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Low Energy Electron – H_2 Molecule Scattering I: Elastic and Rotational Excitation

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Abstract Vibrationally averaged rotationally elastic and inelastic cross sections for electron-H_2 scattering are calculated in the 0.6 - 15 eV energy range. In the present study, the interaction potential formed by static, exchange and polarization contributions is employed to solve the scattering equations at seven internuclear distances. The cross sections, obtained via an adiabatic nuclei approximation, are compared with available experimental data. The good agreement suggests that the present method can be extended to more complex systems.

1. INTRODUCTION

Electron scattering by gaswus atoms and molecules has been a subject of considerable theoretical[1] and experimental[2] investigation during the past decade. Undoubtedly, the hydrogen molecule is certainly the most studied target for a number of reasons: because of its simplicity, some sophisticate ab-initio[3-5] calculations are computationally feasible for H_2 whereas they are practically intractable for more complicated systems. Therefore the electron-H_2 interaction becomes an indispensable test for most theoretical formulations. On the other hand, because of its small reduced mass, the vibrational and rotational energy levels of this molecule are sufficiently spaced and this particularity allows the experimental determination[6-9] of the cross sections for pure elastic scattering, pure rotation excitation and vibrational-rotational excitation of the molecule by electron impact in a wide energy and angular range. This kind of experimental study is

also difficult to be performed for more complicated molecular systems.

Regarding the elaçtic and rotational exeitation cross sections, most of the calculations have been performed[10-12] at the equilibrium internuclear distance of H_2. However, the recent experimental results of the vibrational-rotationally elastic and vibrational-elastic rotational-excitation cross sections justify a more elaborated calculation where the vibrational averaging can be introduced.

In the present study, the vibrationally resolved differential and integral cross sections for elastic and rotational excitation scattering are calculated and presented in the energy range between 0.6-15 eV.

In section 2, we briefly present the theories used. The calculated results are compared against experimental data in section 3. This comparison serves as a check to the theory used. Finally, in section 4 we present the conclusion.

2. THEORY

In the fixed-nuclei (FN) body-frame (BF) formulation, the single-channel Schrödinger equation for electron molecule scattering can be written as

$$(\nabla^2 + k^2)\Psi = U_{int}\,\Psi \tag{1}$$

where k^2 is the energy of the incident electron in rydbergs and U_{int} represents the effective interaction potential betweenelectron and molecule. In this calculation, the interaction potential is composed by the static, exchange and polarization contributions. In the single center partia1 wave expansion, eq.1 can be reduced to a set of coupled radial equations. The expansion is truncated at some number of channels N, which must be determined through convergence studies. The resulting set of N coupled equations has the form

$$\left| \frac{d^2}{dr^2}\vec{1} - \frac{1}{r^2}\vec{L} + k^2\vec{1} \right| \vec{f}(r) = \vec{U}(r) \tag{2}$$

where $\vec{f}$ is an $N\times N$ solution rnatrix, the columns of which correspond to

the N linearly independent solution vectors that are regular at the origin. The solution matrix depends on the good quantum number Λ, which corresponds to the projection of the electron orbital angular momentum along the internuclear axis vector R. However, this label is omitted since the equations are not coupled in A.

In eq. (2), $\vec{L}$ is a diagonal $N\times N$ matrix and has the elements $\ell(\ell+1)\delta_{\ell\ell'}$, $\vec{1}$ is the $N\times N$ unit matrix and $\vec{U}$ is an $N\times N$ potential matrix with its $\ell\ell'$ element, defined as

$$U_{\ell\ell'} = \langle y_{\ell}^{\Lambda}|U|y_{\ell'}^{\Lambda}\rangle \tag{3}$$

Eq. (2) is solved under the usual boundary condition at the origin

$$f_{\ell\ell o}\ (r=0)=0 \tag{4}$$

and K-matrix asymptotic boundary condition i.e.,

$$f_{\ell\ell o}(r) \underset{r\to\infty}{\sim} \sin(kr - \tfrac{\ell\pi}{2})\delta_{\ell\ell o} + K_{\ell\ell o}^{\Lambda} \cos(kr - \tfrac{\ell\pi}{2}) \tag{5}$$

The coupled eq. (2) in the BF-FN theory are solved numerically using an integral-equation algorithm .

In this case, eq. (2) is converted into a coupled integral form

$$\vec{f}(r) = \vec{G}^1(r) - \int_0^\infty G^{12}(r_<,r_>)\vec{U}(r')\vec{f}(r')\,dr' \tag{6}$$

G^1 and G^2 are respectively

$$[\vec{G}^1(r)]_{\ell\ell'} = \hat{j}_\ell(kr)\delta_{\ell\ell'} \underset{r\to\infty}{\sim} \sin(kr - \tfrac{\ell\pi}{2})\delta_{\ell\ell'} \tag{7a}$$

and

$$[\vec{G}^2(r)]_{\ell\ell'} = \frac{1}{k}\,\hat{n}_\ell(kr)\delta_{\ell\ell'} \underset{r\to\infty}{\sim} \frac{1}{k}\cos(kr - \tfrac{\ell\pi}{2})\delta_{\ell\ell'} \tag{7b}$$

The numerical solution of the eq. (6) has been discussed[13] elsewhere. It is important to note that if the interaction potential is fully local, eq. (6) can be solved non-iteratively, however if the non local exchange terms are treated exactly, an iterative integral-

equation algorithm should be used. Morrison[13] suggested that eq. (2) can be written as

$$\left(\frac{d^2}{dr^2}\vec{\mathbb{I}} - \frac{1}{r}\vec{L} + k^2\vec{\mathbb{I}}\right)\vec{f}(r) = 2\left|\vec{V}(r) + \vec{W}(r)\vec{f}^{-1}(r)\right|\vec{f}(r) \tag{8}$$

where $\vec{V}(r)$ is the local part of the interaction potential and $\vec{W}(r)$ is a non-local exchange term expressed as

$$\vec{W}(r) = \int_0^\infty \vec{K}(\vec{r},r')\vec{f}(r')dr' \tag{9}$$

To solve eq. (8), the zeroth-order solution of $\vec{f}(r)$ is obtained using only the local part of the interaction potential, i.e.,

$$\left[\frac{d^2}{dr^2}\vec{\mathbb{I}} - \frac{1}{r^2}\vec{L} - 2\vec{V}(r) + k^2\vec{\mathbb{I}}\right]\vec{f}_0(r) = 0 \tag{10}$$

then the mth iteration for the physical solution is calculated from the $(m-1)^{st}$ iterate as

$$\left|\frac{d^2}{dr^2}\vec{\mathbb{I}} - \frac{1}{r^2}\vec{L} - 2\vec{V}(r) + k^2\vec{\mathbb{I}}\right|\vec{f}_m(r) = \left|\vec{W}_{m-1}(r)\vec{f}_m^{-1}(r)\right|\vec{f}_m(r) \tag{11}$$

and $\vec{W}\vec{f}^{-1}$ provides a local form of the exchange term. Eq. (11) can be solved in a usual manner. However, expressing the exchange contribution in a local form $\vec{W}\vec{f}^{-1}$ implies that one should deal with the singularities which occur at the origin and at the nodes of the scattering function. To avoid these numerical difficulties we have introduced a modified version in which an auxiliary exchange contribution term is defined as

$$\tilde{W}(r) = \int_0^\infty \vec{K}(r,r')\vec{u}(r')dr' \tag{12}$$

where the *auxiliary function* $\vec{u}(r)$ is related to the *physical solution* by a constant transformation

$$\vec{f}(r) = \vec{u}(r)\left[\underline{I}^2(\infty)\right]^{-1} \tag{13}$$

as originally defined by Morrison.

In our calculation, $\tilde{W}(r)$ is treated as an inhomogeneous term to solve the integral equation.

$$u(r) = \vec{G}^1(r)\vec{I}^2(r) - \vec{G}^2(r)\vec{I}^1(r) \tag{14}$$

where I^1 and I^2 are the auxiliary matrices defined by

$$\vec{I}^i(r) = \vec{\mathbb{I}}\,\delta_{i2} + \int_0^r \vec{G}^i(r')\vec{U}(r')\vec{u}(r')dr' \tag{15}$$

and the K-matrices can be determined directly from the asymptotic values of the auxiliary I-matrices as

$$\vec{K} = -\vec{k}^{-1/2}\,\vec{I}^1(\infty)\,|\vec{I}^2(\infty)|^{-1}\,\vec{k}^{-1/2} \tag{16}$$

where

$$k^{-1/2} = k^{-1/2}\,\vec{\mathbb{I}}$$

In practice, the zeroth-order solution of the auxiliary function $\vec{u}^{(0)}(r)$ is obtained solving eq.(14), using only the local part of the interaction potential. $\vec{u}^{(0)}(r)$ is then used to calculate the non-local exchange contribution through eq. (12) and the iterative procedure goes through. The mth-iteration physical solution $\vec{f}(r)$ and the k- matrices are obtained using the mth iteration $u^m(r)$ and eqs.(13) and (16). In the static-exchange approximation the present integral equation algorithm reproduces the K-matrices elements obtained by other theoretical methods[14].

In the present study, the FN-BF scattering equations are solved for seven internuclear distances from 0.8 to 2.0 a_0 with the interval of 0.2 a_0. At each internuclear distance the static potential isderived from a SCF wavefunction for H_2 which is calculated using a $5s\,2p^{14}$ Cartesian Gaussian basis. With this basis, one obtains the ground state SCF -energy at the equilibrium distance ($R_{eq} = 1.4006\ a_0$) of 1.1330 a.u. The Hartree-Fock limit for this geometry is -1.13363 a.u.. Because of the role played by the electron-quadrupole interaction in the rotational excitation, the R-dependent quadrupole moment of the molecule $q(R)$ is of particular importance. In table 1, we show the obtained resultsfor $q(R)$

Tab.1 - The quadrupole moments of H_2 as a function of internuclear distances

R (a_0)	Q (a_0^3)	$Q^{K.W.}$ (a_0^3)
0.8	0.16290	0.1714
1.0	0.2481	0.2571
1.2	0.34607	0.3536
1.4	0.45402	0.4547
1.6	0.57021	0.5646
1.8	0.69249	0.6710
2.0	0.81732	0.7705

K.W.: Kolos and Wolniewicz (ref. 19).

as a function of the internuclear distances. These values compare favorably with the theoretical results calculated by Kolos and Wolniewicz[15], using a sophisticated configuration-interaction method.

In the low energy range ($E \lesssim 13.6$ eV), the inclusion of the polarization potential is essential to calculate the electron-molecule scattering cross sections. Recently, a parameter-free non-penetration polarization potential of H_2 has been calculated by Gibson and Morrison[16-17]. At the equilibrium distance, the authors performed an analytic fit[16] of this potential. In the present study, this analytically fitted form is used to solve the scattering equations for all internuclear distances, however varying only the dipole polarizability of H as a function of R.

The scattering equations are solved for eight symmetries

$$\Sigma_{g,u}\ ,\ \pi_{g,u}\ ,\ \Delta_{g,u} \text{ and } \Phi_{g,u}$$

The number of the partial-wave expansion depends on the incident energy and is truncated at $R_{max=12}$. For the sake of computational time, the exchange effect is treated exactly only for $R \leq 6$, through the iterative procedure; however, for $R > 6$, the K-matrix elements are obtained using only the local part of the potential, through the non-iterative method.

This approximation is expected to be reasonable since the classical turning point of the scattered electron for $R > 6$, because of the centrifugal barrier, is located in the region where the target electronic density is low, therefore the exchange effect is small.

In fact, in some test runs, one notes that the K-matrix elements $K_{\ell\ell'}$ for R, R' $\geq$ 6 obtained in this manner differ only a few percent from those calculated iteratively.

Having calculated the FN-BF K-matrices for each internuclear distance, the corresponding R-dependent T-matrices are obtained by

$$\vec{T} = 2\vec{K}(1 - i\vec{K})^{-1} \tag{17}$$

and consequently, the vibrational excitation T-matrix elements $T_{\nu\nu'}$ are obtained via a R-integration in the interval between $0.6 \leq R \leq 2.4\, a_0$ using a Simpson gradrature with *200* grid points. The ground state vibrational wavefunction χ_0 needed in the R-integration is calculated numerically with the Cooley[18] algorithm, using the H_2 ground state ($\chi^1 \Sigma_g^+$) potential curve calculated by Kolos and Wolniewicz[19]. The errors caused by the interpolation of the T-matrix elements and the numerical integration are believed to be small since the T-matrix elements vary smoothly with R.

The vibrationally elastic differential cross sections are calculated in a j_t-basis expansion[20], in which the components of the scattering amplitudes are classified according to the angular momentum transferred during the collision.

$$\vec{j}_t = \vec{\ell} - \vec{\ell}' \tag{18}$$

With this change of representation, the electron-molecule scattering cross sections can be expressed as an incoherent sum over j_t and are more efficiently evaluated than in the usual manner, thus

$$\frac{d\sigma}{d\Omega} = \sum_{j_t} \left(\frac{d\sigma}{d\Omega}\right)_{j_t} \tag{19}$$

where

$$\left(\frac{d\sigma}{d\Omega}\right)_{j_t} = \frac{\pi}{k^2} \sum_{m_t m_t'} (2j_t + 1)^{-1} \left| B^{j_t}_{m_t m_t'}(\Omega) \right|^2 \tag{20}$$

and

$$B^{j_t}_{m_t m_t'}(\Omega) = \sum_{\ell\ell'\Lambda} (-1)^{\Lambda} (i)^{\ell-\ell'} (2\ell+1)^{1/2} T^{\Lambda}_{\ell\ell'}$$

$$(\ell-\Lambda, \ell'\Lambda | j_t m_{t'})(\ell_0 0, \ell' m_t | j_t m_t) Y_{\ell m_t}(\Omega) \tag{21}$$

where m_t and $m_{t'}$ are projections of j_t along the laboratory andmolecule axes, respectively.

To calculate the rotational excitation cross sections, the adiabatic-nuclei approximation (AN) has been used in the present study. It has been shown recently that the AN approximation breaks down at incident energy near the rotational threshold. Nevertheless, the energy range covered in this work (0.6 - 15 eV) is far enough from this region and the AN approximation is expected to be valid[10] except at very small angles. Within the AN approximation, the rotational excitation cross sections can be expressed as

$$\left(\frac{d\sigma}{d\Omega}\right)_{j\to j'} = \frac{k_{j'}}{k_j} \sum_{j_t} c(jj'j_t) \left(\frac{d\sigma}{d\Omega}\right)_{j_t} \tag{22}$$

where $c(j,jj'_t)$ is an algebraic coefficient, and for transitions involving a $^1\Sigma$ state of a linear molecule, $c(jj'j_t)$ takes the simple form

$$c(jj'j_t) = c(jj_t j';00)^2 \tag{23}$$

where $c(jj_t j';00)$ is a Clebsch-Gordan coefficient.

3. WESULTS AND DISCUSSION

An elastic scattering process results from different rotational states which are not resolved during the experiments, therefore the measured cross sections for it is the average

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = \sum_j P_j \frac{d\sigma(j\to j)}{d\Omega} \tag{24}$$

where P is the fractional population of the jth rotational level. At

room temperature, the fractional occupancies of rotational levels are 0.13, 0.66, 0.12 and 0.09 for j = 0, 1, 2 and 3 and negligible for higher levels. Using these occupancy fractions, our calculated results are also averaged: it has been observed that the elastic cross sections depend weakly on the initial rotational states (<6%).

In figures 1 and 2, the rotationally averaged pure elastic ($v=v'$ and $j=j'$) cross sections are compared against the rotationally-resolved experimental results of Linder and Schmidt[4].

One observes an excellent agreement between theory and experiment in the entire energy range. For impact energies below 2 eV, the differential cross sections are essentially backward peaked and they become more and more forward peaked with the increase of the impact energy. At 0.6 and 1.0 eV our calculated results agree with the experimental data within the quoted errors, except for scattering angles larger than 100°. At 1.5 eV the good agreement is observed in the entire angular range.

In figures 3 and 4 we compare the calculated rotationally unresolved vibrationally elastic differential cross sections against the experimental results obtained by Shyn and Sharp[21], Nishimura *et al*[22] and Srivastava *et al*[23]. in the energy range between 2 eV and 15 eV.

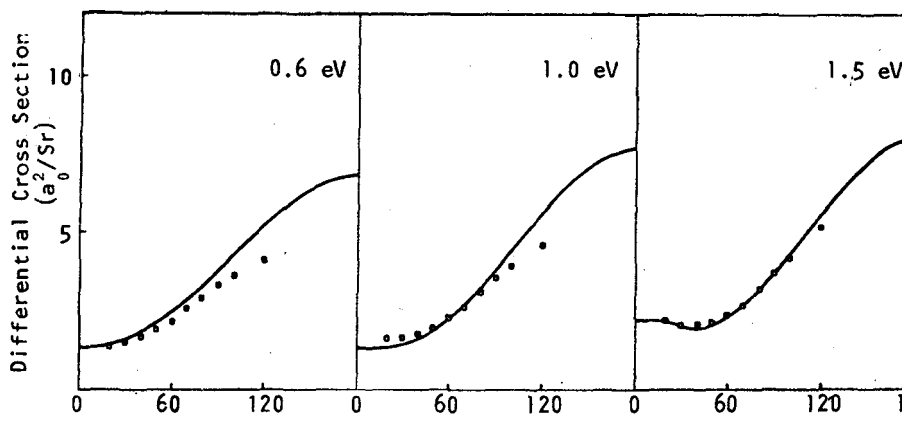


Fig.1 - Differential cross sections for the rotationally averaged pure elastic scattering of electrons by H_2 at 0.6, 1.0 and 1.5 eV. The calculated results (solid line) and the experimental data (open squares) obtained by Linder and Schmidt.

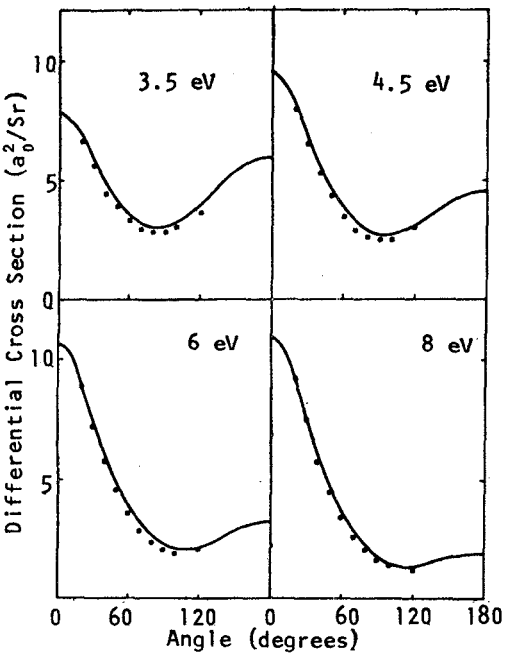


Fig.2 - Same as fig.1, at incident energies of 3.5, 4.5, 6.0 and 8.0 eV.

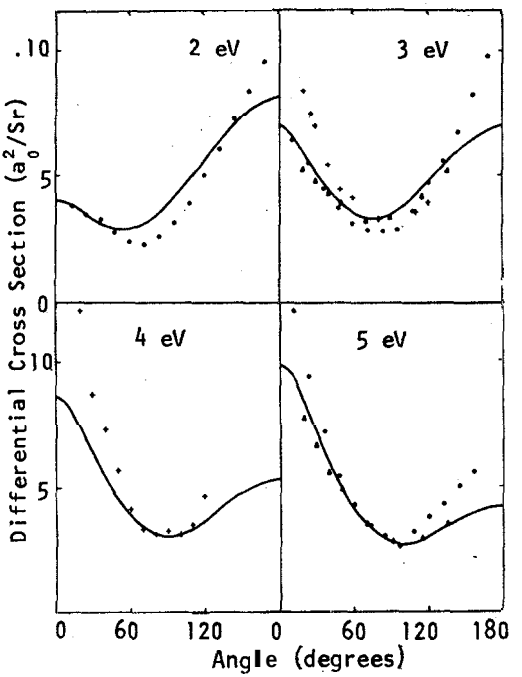


Fig.3 - Differential cross sections for the rotationally unresolved vibrational elastic electron scattering by H_2 at 2.0, 3.0, 4.0 and 5 eV. The calculated results (solid line), the experimental results are from Nishimura et *al* (pluses), Srivastava et *al* (open triangles) and Shyn and Sharp (dark dots)

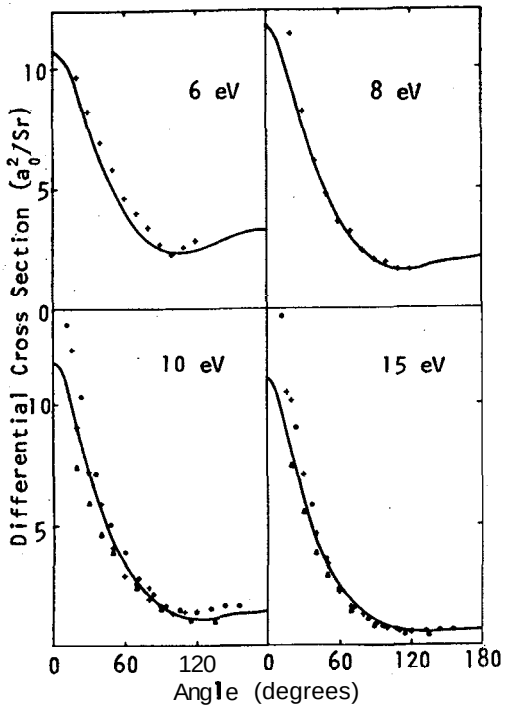


Fig.4 - Same as fig.3, at incident energies of 6.0, 8.0, 10.0 and 15.0 eV.

The calculated rotationally unresolved results were obtained through a summation over the final rotational states and averaging over the initial states.

One notes that there is a good agrsement betweenthecalculated results and experiment. Generally, our results agree very well with the data obtained by Srivastava *et al*[23], for the entire energy and angular ranges. Nevertheless, in the small scattering angles the experimental of Nishimura *et al*[22] lie above the calculated results data. An the contrary, the data of Shyn and Sharp[21] are above our results at large scattering angles. However, the discrepancies between the theory and experiment diminish with the increase of the impact energy.

In fig.5, the comparison of the calculated integrated rotationally unresolved vibrationally elastic cross sections with the experimental data of Srivastava et *al*[23], Shyn and Sharp[21] and Nishumura *et al*[22] is shown; one can note that there is an overall agreement be-

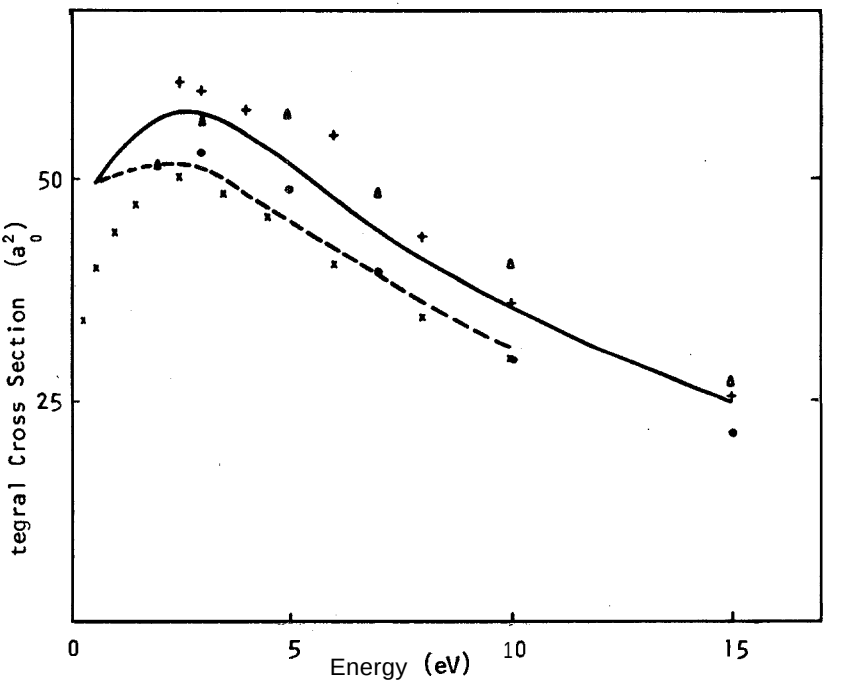
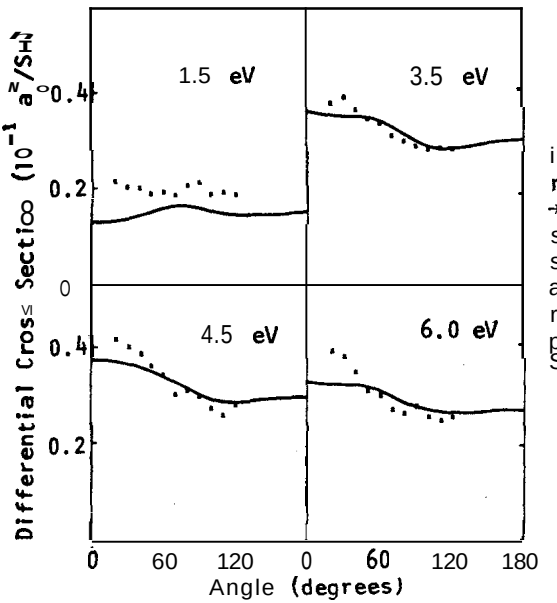


Fig.5 - Integrated vibrationally elastic cross sections for electron H_2 collision. The calculated rotationally unresolved results (solid line) and rotationally elastic results (dashed line). The experimental results for the rotationally elastic scattering of Linder and Schmidt (crosses), the rotationally unresolved results of Shyn and Sharp (open triangles); Nishimura et *al* (pluses) and Srivastava et *al* (dark dots).

tween our results and experiment. In the same figure, we have also shown the calculated pure elastic results in comparison against the rotationally resolved experimental results of Linder and Schmidt[4]; again, a good agreement is observed. The major discrepancies lie in the incident energies below 2 eV and not exceed 5%.

In figures 6 and 7 we compare the calculated rotational excitation cross sections (j=1 → j'=3) of H_2 against the experimental data of Linder and Schmidt[4]; one observes that the agreement between theory and experiments is very good.



iig.6 - Vibrationally elastic rotational excitation (j=1 → j'=3) differential cross sections for electron-H_2 scattering at 1.5, 3.5, 4.5 and 6.0 eV. The calculated results (solid line) and experimental data of Linder and Schmidt (crosses).

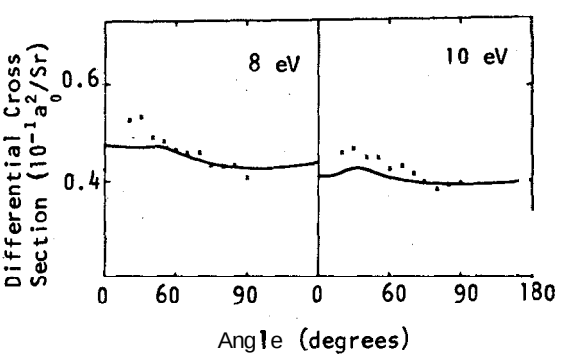


Fig.7 - Same as fig.6, at 8.0 and 10.0 eV.

The major discrepancy occurs at the impact energy of 1.5 eV and even in this case the difference does not exceed 30%. The comparison of the integrated cross sections for two rotational excitations of H_2 ($j=0 \rightarrow j'=2$ and $j=1 \rightarrow j'=3$) is also made against the data obtained by Gibson from the Swarm experiments, and the comparison is shown in fig. 8; in both cases the agreement is excellent.

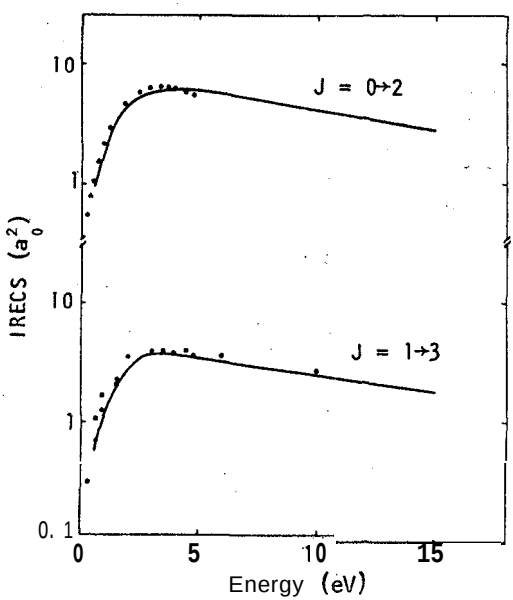


Fig.8 - Integrated cross sections for the pure rotational excitations of H_2 by electron impact. The calculated results (solid line) and the experimental results of Gibson (dark dots) and Linder and Schmidt (open sauares).

4. SUMMARY AND CONCLUSIONS

The calculated vibrationally elastic, rotationally unresolved and resolved cross' sections and the rotational excitation cross sections of H_2 by low energy electron impact have been reported. In the present study, a static-exchange-polarization potential is used and the scattering equation is solved by an iterative integral equation method where the exchange effect is treated exactly.

The calculated results present good agreement when compared against experimental data reported in the literature; the major dis-

crepancy observed refers to the lower energies and the small angular range. The discrepancies seem to reflect that the polarization effect is still not adequately included. On the other hand, the generally good agreement with experiments, particularly in the incident energies above 4 eV shows the possibility of extending the present theory to more complex systems. Studies in this direction are under way.

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Resumo

As secções de choque diferencial e integral do espalhamento de eletrons de baixa energia (0,6 - 15 eV) por molécula de hidrogênio, foram calculadas. Neste estudo, o potencial de interação formado por contribuições do tipo estático-troca-polarização é utilizado para resolver as equações do espalhamento onde o efeito de troca é tratado exatamente. Foram calculadas secções de choque para espalhamento vibrarotacionalmente elástico e vibracionalmente elástico, rotacionalmente inelástico (j=0, j'=2 e j=1, j'=3). Os resultados obtidos mostram boa concordância com os dados experimentais, o que sugere a possível extensão do presente método para sistemas moleculares mais complexos.

IMPRESSÃO E ACABAMENTO

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