Excitation of H_2 vibrational levels ($v \leqslant 4$) by low-energy electron impact†

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Abstract. An *ab initio* L^2-basis-set theory for low-energy electron–molecule scattering is applied to the excitation of the $v = 1, 2, 3$ and 4 vibrational levels of H_2 by slow electrons (1–10 eV), with or without simultaneous rotational excitation. An optical potential including direct, exchange and polarisation terms is expanded in a diagrammatic perturbation series and used in the framework of the T-matrix expansion method of Rescigno, McCurdy and McKoy. Calculated integral and differential cross sections agree well with all available experimental data. The static-exchange approximation, on the other hand, gives poor results (2–4 times too low), with the error increasing as one goes to higher vibrational excitations. Polarisation is thus indispensable in a reliable description of vibrational excitation processes.

1. Introduction

An *ab initio* parameter-free theory of low-energy electron–molecule scattering including static, exchange and polarisation terms has recently been proposed (Klonover and Kaldor 1977, 1978). Application to e–H_2 elastic scattering as well as rotational and lowest vibrational ($v = 0 \rightarrow v = 1$) excitation yielded very satisfactory results (Klonover and Kaldor 1978, 1979a, b). Starting with the T-matrix expansion method of Rescigno *et al* (1974a, b, 1975), we expand the optical potential in Feynman diagrams (Bell and Squires 1959) and insert it in the Lippmann–Schwinger equation for the T matrix, which is then solved in a finite basis of square-integrable functions. The method is applied below to electron impact excitation of higher vibrational levels ($v \leqslant 4$) of H_2. Results are compared with the total cross sections measured by Ehrhardt *et al* (1968) up to 10 eV and with the differential cross sections of Wong and Schultz (1974) at 4·5 eV.

2. Method

The scattering amplitudes are obtained by T-matrix expansion (Rescigno *et al* 1974a, b, 1975) with polarisation included via an optical potential summed to second order. A detailed description of the method has been given elsewhere (Klonover and Kaldor 1978, 1979a) and will not be repeated here. Cross sections for the different possible

processes (elastic, rotational, vibrational) are calculated in the adiabatic-nuclei approximation (Chase 1956, Temkin and Vasavada 1967, Golden *et al* 1971)

$$\frac{\mathrm{d}\sigma\,(vj \to v'j')}{\mathrm{d}\Omega} = \frac{k_f}{k_i}\frac{1}{2j+1}\sum_{mm'}|\langle\chi_{v'}(R)\,Y_{j'm'}(\hat{R})|f(\boldsymbol{R},\theta)|Y_{jm}(\hat{R})\chi_v(R)\rangle|^2 \tag{1}$$

where k_i and k_f are the initial and final wavenumbers of the scattered electron, χ_v and Y_{jm} are vibrational and rotational wavefunctions, f is the scattering amplitude and θ is the scattering angle. The integration on the right-hand side of (1) is carried over the length R and orientation $\hat{R}$ of the molecular axis in the laboratory frame.

3. Calculations

Cartesian Gaussians are used as basis orbitals. The inner set, spanning the molecular orbitals (both occupied and virtual), consists of 30 functions; the outer set, describing the scattered electron, is larger and includes 61 functions of s, pσ, pπ and dπ types. The basis functions are identical with those employed before (Klonover and Kaldor 1979a) and are not listed here. The vibrational eigenfunctions χ_v are obtained from the Kolos and Wolniewicz (1965) potential. The energies of the first five vibrational levels ($v = 0–4$) are 0·0104, 0·0294, 0·0473, 0·0641 and 0·0799 Hartree. Scattering amplitudes are calculated at ten internuclear separations between 0·6 and 3·0 Bohr and interpolated for other R values. As the amplitudes vary smoothly with R and the vibrational functions are calculated directly wherever needed, numerical integration is expected to converge rapidly. Indeed, 60- and 120-point Simpson-rule integrations gave results equal to four or more significant figures. In our previous paper (Klonover and Kaldor 1979a) a smaller integration range (0·8–2·0 Bohr) was used, and the vibrational functions did not quite die off. The present results for the $v = 0 \to v = 1$ excitation are therefore higher by up to 10%.

4. Results and discussion

Integral cross sections for pure vibrational ($v = 0 \to 1$, $\Delta j = 0$) and vibrational–rotational ($v = 0 \to 1$, $j = 1 \to 3$) excitations are shown in figures 1 and 2 respectively. The experimental results of Linder and Schmidt (1971) are given for comparison. In both cases the cross sections calculated with the second-order optical potential (with polarisation included) fall within the experimental error bounds over the whole range (1–10 eV). Similar agreement has been observed for elastic scattering and rotational excitation cross sections when the zero-point vibration of the molecule was taken into account (Klonover and Kaldor 1979b). Static-exchange results are too low in all cases.

No rotationally-resolved integral cross sections for the higher vibrational excitations have been measured. We therefore report total vibrational cross sections, which include all rotational processes. These are shown in figure 3 and compared with the experimental values of Ehrhardt *et al* (1968) for the first three vibrational excitations ($v = 0 \to 1, 2, 3$). The more recent results of Linder and Schmidt (1971) for the lowest excitation are also included to give a measure of the experimental spread. Static-exchange cross sections are not shown; they are 2–4 times lower than the corresponding second-order results shown in figure 3, with the highest excitation showing the largest
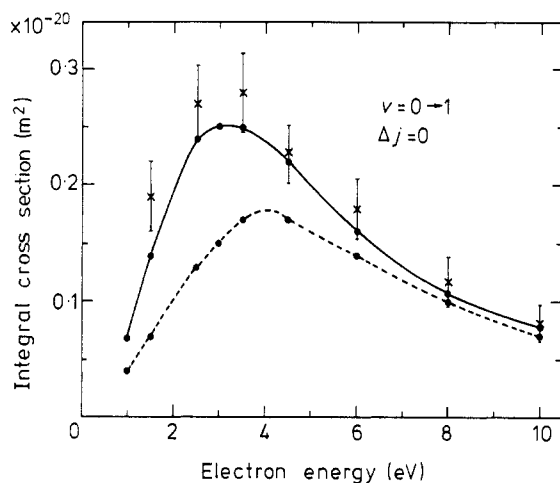
Figure 1. Integral cross sections for vibrational excitation from $v = 0$ to $v = 1$, without changing the rotational quantum number. The broken curve shows the static-exchange results; the full curve includes polarisation. The crosses are the experimental values of Linder and Schmidt (1971).
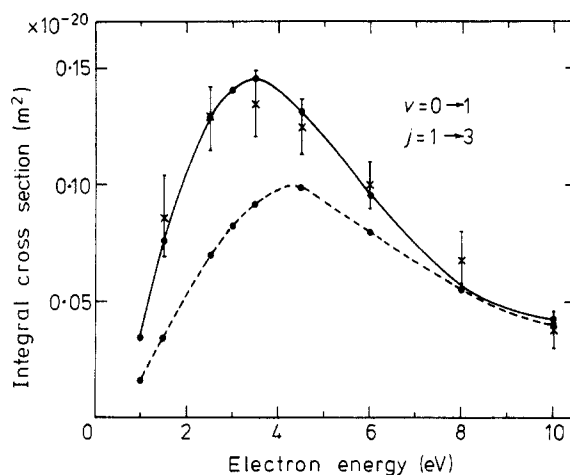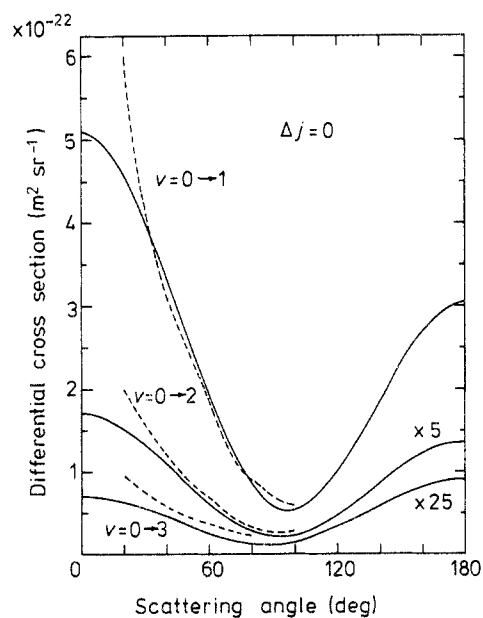

Figure 2. Integral cross sections for excitation from the $v = 0$, $j = 1$ to the $v = 1$, $j = 3$ state. Symbols as in figure 1.

difference. Agreement between theory and experiment is good. This is particularly gratifying if one remembers that vibrational excitation cross sections depend strongly on the detailed behaviour of the scattering amplitude as a function of internuclear separation and therefore provide a stringent test for any theory.
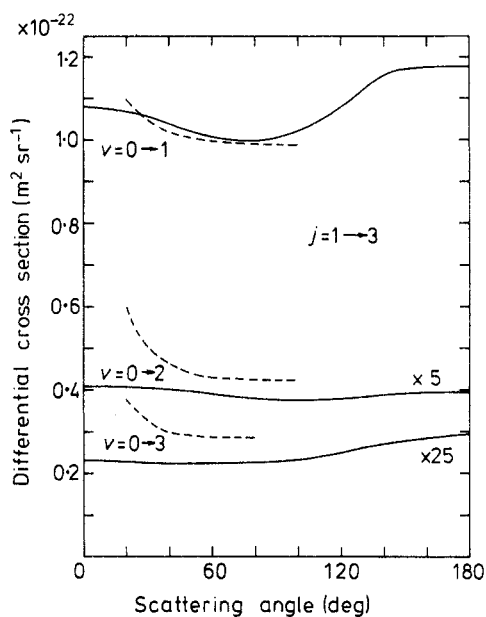
Differential cross sections for excitation of H_2 from the ground $(v = 0)$ to an excited $(v = 1, 2, 3)$ vibrational state by $4 \cdot 5$ eV electrons with or without rotational excitation have been measured by Wong and Schultz (1974). Calculated cross sections for these processes are shown in figures 4 and 5, and ratios between pure vibrational and vibrational–rotational cross sections are given in figure 6. Once again, very satisfactory agreement between theory and experiment is obtained.
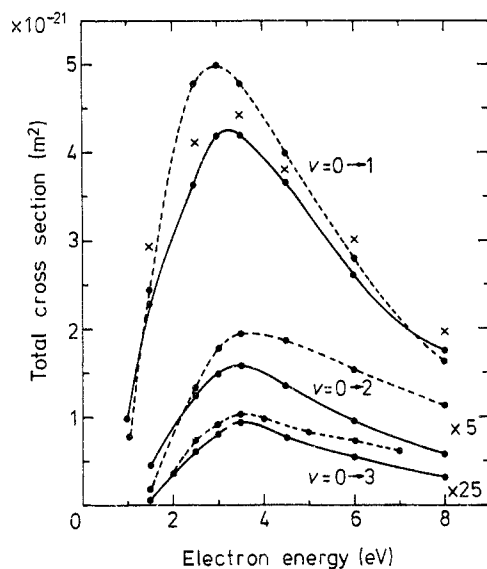
Figure 3. Total cross sections (including all rotational processes) from the $v = 0$ to the $v = 1$, 2 or 3 states of H_2. The full curve shows calculated cross sections, the broken curve gives the measurements of Ehrhardt *et al* (1968), and the crosses are the results of Linder and Schmidt (1971). The $0 \rightarrow 2$ cross sections are multiplied by 5, and the $0 \rightarrow 3$ values are multiplied by 25.

Figure 4. Differential cross sections for excitation from $v = 0$ to $v = 1$, 2 or 3 by 4·5 eV electrons. The rotational quantum number does not change. Full curves: calculated results; broken curve: experiment (Wong and Schultz 1974).

Figure 5. Same as figure 4, but the rotational quantum number goes from 1 to 3.
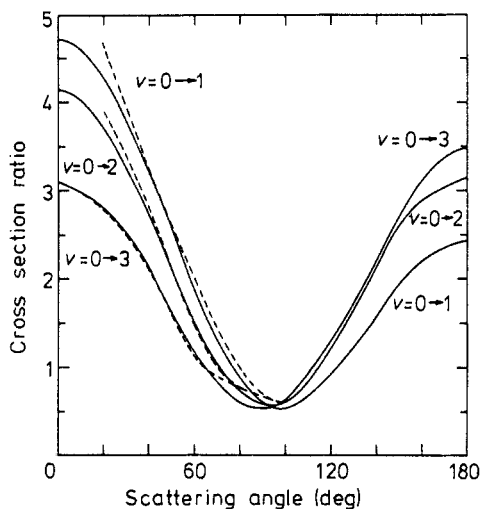
Figure 6. Ratios between pure vibrational ($\Delta j = 0$) and vibrational–rotational ($j = 1 \to 3$) cross sections for different vibrational excitations. Symbols as in figure 4.

Finally, integral cross sections for elastic and pure vibrational processes (no change in rotational quantum number) at several collision energies are collected in table 1. As expected, the cross sections fall off rapidly as the number of vibrational quanta transferred increases. An interesting phenomenon is the disappearance of the broad elastic scattering peak around 3 eV when the scattering molecule is in a high vibrational

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Table 1. Integral cross sections for elastic scattering and vibrational excitation (10^{-20} m^2). The rotational quantum number is not changed in the process.

$v \to v'$ E(eV)	$0 \to 0$	$1 \to 1$	$2 \to 2$	$3 \to 3$	$4 \to 4$	$0 \to 1$	$1 \to 2$	$2 \to 3$	$3 \to 4$	$0 \to 2$	$1 \to 3$	$2 \to 4$	$0 \to 3$	$1 \to 4$	$0 \to 4$
1·5	13·1	14·5	16·4	18·4	18·3	0·14	0·46	1·05	1·51	0·0050	0·037	0·11	0·00014	0·0019	—
2·5	14·1	15·4	16·2	16·4	16·3	0·24	0·56	0·88	1·08	0·014	0·070	0·18	0·0013	0·0083	0·00014
3·5	13·7	14·5	14·8	14·6	14·6	0·25	0·49	0·59	0·60	0·018	0·063	0·13	0·0021	0·010	0·00030
4·5	12·7	13·1	13·2	13·2	13·2	0·22	0·38	0·45	0·47	0·016	0·045	0·078	0·0017	0·0073	0·00027
6	11·7	11·8	11·7	11·7	11·6	0·15	0·26	0·32	0·34	0·012	0·030	0·049	0·0012	0·0046	0·00016
8	10·2	10·2	10·1	10·0	10·0	0·11	0·18	0·22	0·25	0·0070	0·019	0·030	0·0008	0·0027	0·00012

level. As all cross sections reported here are calculated by the adiabatic-nuclei equation (1), this phenomenon simply reflects the behaviour of the scattering amplitude as a function of the energy and internuclear separation.

5. Summary and conclusions

Vibrational excitation of H_2 by low-energy electron impact has been investigated using a completely *ab initio* theory. All terms in the potential (direct, exchange, polarisation) are included via an optical potential expanded in a diagrammatic perturbation series summed to second order in a finite square-integrable basis set. Integral and differential cross sections for excitation from the ground state to the $v = 1, 2$ and 3 states with or without simultaneous rotational excitation are calculated and compared with available experimental data. Very good agreement is obtained in all cases.

Cross sections for the higher vibrational excitations are small and depend very strongly on the derivatives of the scattering amplitude with respect to the internuclear separation. They are therefore rather difficult to predict accurately, and the good agreement of the results presented above with experiment is very gratifying indeed, attesting to the high quality of the calculated scattering amplitudes. The static-exchange approximation is inadequate, producing cross sections 2–4 times too low, with the error increasing as one goes to higher excitations. Polarisation is therefore indispensable for a reasonable description of vibrational excitation.

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