

A Swarm Experiment in He-H₂ Mixtures to Examine Vibrational Excitation of H₂ by Electron Impact

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Abstract

Measurements of electron drift velocities have been made in pure helium and in a helium-hydrogen mixture in order to check the available inelastic cross sections for hydrogen. Although drift velocities in mixtures with helium as the buffer gas are less sensitive to inelastic scattering by hydrogen than those with argon, the accuracy with which the momentum transfer cross section for helium is known enables the check to be made with virtually no error arising from uncertainty in the momentum transfer cross section for the buffer gas, in contrast to the situation when argon is used. A difference technique has been used to minimise the effect of systematic errors in the measurements. The results support the rotational and vibrational cross sections derived from the transport coefficients measured in pure hydrogen.

1. Introduction

In the accompanying paper Morrison *et al.* (1987; present issue p. 239) (see also Petrović 1985; Crompton and Morrison 1987) discuss the present position regarding the cross sections for the elastic and inelastic scattering of low-energy (i.e. less than 2 eV) electrons by molecular hydrogen. These authors point out that in the case of direct (non-resonant) vibrational excitation near threshold there is a significant difference between the results obtained by beam and swarm experiments, and between some of these results and the results of *ab initio* theoretical calculations. This situation is not satisfactory and needs resolution in order to establish confidence in the experimental and theoretical techniques that have been used. In the present paper we present additional evidence, obtained from drift velocity measurements in helium-hydrogen mixtures, which supports the vibrational cross section determined from the analysis of transport coefficients in pure hydrogen. While it cannot be claimed that this new evidence resolves the situation, it is an important independent check on the earlier swarm-derived cross section which is free of objections that could be levelled at similar checks using argon-hydrogen mixtures (Haddad and Crompton 1980).

One of the disadvantages of the swarm technique is the loss of uniqueness of the cross sections determined from an analysis of drift and diffusion data when more than one inelastic cross section has a significant influence on electron transport. This may lead to a significant reduction in accuracy of the cross sections (Huxley and Crompton 1974; Crompton 1983). The most direct method of overcoming this problem is to

supplement the data for the transport coefficients with data for the rate coefficients for specific processes, for example, vibrational excitation (e.g. Bulos and Phelps 1976; Buckman and Phelps 1985) or electronic excitation (e.g. Tachibana and Phelps 1979). Unfortunately some of the advantage of this approach is lost through the difficulty of making accurate rate coefficient measurements.

An alternative approach is through the measurement of transport coefficients in gas mixtures, for example, H_2 and Ar as in the work of Engelhardt and Phelps (1964) and Haddad and Crompton (1980). Because of the very small energy exchange in elastic collisions between electrons and argon atoms, the energy exchange in collisions with hydrogen molecules becomes important or even dominant for quite low concentrations of H_2 ; this is particularly the case when the distribution of energies in the swarm is such that a significant fraction of the electrons have energies exceeding the vibrational threshold. Furthermore, because the fraction of H_2 in the mixture is small, the momentum transfer cross section for the mixture is nearly the same as that for pure Ar except in the vicinity of the Ramsauer–Townsend minimum. It follows that the addition of the hydrogen significantly lowers the mean energy of the swarm and, at higher energies, increases the drift velocity quite spectacularly. The large change in the drift velocity occurs because the onset of vibrational excitation in H_2 coincides with the rapid increase of the momentum transfer cross section in Ar above the Ramsauer–Townsend minimum. As a consequence the lowering of the mean energy of the swarm by vibrational excitation of H_2 greatly reduces the collision frequency for momentum transfer, producing a corresponding increase in the drift velocity. Advantage can be taken of this sensitivity to base the determination of the vibrational excitation cross section solely on drift velocities which are more easily and accurately measured than ratios of the diffusion coefficient to mobility.

Haddad and Crompton (1980) measured electron drift velocities and diffusion coefficient-to-mobility ratios in mixtures containing 0.5% and 4% of H_2 in Ar. Although their work appeared to provide strong support for the vibrational excitation cross section determined from transport data in pure H_2 , this conclusion can be challenged on the basis of some uncertainty in the Ar momentum transfer cross section above the Ramsauer–Townsend minimum (Crompton 1983; Petrović 1985).

In order to overcome this objection it was decided to make measurements in mixtures of hydrogen and helium since the momentum transfer cross section for helium is known very accurately [to within $\pm 2\%$ —see Crompton *et al.* (1970); O'Malley *et al.* (1979); Nesbet (1979)]. However, a major disadvantage is that the momentum transfer cross section is only weakly dependent on the electron energy in the range of interest, and therefore the sensitivity to the inelastic processes is reduced when helium rather than argon is used.

To compensate for the reduced sensitivity an alternative approach based on a difference technique was adopted, thus enabling predictions based on different H_2 cross section sets to be compared with experimental data that were free from most systematic errors. First, drift velocities in pure helium and in a mixture of helium with hydrogen were measured. The differences between the drift velocities measured under identical conditions with and without hydrogen were then determined. Drift velocities were then calculated for pure helium and for the helium–hydrogen mixture, the differences determined, and the comparisons with the experimental data made. By using this procedure the sources of systematic error in the experimental data were considerably reduced, the residual errors being those arising from the determination

of the mixture composition and a possible change of the temperature between the two measurements, and from the small corrections to account for diffusive effects (Huxley and Crompton 1974).

2. Measurements of Drift Velocities in Pure He and in an He-H₂ Mixture

The Bradbury-Nielsen method as described by Crompton *et al.* (1970) was used to measure drift velocities. Previously described procedures were followed in order to produce results of high accuracy (see Elford 1972; Huxley and Crompton 1974). Research grade helium was used, while hydrogen was purified through a heated palladium osmosis thimble (Crompton and Elford 1962). The gas number density was determined from accurate pressure and temperature measurements. A calibrated quartz spiral manometer (Texas Instruments) was used for the pressure measurements enabling pressures to be measured to within $\pm 0.1\%$. The temperature of the water bath in which the drift tube was immersed was measured to within 0.25°C at the time the tube was filled and valved off from the vacuum system. The temperature variation was less than 0.3°C during the course of the experiment.

A mixture of 10.69% of hydrogen in helium was prepared by volume sharing using a mixing vessel similar to that described by Haddad (1983). The volume ratio was determined by a volume-sharing technique which took advantage of the very large range of pressures that can be accurately measured with the quartz spiral manometer. The choice of the abundance (10.69%) was determined by the pressures at which the gauge had been calibrated and the volume ratio of the mixing vessel. The vessel was immersed in a water bath, thus keeping the temperature stable during the mixture preparation. Sufficient time was allowed at each stage for the gas to reach thermal equilibrium with its surroundings and for thorough mixing. The estimated uncertainty in the mixture composition is $\pm 0.2\%$.

Corrections for diffusive effects were made using the procedure previously described (Elford 1972). Values of the characteristic energy for the mixture, which were required to make the corrections, were calculated using published cross sections for H₂ and He. The corrections were always less than 0.4% and were applied to the raw data to obtain the results shown in Tables 1 and 2.

Measurements in pure helium were made for values of E/N up to 3 Td. The results, presented in Table 1, agree with the data of Crompton *et al.* (1967) and Milloy and Crompton (1977) to within 0.3%. A conservative estimate of the uncertainty of our data is $\pm 1.0\%$. Although not justified on the basis of this error estimate, the data are presented to four significant figures to avoid the effects of round-off errors in the subsequent analysis.

The results for the mixture are presented in Table 2. The error bounds for these data are slightly larger due to the uncertainty of the mixture composition.

3. Discussion

Before discussing the results derived from the application of the difference technique, it is interesting to examine the results obtained directly from the measurements. The results for pure helium and for the He-H₂ mixture are shown in Fig. 1. Also shown are curves for calculated drift velocities corresponding to these experimental data. The dashed curve for pure He is based on the swarm-derived He momentum transfer cross section; curve (a) for the mixture is calculated using this cross section and the set of cross sections for H₂ (i.e. for momentum transfer, rotation, and vibration) derived

The calculations were made using a standard two-term Boltzmann code. The errors in the calculated drift velocities for the mixture resulting from the two-term approximation were found by recalculating the drift velocities using a multiterm code (Lin *et al.* 1979) and the same set of cross sections. For values of E/N between 0.25 and 7 Td, that is, for values of E/N covering the region most sensitive to the $v = 0 \rightarrow 1$ vibrational excitation cross section, the errors were less than 0.1%.

The measured drift velocities in the mixture agree with the calculated values to within 1% when the swarm-derived cross sections are used. However, differences of up to 5% occur when the swarm-derived σ_v is replaced by the theoretical cross section (Morrison *et al.* 1987).

The significance of the test of the vibrational cross sections can be enhanced by taking advantage of the difference techniques described in Section 1. Because of the cancellation of most of the systematic errors, the uncertainty in the difference between the drift velocities measured in pure helium and in the mixture is reduced to $\pm 0.5\%$. Therefore, in Fig. 2, we plot the relative differences Δv_{dr} , defined as

$$\Delta v_{dr} = |v_{dr}^{\text{He}} - v_{dr}^{\text{mix}}| / v_{dr}^{\text{He}},$$

against E/N and compare these data with those calculated using the swarm-derived and theoretical vibrational cross sections.

Our measurements in pure He terminate at $E/N = 3$ Td, thus we cannot apply arguments based on difference measurements above this value. Nevertheless, we include data between 3 and 7 Td based on Milloy and Crompton's (1977) measurements in helium to provide supporting evidence at higher swarm energies.

Between 0.7 and 3.0 Td, where there is an increasing influence of σ_v on the drift velocity in the mixture, there is a monotonic increase in Δv_{dr} . At $E/N = 3$ Td the measured Δv_{dr} is about 31% with an uncertainty of $\pm 0.5\%$. This is to be compared with a calculated value that is about 6% higher (i.e. $\Delta v_{dr} = 37\%$) when the theoretical vibrational cross section is used but less than 1% higher when the swarm derived cross section is used. Fig. 2 shows that this trend holds generally throughout the range. Thus the theoretical cross section predicts values that lie well outside the limits of uncertainty of the experimental data, while the earlier swarm-derived cross section leads to values that are within these limits or just outside them. Small adjustments of the momentum transfer cross sections for He and H_2 (within the error limits claimed for these cross sections) can be made which bring the calculated values of Δv_{dr} within the error limits of the experimental data when the swarm-derived σ_v is used. However, the calculated and experimental data cannot be reconciled in this way for the theoretical σ_v .

4. Conclusions

New experimental results are presented in this paper to test the validity of experimental and theoretical vibrational excitation cross sections near threshold. The four features of the work that add weight to the conclusions drawn from it are the following:

- (i) a mixture technique has been used to separate more effectively the effects of elastic and inelastic scattering on electron transport;
- (ii) helium was used as the buffer gas because of the high accuracy with which its momentum transfer cross section is known at low energies;

- (iii) a difference technique was used to reduce the uncertainty due to systematic errors;
- (iv) the conclusions are based on the measurement and analysis of electron drift velocities. Drift velocities are the most accurately measurable of the transport coefficients, and in this instance subject to negligible error (<0.1%) when calculated using conventional (two-term) transport theory.

When combined with conclusions based on a large body of data for pure H₂ and Ar-H₂ mixtures, the new results give a high degree of confidence in the swarm-derived $v = 0 \rightarrow 1$ vibrational excitation cross section near threshold, highlighting the need for further evidence from accurate low-energy beam experiments to help resolve the questions raised in the companion paper by Morrison *et al.*

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