LETTER TO THE EDITOR

Vibrationally elastic and inelastic (0 → 1) scattering of electrons by H₂—a coherent renormalised multicentre potential model approach

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Abstract. The coherent renormalised multicentre potential model including intramolecular multiple scattering has been extended, for the first time, to study the vibrationally elastic and inelastic scattering of electrons by linear molecules in the intermediate energy range. Our calculated vibrationally elastic cross sections for $e^- $-$H_2$ scattering agree very well with experiments and the vibrational excitation cross sections agree qualitatively with the measurements. Our results also show that the inclusion of the multiple-scattering effect in the calculation is important at lower incident energies.

Recently, the coherent version of the renormalised multicentre potential model (CRMPM) including the intramolecular multiple-scattering (IMS) effect has been applied (Jain *et al* 1983, 1984, Botelho *et al* 1984) with relative success to the study of the elastic scattering of electrons by several linear molecules in the intermediate and high energy range. Contrary to the usual independent-atom model (IAM) and its modified versions (Jain and Tayal 1982), in the CRMPM approach, the static electron–molecule interaction potential is derived directly from the target molecular wavefunctions and, therefore, the bonding effects are implicitly included. This bonding effect contributes significantly to the cross sections at lower energies, as we have shown previously (Lee Mu-Tao and Freitas 1981, Botelho *et al* 1984). Moreover, our theory requires little computational effort and its application can be straightforwardly extended to treat scattering problems involving non-linear polyatomic molecules. In view of the enormous computational efforts required to study such problems in an *ab initio* approach, it is clearly of interest to extend the applicability of CRMPM-IMS either to lower impact energies or to study more complex physical problems. In this letter, the CRMPM-IMS is extended to the study of the vibrational excitation of linear molecules by electron impact. As our first investigation, we have applied the theory to obtain the vibrationally elastic and inelastic (0 → 1) cross sections of electrons scattered by H_2 in the 20–81.6 eV range.

Vibrationally elastic and inelastic electron–H_2 scattering has been previously studied by Truhlar and Rice (1970) in the Born-type approximation, by Lee Mu-Tao and Freitas (1981) in the incoherent renormalised multicentre potential mode (IRMPM) and by LaGatutta (1980) in the Glauber approximation. In the present study, we have derived mathematical expressions based on the adiabatic nuclei approximation and the CRMPM-IMS formalism. These expressions allow us to obtain the vibrationally

elastic and inelastic cross sections and therefore to elucidate the importance of the IMS contribution in these processes. Since the CRMPM-IMS formalism has been discussed in detail elsewhere (Jain *et al* 1983, 1984), we will present briefly the theory used in this calculation.

In the adiabatic-nuclei approximation, the electron impact differential cross section for the molecular transition from the vibrational level v to v', in the same electronic state, is given as:

$$\left(\frac{d\sigma}{d\Omega}\right)_{v \to v'} = \frac{1}{4\pi} \frac{k_f}{k_i} \int d\hat{R} \, |F_{vv'}|^2 \tag{1}$$

where the integral refers to the averaging over the molecular orientations. The vibrational transition scattering amplitude $F_{vv'}$ is expressed as:

$$F_{vv'} = \langle \chi_{v'}(R)|f(\theta;R)|\chi_v(R)\rangle \tag{2}$$

here, the $\chi_{v'}(R)$ and $\chi_v(R)$ are respectively the final and initial vibrational wavefunctions. The $f(\theta;R)$ is the adiabatic elastic scattering amplitude, which in our approach depends parametrically on the geometry of the molecule.

In the CRMPM the $f(\theta,R)$ is given as:

$$f(\theta;R) = \sum_{\alpha} f_{\alpha}(\theta;R) \exp(iS \cdot R_{\alpha}) + f^{\text{pol}}(\theta;R) + \sum_{\alpha} f_{\text{pol},\alpha} + \sum_{\alpha \neq \beta} f_{\alpha\beta} + \ldots \tag{3}$$

where the $f_{\alpha}(\theta;R)$ is the adiabatic single-scattering amplitude of the centre α and $f^{\text{pol}}(\theta;R)$ is the elastic scattering amplitude due to the polarisation of the molecule by the incident electron. Both $f_{\alpha}(\theta;R)$ and $f^{\text{pol}}(\theta;R)$ are parametrically dependent on the internuclear distance of the molecule. The $f_{\alpha,\text{pol}}$ refers to the double-scattering amplitude between the atomic scatterer α and the polarisation potential, centred at the origin of the coordinates and $f_{\alpha\beta}$ corresponds to the double-scattering amplitude between two atomic scatterers α and β. In this study, the terms of high order of the multiple scattering were not included in the calculation. After carrying out some integrals, one finds that the differential cross sections corresponding respectively to the single and single–double scatterings for linear molecules are given by:

$$I_{\text{SS}} = \frac{k_n}{k_0} \sum_{\alpha,\beta} \sum_{l} (2l+1) P_l(\cos\theta_q) \langle \chi_v|j_l(C_\alpha q) f_\alpha|\chi_{v'}\rangle \langle \chi_{v'}|j_l(C_\beta q)|\chi_v\rangle \tag{4a}$$

and

$$I_{\text{SD}} = \frac{k_n}{k_0} \frac{4\pi}{k_0} \sum_{\alpha} \sum_{\beta \neq \gamma} \sum_{l_1 l_2 l_3 l_4 l_5, m_1} (-1)^{m_1}(i)^{l_3+l_5-l_4+1}(2l_1+1)(2l_2+1)(2l_5+1)$$

$$\times |(2l_3+1)(2l_4+1)|^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & 0 & -m_1 \end{pmatrix} \begin{pmatrix} l_1 & l_4 & l_5 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} l_1 & l_4 & l_5 \\ m_1 & 0 & -m_1 \end{pmatrix} Y^*_{l_1,m_1}(\hat{k}_n) Y_{l_4,m_1}(\hat{q}) P_{l_5}(\cos \hat{W}_{\beta\gamma}) \langle \chi_v|j_{l_4}(C_\alpha q) f_\alpha|\chi_{v'}\rangle$$

$$\times \langle \chi_{v'}|j_{l_3}(C_{\alpha\beta} q) j_{l_5}(W_{\beta\gamma}) a_{l_1}(k_n, q, C_\alpha \hat{R}) a_{l_2}(q, k_0, C_\beta \hat{R})|\chi_v\rangle. \tag{4b}$$

Here, q is the momentum transfer vector, defined as

$$q = k_0 - k_n \tag{5}$$

C_α is a constant and is related to the coordinate of the scattering centre α by

$$R_\alpha = C_\alpha \hat{R} \qquad (6)$$

and $\hat{R}$ is the orientation of the molecular axis; the vector $W_{\alpha\beta}$ is defined as:

$$W_{\alpha\beta} = C_\alpha k_n - C_\beta k_0 \qquad (7)$$

and the a_l in equation (4b) are related to the phaseshifts by

$$a_l = \sin \delta_l \exp(\mathrm{i}\delta_l). \qquad (8)$$

Since the previous studies (Jain *et al* 1983, Botelho *et al* 1984) showed that the contribution of the double–double scattering is not important, it is not included in this study.

To obtain the adiabatic elastic scattering amplitude of the atomic centres, we employed the partial-wave expansion method in which the short-range interaction potentials are derived from the R-dependent valence-bond-type wavefunction, calculated by Rosen (1931). The $f_\alpha(\theta; R)$ were obtained for three internuclear distances (0.7, 1.4 and 2.1 a_0) respectively.

The scattering amplitude $f^{\mathrm{pol}}(\theta; R)$ is also obtained in the partial-wave approach using only the spherical part of the potential; in this case, an R-dependent polarisation potential is constructed using the R-dependent polarisability calculated by Gibson and Morrison (1984) in a non-penetrating form (Henry and Lane 1969). The convergence of the calculated phaseshifts for the short-range potentials is better than 10^{-5}. However, for the long-range potentials, the phaseshifts were calculated up to 10^{-3} in this study. To perform the integration of equation (2), a Simpson quadrature of 25 points has been used in the internuclear distances between 0.65 and 2.15 a_0 with a step size of 0.0625 a_0. For this proposal, a interpolation technique has been used to calculate $f_\alpha(\theta; R)$, $f^{\mathrm{pol}}(\theta; R)$ etc, on the mesh points. The Morse (1929) functions are used to represent both the initial and final vibrational wavefunctions.

Figure 1 compares the vibrationally elastic differential cross sections (VEDCS) obtained by CRMPM-IMS with the experimental results of Trajmar *et al* (1970a) at impact energies of 20, 45, 60 and 81.6 eV. For the first three energies, we have also shown the experimental results of Shyn and Sharp (1981). Although the measurements of Shyn and Sharp (1981) are not vibrationally resolved, the direct comparison can be made since the contribution of the vibrational excitation cross section are, in general, negligibly small in relation to the VEDCS. One notes that there is agreement between our theory and the experiments. The comparison with our previous IRMPM results shows that the introduction of the multiple-scattering effects improves the agreement with experiments at lower energies, although the IMS does not significantly affect the DCS at higher energies. In figure 2, we show the ratio between the contributions of the single–double scattering and the single scattering only at 20 and 60 eV. At 20 eV, the single scattering contributes up to 40% at the large scattering angles, whereas at 60 eV, the contribution of the I^{SD} does not exceed 4% in the entire angular range.

In figure 3, we compare the theoretical transition $(0 \to 1)$ differential cross sections (VTDCS) obtained using the CRMPM-IMS with the experimental measurements of Trajmar *et al* (1970b) at 20, 45 and 81.6 eV. One notes that our theory reproduces quite well the shape of the experimental data but overestimates the magnitude of the DCS. The Born-type approximation (Truhlar and Rice 1970) did not reproduce the shape correctly, whereas the previous IRMPM results (Lee Mu-Tao and Freitas 1981) show a better agreement with experiments. In order to understand this discrepancy, in figure
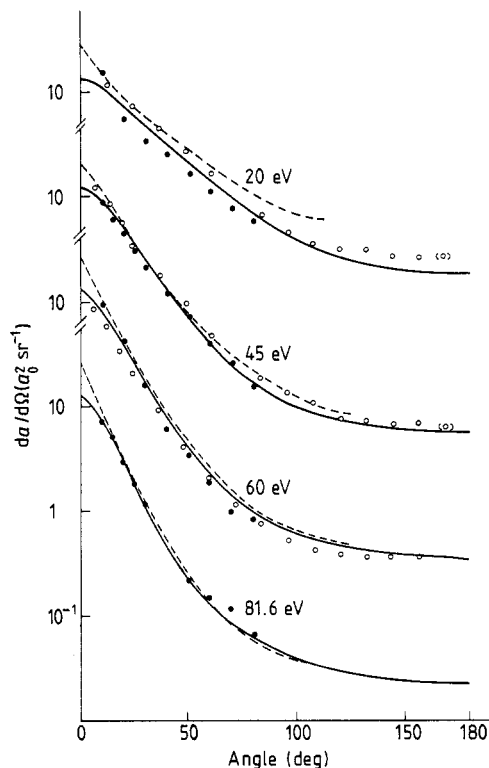
Figure 1. The vibrationally elastic DCS at 20, 45, 60 and 81.6 eV. The results of the present study are represented by full curves. The broken curves give the results of IRMPM (Lee Mu-Tao and Freitas 1981). The experimental results are from Shyn and Sharp (1981) (open circles) and from Trajmar *et al* (1970a) (full circles).
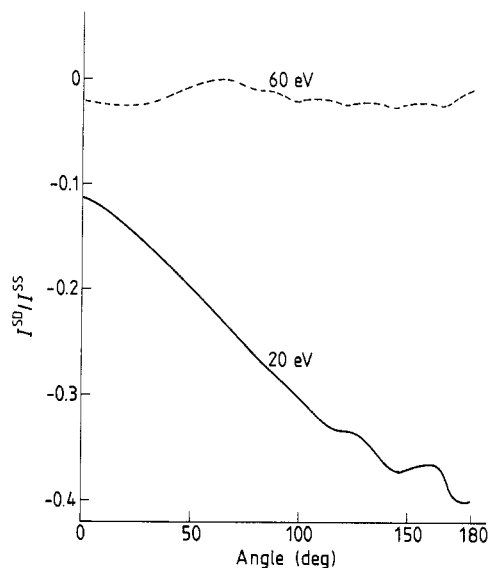
Figure 2. The ratios between the I^{SD} and I^{SS} (see text) for vibrationally elastic scattering at 60 and 20 eV.

4 we present the VTDCS at 60 eV, obtained by CRMPM-IMS, employing the short-range (static) potential only and the static plus polarisation potential respectively. The DCS, using only the static potential, agree very well with the experimental data for scattering angles above 15°; at the smaller angles, the experimental DCS is forward-peaked indicating charge polarisation of the target by the incident electron. Nevertheless, when the polarisation effect is included in the calculation, the coherent sum between the contributions of the short-range and the polarisation potentials produces interference which leads to the overestimation of the DCS. This is probably the reason for the better agreement between the IRMPM results and experiments, since in the IRMPM approach, the interference is not taken into account (although the CRMPM is physically more consistent).

An alternative cause of the discrepancy between our theory and the experimental data is the fact that VTDCS is very sensitive with respect to the polarisation potential. In order to verify this sensitivity of the VTDCS and the VEDCS, we have also carried out the calculation of both cross sections, at 60 eV, with the polarisation potential used by Lee Mu-Tao and Freitas (1981). The VEDCS obtained by using the different polarisation potentials are almost the same (discrepancy less than 5%), however, as
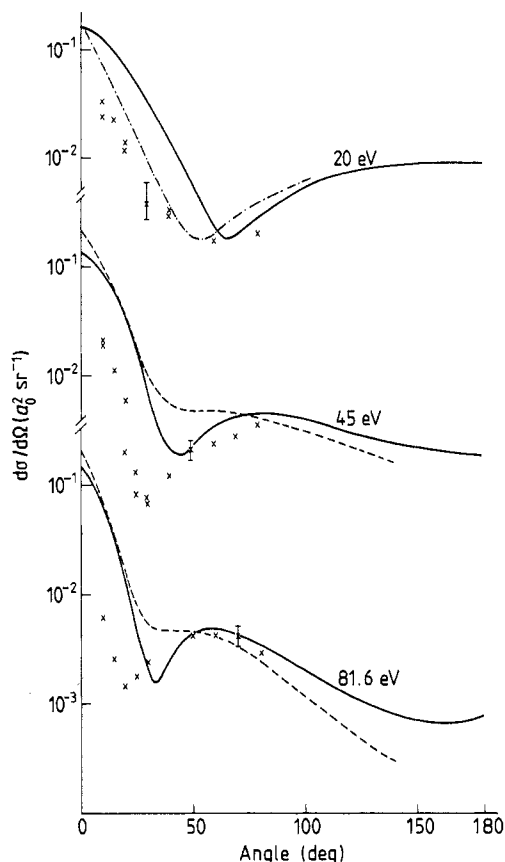
Figure 3. The vibrational excitation DCS of e^--H_2 scattering at 20, 45 and 81.6 eV. The full curves give the present results; the results from the Born approximation are represented by broken curves and the results from IRMPM (Lee Mu-Tao and Freitas 1981) are represented by a chain curve. The experimental results (crosses) are from Trajmar *et al* (1970b).
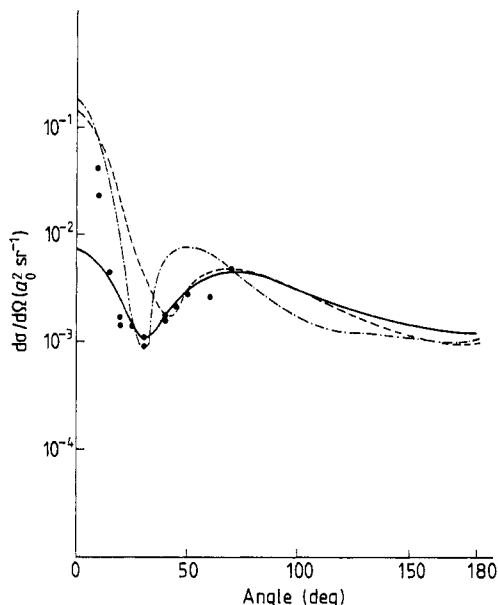
Figure 4. The vibrational excitation DCS of e^--H_2 at 60 eV. The results obtained usng the short-range potential only are given by a full curve; the results with the polarisation potential of Gibson and Morrison (1984) by a broken curve; the results with the polarisation potential of Lee Mu-Tao and Freitas (1981) by a chain curve and the experimental results by full circles.

one can see in figure 4, the VTDCS obtained using these two polarisation potentials are significantly different. That means that the VTDCS is very sensitive with respect to the polarisation effect and the discrepancy between our theory and experiments might be caused by the inadequancy of the polarisation potential used.

In figure 5, the ratio between the I^{SD} and I^{SS} for the vibrational excitation $(0 \to 1)$ at 20 and 60 eV is shown. One notes that the multiple scattering contributes significantly in both cases. Finally, in table 1, we show the integral cross sections for the vibrationally elastic (VEICS) and inelastic (VIICS) scatterings in comparison with the experimental results (Trajmar *et al* 1970a, b) and the values of the Born-type approximation (Truhlar and Rice 1970). Our values of VEICS agree well with the experimental data whereas the results of Born-type approximation are larger than ours by about 25%. For the vibrationally inelastic scatterings, our results are similar to those of Born's approximation and, as expected, both theories overestimate the cross sections.
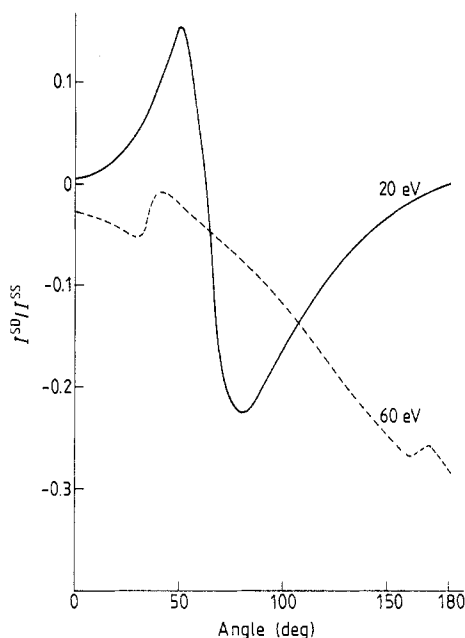
Figure 5. The ratios between I^{SD} and I^{SS} for vibrational excitation cross sections at 20 and 60 eV.

Table 1. The integral cross sections for vibrationally elastic (VEICS) and inelastic (VIICS) integral cross sections of electrtons scattered by H_2.

Energy (eV)	VEICS (a_0^2)			VIICS (a_0^2)		
	This work	BOR/P[a]	Expt[b]	This work	BOR/P[b]	Expt[b]
20	16.5395	20.55	14.70	0.1333	0.148	0.0456
45	7.9292	9.383	7.86	0.0767	0.081	0.0396
60	5.9545	7.15	5.97	0.0617	0.0608	0.032
81.6	4.3011	5.06	4.44	0.0498	0.0468	0.030

BOR/P is the Born–Ochkur–Rudge polarisation approximation.
[a] Truhlar and Rice (1970).
[b] Trajmar *et al* (1970a, b).

In summary, the CRMPM-IMS has been extended to study the vibrationally elastic and inelastic scattering of electron by H_2 in the 20–81.6 eV range. The VEDCS and VEICS obtained in this study agree very well with the experimental data, implying that the CRMPM-IMS is very promising for such studies. The VTDCS also agree qualitatively with the experiments, however our theory overestimates the magnitude of the DCS. Since the VTDCS is very sensitive with respect to the polarisation potential used in the calculation, the discrepancy might be caused by the use of inadequate polarisation potentials. Further studies will be needed in order to clarify this fact. On the other hand, the sensitive dependence of the VTDCS on the polarisation effect can be applied to study the quality of the model polarisation potentials.

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