in the said collision process as reflected of the cross sections for $\Delta j = 2$ transition has been discussed on the basis of their relative values. The values of the energy gap $\Delta E = E_{j'} - E_j$ and the corresponding excitation cross sections are given in Table 4 at the incident energy of 0.40 eV. The results show the same kind of

Table 3. Ratio of $\sigma(0-2)/\sigma(1-3)$ at J_{\max}^1 .

| Energy in eV | $\sigma(0-2)$ in \AA^2 at J_{\max}^1 | $\sigma(1-3)$ in \AA^2 at J_{\max}^1 | $\sigma(0-2)/\sigma(1-3)$ at J_{\max}^1 |
|-----------------|--|--|--|
| 0.125 | 0.550 | 0.056 | 9.820 |
| 0.199 | 1.292 | 0.357 | 3.690 |
| 0.312 | 2.704 | 1.056 | 2.560 |
| 0.499 | 5.361 | 2.588 | 2.090 |

behaviour as already discussed by Zarur and Rabitz [2]. The magnitude of the cross section varies inversely with ΔE . According to this, $\sigma(0-4)$ should be greater than $\sigma(4-6)$ since

$E_4 - E_0 = 0.1450$ eV while $E_6 - E_4 = 0.1595$ eV. An examination of Figure 1 for $E > 0.40$ eV shows that $\sigma(4-6)$ is slightly larger than $\sigma(0-4)$. It is because [2] $0-4$ transition is a first

Table 4. Energy transfer behaviour of the $\Delta J = 2$ cross sections.

| Transition | Cross sections in \AA^2 at 0.40 eV | $\Delta E = E_{J'} - E_J$ |
|------------|--|---------------------------|
| 0-2 | 1.1656 | 0.0435 |
| 1-3 | 0.4925 | 0.0725 |
| 2-4 | 0.2227 | 0.1015 |
| 3-5 | 0.0617 | 0.1305 |
| 4-6 | 0.0617 | 0.1595 |
| 5-7 | — | 0.1825 |
| 0-4 | 0.8523×10^{-2} | 0.1450 |
| 1-5 | 0.1218×10^{-2} | 0.2030 |
| 2-6 | 0.7532×10^{-4} | 0.2610 |

order forbidden and its cross section is reduced in magnitude due to second order coupling effect. Similar argument can be applied to $\sigma(1-5)$ and $\sigma(5-7)$ at a energy sufficiently far from the threshold.

5. Conclusions

The centrifugally decoupled exponential distorted wave (CDEDW) [20] method used in the present work, substantially reduces the computational efforts. The $R-T$ energy transfer mechanism in the He-H₂ system for ortho and para hydrogen has been discussed on the basis of partial cross sections. With the value of the propagation control parameter EPS = 0.002 in the computer program and without using the WKB approximation, a relative accuracy of better than 1% in the calculated partial cross sections has been achieved.

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