

A Study of the Vibrational Excitation of H_2 by Measurements of the Drift Velocity of Electrons in H_2 -Ne Mixtures

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Abstract

Measurements of electron drift velocities have been made in 1.160% and 2.892% hydrogen–neon mixtures at 294 K and values of E/N from 0.12 to 1.7 Td. The measurements are highly sensitive to the region of the threshold of the $v = 0 \rightarrow 1$ vibrational excitation cross section for hydrogen and have enabled more definitive tests of proposed cross sections to be made than was possible using drift velocity data for H_2 -He and H_2 -Ar mixtures. The theoretical $v = 0 \rightarrow 1$ vibrational excitation cross section of Morrison *et al.* (1987) is shown to be incompatible with the present measurements. A new set of hydrogen cross sections has been derived from the available electron swarm measurements in pure hydrogen and hydrogen mixtures.

1. Introduction

In a recent, comprehensive study of low energy electron–hydrogen scattering, Morrison *et al.* (1987) showed that there is satisfactory agreement between the $J = 0 \rightarrow 2$ and $1 \rightarrow 3$ rotational excitation cross sections derived from electron swarm studies (Crompton *et al.* 1969; Gibson 1970; Crompton *et al.* 1970) and theoretical predictions. In contrast they demonstrated that there is significant disagreement between the swarm-derived and theoretical cross sections for the case of the $v = 0 \rightarrow 1$ vibrational excitation, although the theoretical cross section is in good agreement with the cross section obtained from beam measurements (Ehrhardt *et al.* 1968).

Two previous sets of measurements have been used to investigate the disagreement between the swarm derived cross sections and those obtained from beam experiment or from theory. Haddad and Crompton (1980) measured electron drift velocities and the ratio D_T/μ (where D_T is the transverse diffusion coefficient and μ the electron mobility, $\mu = v_{dr}/E$, with v_{dr} the drift velocity and E the electric field strength) for two mixtures of H_2 in Ar. They found that the $v = 0 \rightarrow 1$ vibrational cross section derived from swarm experiments and the best estimate values for cross sections for all other relevant processes could be used to predict their experimental values to within the experimental uncertainty. When the values for the $v = 0 \rightarrow 1$ vibrational cross section obtained from beam experiments were used with the same cross sections for the other processes, the calculated drift velocities and D_T/μ values were found to be incompatible with the experimental values. Petrović (1985) has since shown that the theoretical $v = 0 \rightarrow 1$ vibrational cross section is also unable

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to predict the experimental data for the H_2 -Ar mixtures. Petrović and Crompton (1987) measured electron drift velocities in a H_2 -He mixture. They also compared the experimental values with values predicted using the theoretical $v = 0 \rightarrow 1$ vibrational excitation cross section and concluded that the theoretical vibrational cross section was incompatible with the experimental results.

The addition of hydrogen to monatomic gases causes an increase in the measured drift velocity for a given value of E/N (N is the gas number density) due to the reduction of the mean collision frequency, $\langle \nu_m \rangle = N \langle \sigma_m c \rangle$, where the angle brackets indicate an average over the electron energy distribution function, ν_m is the collision frequency for momentum transfer, σ_m is the momentum transfer cross section for the inert gas or gas mixture, and c is the electron speed. This reduction in $\langle \nu_m \rangle$ is caused by the lowering of the electron swarm energy primarily by the absorption of energy in the excitation of rotation and vibration of the hydrogen molecules. When σ_m varies only slightly with energy, the reduction in $\langle \nu_m \rangle$ is caused primarily by the reduction of c . However, when σ_m decreases rapidly with decreasing c , there is an enhanced reduction in $\langle \nu_m \rangle$ and an enhanced sensitivity to inelastic energy loss processes. The importance of the sensitivity to the study of the vibrational excitation cross section of hydrogen is that low concentrations of hydrogen can be used and, thus, the uncertainties in $\sigma_m(\text{H}_2)$ have little influence on the uncertainties of the calculated values of the transport parameters.

The studies using H_2 -He and H_2 -Ar mixtures were less definitive than desired. In the case of helium mixtures, the relatively small variation of the helium momentum transfer cross section with energy causes the sensitivity of the drift velocity to the vibrational cross section to be small, and relatively large concentrations of hydrogen are required to obtain an adequate change in the drift velocity. As a consequence, the uncertainty in the calculated values due to the uncertainty in the hydrogen momentum transfer cross section is increased. In the case of argon mixtures, although the argon momentum transfer cross section changes rapidly with energy, its value is not known to the desired accuracy in the region of the Ramsauer-Townsend minimum. This again led to increased uncertainty in the calculated transport parameters.

In the case of H_2 -Ne mixtures, not only is there a relatively large variation of the neon momentum transfer cross section with energy in the region of the threshold of the $v = 0 \rightarrow 1$ vibrational excitation cross section for hydrogen (approximately 0.5 eV), giving rise to a higher sensitivity to the vibrational cross section but, also, the uncertainty in the momentum transfer cross section for neon (Robertson 1972) is less than that for argon.

2. Measurements of Drift Velocities in H_2 -Ne Mixtures

The electron drift velocities were measured by the Bradbury-Nielsen method using the apparatus and procedures described by Elford (1972) and Huxley and Crompton (1974). The hydrogen was purified by passage through a heated palladium osmosis thimble (Crompton and Elford 1962) and the neon was Matheson Research Grade gas used without further purification. The gas pressures were measured with an estimated uncertainty of $\pm 0.1\%$ using a calibrated quartz spiral manometer (Texas Instruments Ltd). The drift tube was immersed in a water bath to maintain temperature stability. The gas temperature, as measured by internal thermocouples, varied by less than 0.2 K about 293.5 K over the duration of the experiment.

**Table 1. Drift velocities (in units of 10^5 cm s^{-1}) measured at 293.5 K
in two H₂-Ne mixtures**

E/N (Td)	Pressure (kPa)			Corrected for diffusion	
	10.33	13.43	20.08	26.85	
(a) 1.160% H ₂ -Ne					
0.12			3.852	3.850	3.837
0.14			4.113	4.109	4.097
0.17			4.489	4.486	4.474
0.20			4.857	4.850	4.839
0.25			5.421	5.417	5.404
0.30		5.956	5.948	5.944	5.931
0.35	6.470	6.456	6.457	6.443	6.434
0.40	6.915	6.927	6.922	6.916	6.903
0.50	7.816	7.815	7.797	7.793	7.781
0.60	8.632	8.619	8.609	8.600	8.591
0.70	9.379	9.364	9.356	9.351	9.337
0.80	10.074	10.067	10.056		10.036
1.0	11.324	11.322	11.314		11.289
1.2	12.414	12.408			12.373
1.4	13.323	13.335			13.290
1.7	14.422				14.376
(b) 2.892% H ₂ -Ne					
0.12			4.478	4.473	4.454
0.14			4.733	4.729	4.709
0.17			5.101	5.094	5.074
0.20			5.457	5.449	5.430
0.25		6.045	6.025	6.018	6.000
0.30		6.584	6.573	6.563	6.543
0.35	7.110	7.105	7.093	7.083	7.061
0.40	7.619	7.604	7.590	7.583	7.561
0.50	8.549	8.545	8.526	8.518	8.496
0.60	9.428	9.410	9.398	9.384	9.365
0.70	10.237	10.228	10.219	10.200	10.180
0.80	11.020	11.003	10.986		10.956
1.0	12.454	12.436	12.420		12.388
1.2	13.767	13.750			13.699
1.4	14.980	14.956			14.907
1.7	16.627				16.555

The mixtures of H_2 in Ne were made using volume sharing in a mixing vessel similar to that used by Haddad (1983). The particular H_2 concentrations of 1.160% and 2.892% were chosen as the result of preliminary calculations to establish the concentrations and ranges of E/N where the drift velocity was highly sensitive to the vibrational cross section. When making the mixtures, pressures corresponding to gauge calibration points were used to reduce errors from interpolation. The mixing vessel was immersed in a water bath to ensure temperature stability. A period of 40 hours was allowed for mixing before gas samples were taken from the vessel. This mixing time was shown to be adequate by comparing drift velocity measurements with measurements using a gas sample taken from the mixing vessel a week later. The estimated uncertainty in the mixture compositions is 0.2%.

Drift velocities were measured at values of E/N between 0.12 and 1.7 Td (1 Td $\equiv 10^{-17}$ V cm²); the values obtained are shown in Table 1. For each value of E/N where more than two pressures were used, the drift velocities were plotted against $1/p$ (p is the gas pressure) and linear extrapolations made to $1/p = 0$ to obtain values corrected for diffusion. For those values of E/N where values at only two pressures were available, the following correction procedure was employed. The relation (Elford 1972)

$$v_{\text{dr}}(\text{meas}) = v_{\text{dr}} \left(1 + C \frac{D_{\text{T}}/\mu}{E/N} \frac{1}{Nd} \right),$$

was used together with calculated values for the ratio D_{T}/μ in order to find estimates for the constant C at those values of E/N where data for more than two pressures were available. A value of 0.89 ± 0.05 was obtained for the 1.160% mixture and 1.81 ± 0.05 for the 2.892% mixture. In both cases C was independent of E/N . These values of C were then used to correct the drift velocities at values of E/N where data for only two pressures were available. The corrected drift velocities are shown in Table 1. The corrections in all cases were less than 1.0% and are estimated to cause an uncertainty in the corrected values of $< \pm 0.1\%$. The reasons for the different values of C for the two different mixtures are not understood but may be due in part to differences in the ratio of the longitudinal and transverse diffusion coefficients for each mixture.

The errors in the drift velocity measurements have been discussed in detail by Elford (1972). Contributions to the total error are summarised in Table 2. By adding the systematic errors in quadrature and then adding the random error, the uncertainty in the data was estimated to be $< \pm 0.5\%$. Thus, although not all of the four or five figures of each value in Table 1 are significant, they have been presented so that round-off errors were not incurred in the subsequent analysis.

3. Comparisons of Experimental and Calculated Values

The calculations of transport coefficients for the H_2 -Ne mixtures were carried out using a computer code which solves the Boltzmann equation iteratively using the two-term approximation (see for example Crompton *et al.* 1969). The errors in the calculated drift velocities for the present mixtures due to the use of a two-term code are believed to be negligible. Previous studies have shown such errors to be less than 0.1% (Petrović and Crompton 1987).

The momentum transfer, rotational, and $v = 0 \rightarrow 2$ and $0 \rightarrow 3$ vibrational cross sections assumed in the calculations were considered to be the best available. The

Table 2. Contributions to the absolute error

Source of error	Maximum effect on v_{dr} (%)
(a) Systematic errors	
Voltages between shutters	0.05
Temperature	0.10
Pressure	0.10
Drift distance	0.10
Diffusion correction	0.10
Mixture composition	0.05
Total systematic	<0.30
(b) Random error	0.15
Total error	< ± 0.5

neon momentum transfer cross section used was that derived by Robertson (1972) and that for hydrogen was from Crompton *et al.* (1969). The hydrogen inelastic cross sections were described by Morrison *et al.* (1987). The lowest two rotational cross sections, $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$, are the swarm-derived cross sections up to an energy of 0.35 eV. At higher energies they are merged to the theoretically derived cross sections. The $J = 2 \rightarrow 4$ and $J = 3 \rightarrow 5$ rotational cross sections were derived theoretically by Morrison (1986, personal communication) and the $v = 0 \rightarrow 2$ and $v = 0 \rightarrow 3$ vibrational cross sections were those of Ehrhardt *et al.* (1968) obtained by beam measurements. Neon inelastic cross sections were not included in the calculations because the lowest threshold (16.62 eV) was higher than the maximum energy required in the calculations. Higher inelastic processes for hydrogen were included although their effects on the H₂-Ne calculations were negligible except at 1.7 Td where v_{dr} was changed by less than 0.5% by their inclusion.

The differences between calculated and measured drift velocities are shown in Fig. 1. The points (a) and (b) were obtained using the theoretical $v = 0 \rightarrow 1$ vibrational excitation cross section, and (c) and (d) using the cross section derived from swarm data (Petrović 1986, personal communication), all other cross sections being the same. Ro-vibrational splitting of both $v = 0 \rightarrow 1$ vibrational cross sections was included in the calculations (Morrison *et al.*). The differences of up to 6%, 12 times the estimated experimental error, shown in (a) and (b) support the conclusion drawn from the two previous studies, i.e. that the theoretical cross section is too large near threshold.

Although the differences, (c) and (d), show that the swarm derived vibrational cross section gives much better agreement with experiment, the differences are still not within the stated experimental error limits, being as large as 1.7% for the 2.89% H₂-Ne mixture. The peaks in the differences at about 0.2 Td correspond to the onset of vibrational excitation. When differences of the same type were plotted for a 10.69% H₂-He mixture using the data of Petrović and Crompton (1987) (see Fig. 2), a peak was found at approximately 1.2 Td where the mean swarm energy is 0.4 eV.

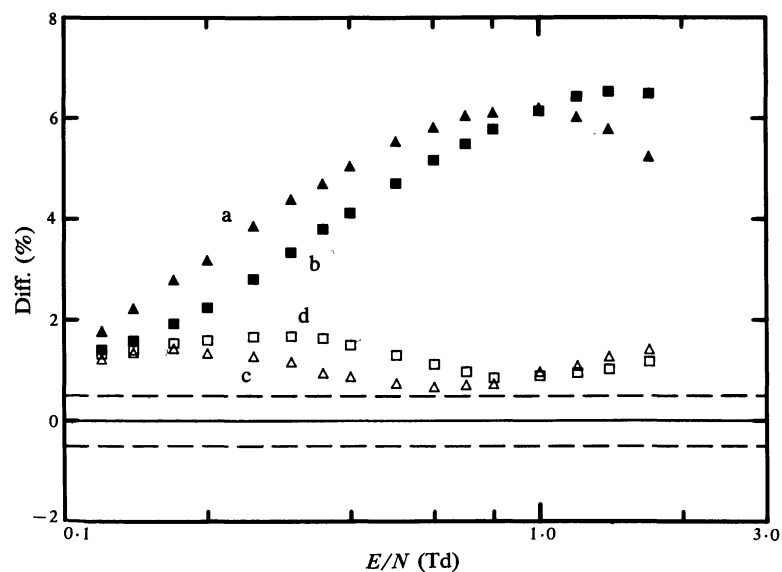


Fig. 1. Differences between calculated and experimental drift velocities,

$$\text{Diff.} = \{v_{\text{dr}}(\text{calc}) - v_{\text{dr}}(\text{exp})\} / v_{\text{dr}}(\text{exp}),$$

using the theoretical $v = 0 \rightarrow 1$ vibrational excitation cross section (a) for 1.160% H_2 -Ne (closed triangles) and (b) for 2.892% H_2 -Ne (closed squares); and using the swarm derived vibrational excitation cross section (c) for 1.160% H_2 -Ne (open triangles) and (d) for 2.892% H_2 -Ne (open squares).

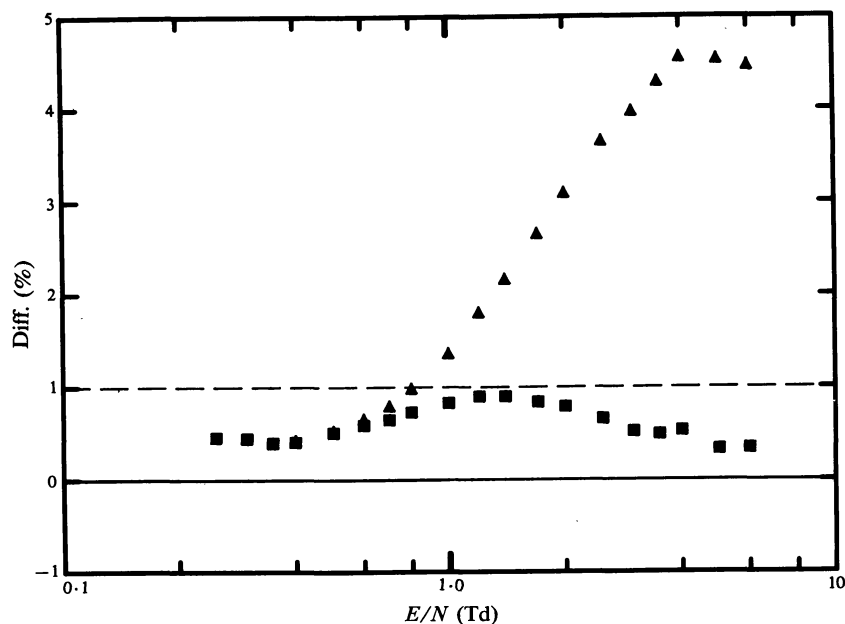


Fig. 2. Differences between calculated and experimental drift velocities for 10.69% H_2 -He using the theoretical $v = 0 \rightarrow 1$ vibrational excitation cross section (triangles) and the swarm derived vibrational excitation cross section (squares). The dashed line shows the estimated experimental uncertainty.

This is about the same mean energy as for the value of E/N for the peak in the H₂-Ne differences. Petrović and Crompton also found that the agreement with experiment, after taking differences from pure He drift velocity measurements, was not always within their experimental uncertainty when the swarm derived vibrational cross section was assumed. Thus, there are strong similarities between the present findings and those of Petrović and Crompton. They stated that any differences outside experimental error could be removed by making small adjustments to the momentum transfer cross sections for helium and hydrogen. Similar adjustments can be made in the present calculations. By raising the neon momentum transfer cross section by 1.8%, most of the differences could be reduced to within the experimental uncertainty. Robertson (1972) quoted the cross section as accurate to $\pm 3\%$, so a change of 1.8% is within the uncertainty in the cross section. In fact, after this adjustment the agreement with the experimental drift velocities of electrons in pure neon at 293 K is still generally within 1.0%.

This explanation for the differences is not considered satisfactory, however, because the differences exhibit a variation with E/N which is much larger than the random scatter of the experimental results and which could not be removed by adjustments to the momentum transfer cross sections.

These arguments led to a reassessment of the calculations involved in the original derivation of the hydrogen cross sections. Transport data for pure hydrogen were originally fitted without making corrections to the calculated values to account for errors introduced by the use of the two-term approximation. Correction factors have since been calculated by comparing the results of two-term calculations with the results from multi-term calculations (Haddad *et al.* 1981; Petrović 1985). The corrections increase with increasing E/N values and, at 34 Td, they are as large as 1.4% for D_T/μ values but are negligible for drift velocities in pure hydrogen. These corrections must be taken into account in the derivation of the cross sections. This had not been done in studies carried out before that of Petrović (1985).

A re-derivation of the H₂ cross sections has therefore been carried out taking into account corrections due to the two-term approximation and using a much more extensive data bank than was available in the original derivation, i.e. including mixture measurements.

4. Derivation of a Revised Set of Cross Sections for Hydrogen

For a cross section set to be considered satisfactory, the calculated transport coefficients were required to predict the following experimental data sets to within the experimental uncertainty:

- (a) drift velocities and D_T/μ values for parahydrogen at 77 K (Robertson 1971; Crompton and McIntosh 1968);
- (b) drift velocities and D_T/μ values for normal hydrogen at 77 K (Robertson 1971; Crompton *et al.* 1968);
- (c) drift velocities and D_T/μ values for normal hydrogen at 293 K (Lowke 1963; Robertson 1971; Crompton *et al.* 1966, 1968);
- (d) drift velocities for 0.5% and 4.0% H₂-Ar mixtures at 293 K (Haddad and Crompton 1980);

(e) drift velocities for a 10.69% H_2 -He mixture at 293.4 K (Petrović and Crompton 1987); and

(f) the present drift velocities for 1.160% and 2.892% H_2 -Ne mixtures at 293 K.

Another important requirement of the derived cross sections was that they should be smoothly varying with energy.

Below 0.4 eV, the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ rotational cross sections can be derived uniquely. For energies above 0.4 eV, however, the onset of vibrational excitation causes a problem of uniqueness and, to derive the vibrational cross section, the rotational cross sections must be extrapolated to energies above 0.4 eV (Crompton *et al.* 1969). Haddad and Crompton (1980) and Petrović (1985) have used the theoretically derived rotational cross sections to extrapolate the swarm derived rotational cross sections to energies above 0.35 eV. This has not been done in the present work as will now be explained.

The procedure used to obtain the cross sections and the differences between the new and previous cross sections are listed below.

(i) Because of the assumption that the cross sections should be smoothly varying with energy, there are limitations imposed on modifications that can be made to the rotational and vibrational cross sections in order to eliminate the structure in the difference curves for the H_2 -Ne mixtures (Fig. 1). If the introduction of unlikely features in the rotational cross sections was to be avoided, it was necessary to lower the vibrational cross section at energies very close to threshold. In this way, a $v = 0 \rightarrow 1$ vibrational cross section was found which removed most of the peak in the mixture difference curves (i.e. for v_{dr} values in 1.160 and 2.892% H_2 -Ne). The theoretical values of Morrison *et al.* (1987) for the rotational splitting of this cross section were used to obtain the rotationally elastic and inelastic parts. The $v = 0 \rightarrow 1$ vibrational cross section agrees with the previous swarm derived cross section to within 10% except at energies in the range from threshold to 0.65 eV where it is as much as 35% lower. The newly derived cross section is lower than the previous cross section which was itself lower than the theoretical cross section.

The additional information about the threshold behaviour of the vibrational cross section, which is now available due to the higher precision of the present experimental results, is a significant new contribution to the derivation of H_2 cross sections. The closer limits on the threshold behaviour of the cross section resulting from the analysis of the new H_2 -Ne data enables the rotational cross sections derived from swarm measurements to be extended to higher energies than was previously possible.

(ii) A $J = 0 \rightarrow 2$ rotational cross section was derived which gave a satisfactory fit to the parahydrogen data using the new vibrational cross section [from point (i)]. For energies between threshold and 0.4 eV, the new $J = 0 \rightarrow 2$ cross section is equal to or less than the original, the maximum difference being less than the quoted error of $\pm 5\%$. For energies between 0.4 and 0.9 eV, the $J = 0 \rightarrow 2$ cross section was obtained by merging smoothly to the theoretical cross section. The fit was improved by a small decrease (0.6%) in the hydrogen momentum transfer cross section for all energies [the decrease is much smaller than the quoted error limits for this cross section, i.e. $\pm 5\%$, see Crompton *et al.* (1969)].

(iii) The $J = 1 \rightarrow 3$ rotational cross section was adjusted to improve the fit to data in normal hydrogen at 77 K using the cross sections from points (i) and (ii). For energies between threshold and 1.3 eV, the $J = 1 \rightarrow 3$ cross section is lower than the

original but, in general, is within 10% and is closer to the theoretical cross section. The cross section between 1.3 and 2.5 eV was merged smoothly to the theoretical cross section.

(iv) Higher rotational cross sections were obtained using the $J = 0 \rightarrow 2$ rotational cross section and smoothed values for their ratios from the theoretical

Table 3. Present H₂ rotational excitation cross sections (in Å²)

Energy (eV)	$J = 0 \rightarrow 2$ (Å ²)	Energy (eV)	$J = 1 \rightarrow 3$ (Å ²)	Energy (eV)	$J = 2 \rightarrow 4$ (Å ²)	$J = 3 \rightarrow 5$ (Å ²)
0.0439	0.0	0.0727	0.0	0.1008	0.0	
0.047	0.0185	0.075	0.0070	0.1280		0.0
0.050	0.027	0.080	0.0140	0.15	0.0272	0.016
0.055	0.035	0.085	0.0198	0.20	0.0424	0.037
0.060	0.042	0.090	0.0237	0.25	0.0557	0.051
0.065	0.048	0.095	0.0265	0.30	0.0663	0.062
0.070	0.053	0.10	0.0280	0.35	0.0766	0.072
0.080	0.062	0.11	0.0330	0.40	0.0872	0.082
0.090	0.068	0.12	0.0364	0.45	0.0955	0.093
0.10	0.074	0.13	0.0394	0.50	0.1054	0.104
0.11	0.079	0.15	0.0450	0.60	0.132	0.129
0.13	0.088	0.20	0.0580	0.70	0.162	0.160
0.15	0.097	0.25	0.0719	0.80	0.193	0.194
0.20	0.115	0.30	0.0860	0.90	0.227	0.233
0.25	0.132	0.35	0.1000	1.0	0.266	0.271
0.30	0.152	0.40	0.1140	1.5	0.463	0.478
0.35	0.175	0.45	0.1285	2.0	0.619	0.637
0.40	0.200	0.50	0.1439	2.5	0.719	0.742
0.45	0.228	0.56	0.1633	3.0	0.774	0.799
0.50	0.260	0.60	0.1776	3.5	0.799	0.825
0.60	0.323	0.66	0.1996	4.0	0.802	0.828
0.70	0.394	0.70	0.2135	4.5	0.790	0.818
0.80	0.469	0.80	0.2518	5.0	0.771	0.797
0.90	0.555	0.90	0.2919	5.5	0.748	0.774
1.0	0.636	1.01	0.3338	6.0	0.721	0.747
1.2	0.796	1.2	0.420	7.0	0.669	0.692
1.5	1.036	1.4	0.510	8.0	0.617	0.640
2.0	1.370	1.6	0.610	10.0	0.529	0.548
2.5	1.585	1.8	0.700			
3.0	1.704	2.0	0.786			
3.5	1.755	2.5	0.937			
4.0	1.758	3.0	1.014			
4.5	1.732	3.5	1.046			
5.0	1.689	4.0	1.050			
6.0	1.579	4.5	1.036			
7.0	1.462	5.0	1.011			
8.0	1.350	6.0	0.946			
9.0	1.248	7.0	0.876			
10.0	1.156	8.0	0.809			
15.0	0.730	9.0	0.748			
		10.0	0.694			
		15.0	0.450			

cross sections. These were then adjusted below 1.0 eV to improve the agreement of calculated with experimental values for normal hydrogen at 293 K and H₂-Ne mixtures. The $J = 2 \rightarrow 4$ rotation was also multiplied by a normalising factor of about 0.9.

The new cross sections for rotational and vibrational excitation together with that for momentum transfer are listed in Tables 3 to 5.

The revised $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ rotational cross sections differ from the cross sections used by Petrović and Crompton (1987) by less than 10% except for the $J = 1 \rightarrow 3$ cross section at energies close to the threshold. The differences of the new from the theoretically derived rotational cross sections are generally less than $\pm 10\%$

Table 4. Present H₂ $v = 0 \rightarrow 1$ vibrational excitation cross sections (in Å²)

Energy (eV)	$v = 0 \rightarrow 1, \Delta J = 0$ (Å ²)	$v = 0 \rightarrow 1, \Delta J = 2$ (Å ²)
0.516	0.0	
0.558		0.0
0.56	0.0028	
0.575		0.0005
0.60	0.0053	0.0013
0.65	0.0082	0.0032
0.75	0.0143	0.0078
0.85	0.0206	0.0134
0.95	0.0280	0.0205
1.00	0.0322	0.0248
1.05	0.0363	0.0287
1.10	0.0407	0.0333
1.15	0.0450	0.0380
1.20	0.0499	0.0437
1.30	0.0594	0.0549
1.40	0.0688	0.0653
1.60	0.0865	0.0892
1.80	0.1038	0.1139
2.2	0.1394	0.1639
2.4	0.1561	0.1869
2.6	0.1709	0.2121
3.0	0.1916	0.2494
3.5	0.2008	0.2672
4.0	0.1860	0.2540
4.5	0.1630	0.2270
5.0	0.1460	0.2040
6.0	0.1160	0.1640
7.0	0.0876	0.1224
8.0	0.0637	0.0879
9.0	0.0506	0.0684
10.0	0.0376	0.0498
11.0	0.0292	0.0388
12.0	0.0215	0.0285
13.0	0.0180	0.0200
14.0	0.0170	0.0150
15.0	0.0150	0.0100

except for the $J = 2 \rightarrow 4$ rotational cross section where the new cross section values are as much as 18% less than the theoretical cross section.

The revised $v = 0 \rightarrow 1$ vibrational cross section differs from the cross section used by Petrović and Crompton by less than 10% except at energies close to the threshold energy. On the other hand, the new cross section is as much as 40% less than the theoretical cross section. A comparison of the rotationally elastic $v = 0 \rightarrow 1$ vibrational cross sections is shown in Fig. 3.

Table 5. Present H₂ momentum transfer cross section (in Å²)

Energy (eV)	Momentum transfer (Å ²)	Energy (eV)	Momentum transfer (Å ²)
0.0	6.36	0.60	15.51
0.01	7.26	0.70	16.20
0.02	7.95	0.90	17.00
0.03	8.45	1.0	17.30
0.04	8.91	1.1	17.59
0.046	9.05	1.4	18.09
0.05	9.22	1.5	18.14
0.06	9.50	1.6	18.19
0.07	9.79	1.8	18.09
0.08	10.04	2.0	17.89
0.09	10.24	2.5	17.69
0.10	10.44	3.0	16.90
0.13	10.93	4.0	14.71
0.15	11.33	5.0	12.92
0.20	11.93	6.0	11.93
0.30	12.92	10.0	7.60
0.40	13.82	25.0	1.49
0.50	14.61		

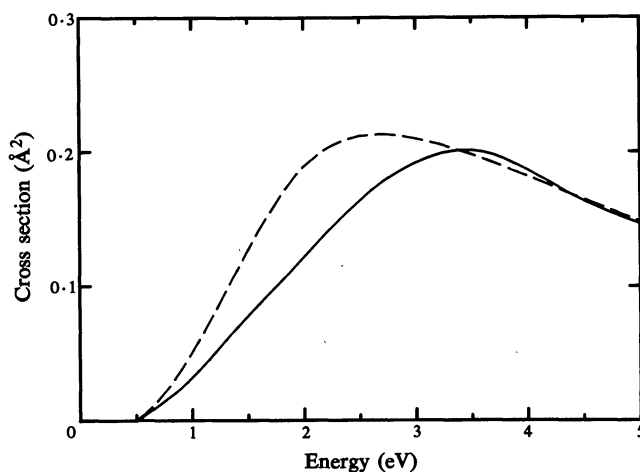


Fig. 3. Rotationally elastic $v = 0 \rightarrow 1$ vibrational excitation cross section: the full curve is the present cross section and the dashed curve is the theoretical cross section.

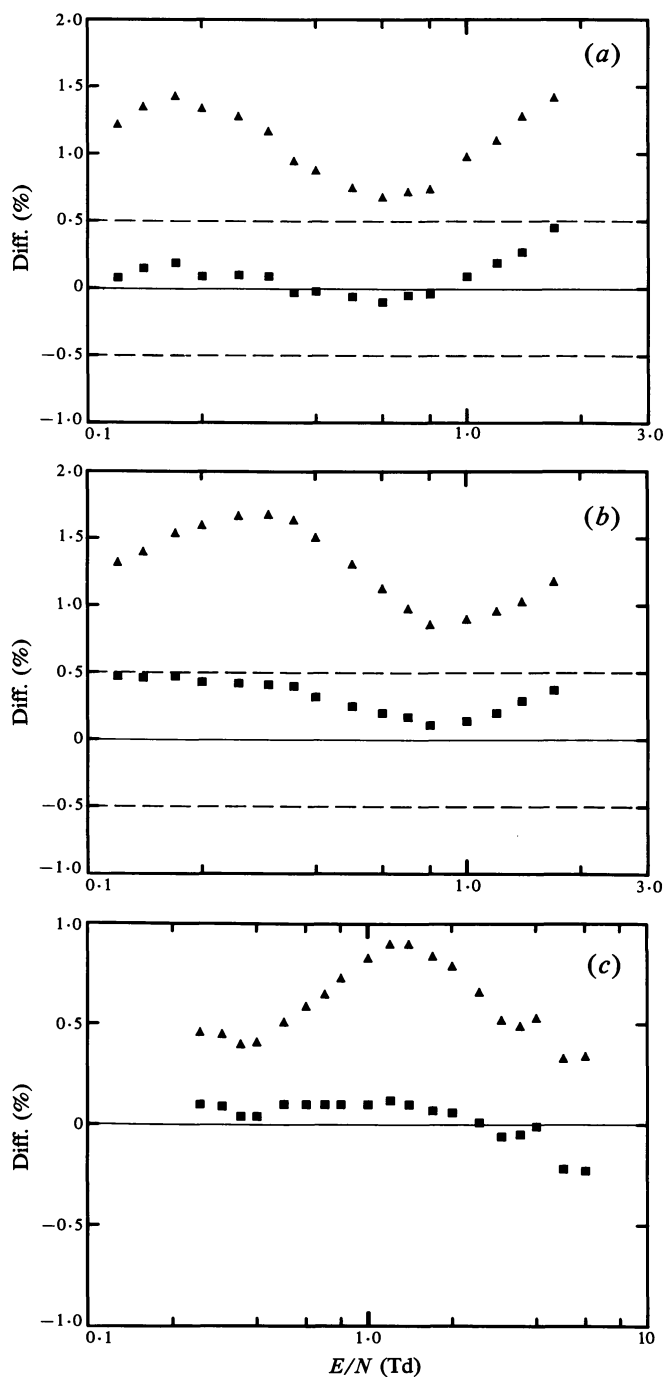


Fig. 4. Differences between calculated and experimental drift velocities using the present H_2 cross sections (squares), and using the previous best H_2 cross sections (including the previous swarm-derived $v = 0 \rightarrow 1$ vibrational excitation cross section, see Section 3) (triangles) for: (a) and (b) 1.160% and 2.892% H_2 -Ne respectively, where the dashed lines show the experimental uncertainties; (c) 10.69% H_2 -He drift velocities, where the experimental uncertainty is $\pm 1\%$.

The $v = 0 \rightarrow 2$ and $v = 0 \rightarrow 3$ vibrational cross sections were not changed since the sensitivity of the transport coefficients to these cross sections is very small—complete removal of them leads to negligible changes except at the highest E/N values.

The differences between calculated and experimental drift velocities for H₂–Ne and H₂–He mixtures are shown in Fig. 4. The new set of cross sections gives agreement between calculated and experimental values to within the experimental uncertainties for all the data sets listed in Section 4.

5. Conclusions

Measurements of the drift velocities of electrons in two H₂–Ne mixtures have been carried out to test the validity of experimental and theoretical vibrational excitation cross sections near threshold. It was found that the theoretical cross section was incompatible with the measurements. This result is consistent with previous studies of the same type (Haddad and Crompton 1980; Petrović and Crompton 1987); however, more weight can now be put on the conclusion due to the absence of problems of reduced sensitivity to the vibrational cross section in the H₂–He study and of larger uncertainties in the H₂–Ar study due to the uncertainties in the momentum transfer cross section of argon.

The agreement of the experimental drift velocities with values calculated using the earlier cross sections derived from swarm measurements, although much better than that obtained using the theoretical cross section, was not within the present estimated experimental errors. The results for H₂–He of Petrović and Crompton showed similar discrepancies. The hydrogen cross sections have therefore been rederived using the available transport data for normal hydrogen, parahydrogen and H₂–He and H₂–Ne gas mixtures. Corrections for the use of the two-term approximation in the calculations were applied.

The newly derived cross sections in general do not differ from the original cross sections, including the earlier swarm derived vibrational cross section, by more than 10%. The new cross section set provides improved agreement with experimental transport parameters for electrons in parahydrogen (77 K), normal hydrogen (77 and 293 K), a H₂–He mixture and the present H₂–Ne mixtures, and retains satisfactory agreement with data from H₂–Ar mixtures.

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