

# THE CROSS SECTION FOR THE $J = 0 \rightarrow 2$ ROTATIONAL EXCITATION OF HYDROGEN BY SLOW ELECTRONS

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## Summary

The results of electron drift and diffusion measurements in parahydrogen have been analysed to determine the cross sections for momentum transfer and for rotational and vibrational excitation. The limited number of possible excitation processes in parahydrogen and the wide separation of the thresholds for these processes make it possible to determine uniquely the  $J = 0 \rightarrow 2$  rotational cross section from threshold to 0.3 eV. In addition, the momentum transfer cross section has been determined for energies less than 2 eV and it is shown that, near threshold, a vibrational cross section compatible with the data must lie within relatively narrow limits. The problems of uniqueness and accuracy inherent in the swarm method of cross section analysis are discussed. The present results are compared with other recent theoretical and experimental determinations; the agreement with the most recent calculations of Henry and Lane is excellent.

## I. INTRODUCTION

In recent years considerable interest has been shown in the rotational excitation of hydrogen molecules by slow electrons. Beginning with the work of Morse (1953) and Carson (1954) there has been a succession of theoretical calculations (Gerjuoy and Stein 1955; Dalgarno and Moffett 1963; Dalgarno and Henry 1965; Sampson and Mjolsness 1965; Takayanagi and Geltman 1965; Geltman and Takayanagi 1966; Lane and Geltman 1967) leading to the latest calculation of Henry and Lane (1969) that takes account of both polarization and exchange effects.

Because the electron energies required for rotational excitation of molecules are so low ( $< 0.1$  eV), it is difficult to use a beam experiment to make a direct determination of the cross sections for these processes in the near-threshold region. Ehrhardt and Linder (1968) have recently succeeded in determining the cross section for the  $J = 1 \rightarrow 3$  excitation in hydrogen but their results do not extend below 1 eV. Furthermore, in experiments of this type there is a fundamental difficulty in making an absolute determination of the cross section; for example in Ehrhardt and Linder's work the results were normalized to the absolute total cross section measured by Golden, Bandel, and Salerno (1966). Despite the success of Ehrhardt and Linder's recent experiment, the need still remains for an absolute determination of the cross section, particularly for energies between threshold and 1 eV.

Prior to 1962, the alternative approach to the problem, through the interpretation of swarm experiments (i.e. experiments to determine the average behaviour of electrons drifting and diffusing through a gas), was rather indirect but it had yielded

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valuable qualitative and semiquantitative information about the inelastic loss processes. For example, Gerjuoy and Stein (1955) showed that the inclusion of the electron quadrupole interaction in calculations of the rotational excitation of hydrogen considerably improved the agreement between theory and experiment. Gerjuoy and Stein made their comparison through the "mean fractional energy loss" deduced from the experimental results. Because of the assumptions which had to be made to estimate the electron energy distribution function necessary for the calculation of the mean fractional energy loss, such an approach could not provide an accurate and detailed comparison between theory and experiment. This situation was changed completely by the work of Frost and Phelps (1962). These authors took advantage of the development of high speed computing methods to obtain numerical solutions to the Boltzmann equation using an extension of the theory of Holstein (1946) and Margenau (1946). In a series of papers (Frost and Phelps 1962; Engelhardt and Phelps 1963; Engelhardt, Phelps, and Risk 1964; Frost and Phelps 1964; Hake and Phelps 1967) Phelps and his colleagues at the Westinghouse Laboratories applied this technique to a study of low energy collision processes in a number of gases, the work described in the first two papers providing the first definitive experimental test of some of the theoretical cross sections listed above. On the basis of their analysis of the low temperature swarm data of Pack and Phelps (1961) and Warren and Parker (1962), Frost and Phelps suggested that either the Gerjuoy and Stein treatment of rotational excitation was inadequate or that the quadrupole moment of Harrick and Ramsey (1952) was seriously in error. Since this analysis in 1962, the theoretical treatments have become increasingly refined but there have been no new experimental data of adequate accuracy to test the completeness of the theories and the validity of the approximations that have been made.

A fundamental problem in determining cross sections from transport data is that of determining the accuracy and uniqueness of the results. Lack of uniqueness is an inherent problem when, as in the low energy region, cross sections for a number of competing inelastic processes must be determined from relatively limited experimental data, i.e. data for two or three transport coefficients. Similar problems arise from the use of experimental data of limited accuracy. The related problems of uniqueness and accuracy are discussed in Section III.

In order to make the best use of the swarm technique we have analysed the results of swarm experiments in parahydrogen (Crompton and McIntosh 1968). These experiments were designed to yield precise transport measurements in a situation in which the thresholds for the inelastic processes are relatively widely spaced, the only inelastic processes of significance for low energy electrons in parahydrogen being the  $J = 0 \rightarrow 2$  rotational transition and the first vibrational excitation for which the thresholds are 0.044 and 0.52 eV respectively. The techniques developed by Frost and Phelps (1962) and Engelhardt and Phelps (1963) have been used for the analysis.

The primary experimental data used are the measurements of the electron drift velocity  $W$  and the ratio of diffusion coefficient to mobility  $D/\mu$ . Although other electron transport coefficients have been used for such analyses, e.g. the magnetic deflection coefficient (Engelhardt and Phelps 1963; Crompton, Elford, and Jory 1967), the quantities that were selected for measurement and analysis in this instance are those which are capable of being measured with the greatest accuracy.

As a result of our analysis we have concluded that the rotational cross section can be determined to within about 5% from the threshold to 0.3 eV and to within 10% to 0.4 eV. In order to arrive at the error limit at 0.4 eV a reasonable estimate of the vibrational cross section had to be made; nevertheless we believe that the limit is a somewhat generous overestimate. Above this energy the accuracy and uniqueness of the cross section rapidly deteriorate owing to the increasing importance of vibrational excitation in determining the energy distribution function for the swarm.

At sufficiently high energies, vibrational excitation becomes so dominant that the cross section for this process can be determined even though two inelastic processes are now operative. We have therefore been able to determine a vibrational cross section which, while not unique, is compatible with the swarm data in parahydrogen and we give reasons for suggesting that this cross section may be more accurate near threshold than that recently reported by Ehrhardt *et al.* (1968).

## II. THEORY

The energy distribution of electrons in a gas subject to an electric field has been treated by many authors (e.g. Holstein 1946; Margenau 1946; Allis 1956). The particular form of the Boltzmann equation derived by Holstein and modified by Margenau to include the effect of the molecular energy distribution is (Frost and Phelps 1962)

$$\begin{aligned} \frac{E^2 e^2}{3} \frac{d}{d\epsilon} \left( \frac{\epsilon}{N q_m(\epsilon)} \frac{df}{d\epsilon} \right) + \frac{2m}{M} \frac{d}{d\epsilon} \left( \epsilon^2 N q_m(\epsilon) f(\epsilon) \right) + \frac{2mkT}{M} \frac{d}{d\epsilon} \left( \epsilon^2 N q_m(\epsilon) \frac{df}{d\epsilon} \right) \\ + \sum_j \{ (\epsilon + \epsilon_j) f(\epsilon + \epsilon_j) N q_j(\epsilon + \epsilon_j) - \epsilon f(\epsilon) N q_j(\epsilon) \} \\ + \sum_j \{ (\epsilon - \epsilon_j) f(\epsilon - \epsilon_j) N q_{-j}(\epsilon - \epsilon_j) - \epsilon f(\epsilon) N q_{-j}(\epsilon) \} = 0. \quad (1) \end{aligned}$$

The solution of this equation gives the steady state energy distribution  $f(\epsilon)$  of a swarm of electrons drifting and diffusing through a gas at temperature  $T$  under the influence of a uniform electric field  $E$ .  $N$  is the gas number density,  $q_m(\epsilon)$  is the energy-dependent momentum transfer cross section,  $q_j(\epsilon)$  is a rotational, vibrational, or electronic excitation cross section with an excitation energy  $\epsilon_j$ , and  $q_{-j}(\epsilon)$  is the cross section for collisions of the second kind in which an electron gains the excitation energy  $\epsilon_j$  from a molecule. The other symbols are for the electronic charge  $e$ , the electronic mass  $m$ , the molecular mass  $M$ , and Boltzmann's constant  $k$ . The distribution function is normalized through the relation

$$\int_0^\infty \epsilon^{\frac{1}{2}} f(\epsilon) d\epsilon = 1.$$

In principle it is possible to measure  $f(\epsilon)$  directly and to compare the results with solutions of equation (1) using trial sets of cross sections. Up to the present time, however, electron energy distribution functions have been measured directly only in a few cases at relatively high values of  $E/N$  (see e.g. Roberts and Burch 1966). An

alternative procedure that has been adopted is to compare experimental and calculated values of electron drift velocities and diffusion coefficients. These coefficients are comparatively straightforward integrals of functions of the momentum transfer cross section and the energy distribution function. Written in terms of the energy distribution function of equation (1) these integrals are

$$W = \frac{-eE(2/m)^{\frac{1}{2}}}{3N} \int_0^{\infty} \frac{\epsilon}{q_m(\epsilon)} \frac{df}{d\epsilon} d\epsilon, \quad (2)$$

$$D = \frac{(2/m)^{\frac{1}{2}}}{3N} \int_0^{\infty} \frac{\epsilon f(\epsilon)}{q_m(\epsilon)} d\epsilon$$

from which the ratio of diffusion coefficient to mobility ( $\mu = W/E$ ) is found to be

$$De/\mu = - \int_0^{\infty} \frac{\epsilon f(\epsilon) d\epsilon}{q_m(\epsilon)} \bigg/ \int_0^{\infty} \frac{\epsilon}{q_m(\epsilon)} \frac{df}{d\epsilon} d\epsilon. \quad (3)$$

The determination of cross sections by the swarm method therefore consists of taking a trial set of cross sections, calculating  $f(\epsilon)$  from equation (1), evaluating  $W$  and  $D/\mu$  using equations (2) and (3), comparing calculated and measured values over as large a range of  $E/N$  as possible, and adjusting the cross sections until the agreement matches the accuracy of the experimental data. The uniqueness and accuracy of the cross sections derived in this way are discussed in the following section.

### III. DETERMINATION OF THE CROSS SECTIONS; UNIQUENESS AND ACCURACY

#### (a) *General Considerations*

As in all analyses which rely on an unfolding technique it is necessary to examine closely the uniqueness of the results obtained by the method outlined in the preceding section. Only in exceptional cases (see e.g. Crompton, Elford, and Jory 1967; Robertson, Elford, and Crompton, in preparation) does the uniqueness depend ultimately on the accuracy of the experimental results for the transport coefficients; in general uniqueness is lost to a greater or lesser degree by there being insufficient experimental data to determine the cross sections for a number of simultaneously occurring processes.

It is possible to use the present method for determining cross sections only because of the relatively restricted energy range which characterizes the energy distribution of electrons in a swarm for a given set of experimental conditions. The fact that the energies are rather narrowly distributed about the mean energy means that, in calculating the transport integrals, there is an effective range extending from zero to about twice the mean energy within which nearly all the integral is contained. The energy distribution and transport coefficients at each value of  $E/N$  are determined by the values of the cross sections over this small energy range and it is therefore possible to examine the energy dependence of these cross sections by analysing the data recorded at a series of values of  $E/N$ .

The simplest case to consider is that of elastic scattering only. While it is true that for any value of  $E/N$  there are many alternative cross section curves which

would yield the correct transport integrals, the choice narrows when experimental results are available for a range of values of  $E/N$ . In this case the results apply to swarms having a range of values of mean energy, and, consequently, a cross section that is specified within narrow limits over a range of energy is required to fit the experimental data at all values of  $E/N$ . The wider the range of  $E/N$  employed and the more precise the experimental measurements the wider will be the energy range for which the cross section is known within given limits.

The simplest extension to the case already described is that in which elastic scattering is accompanied by only one inelastic process. If two different transport coefficients are measured over the chosen range of  $E/N$ , unique curves for the cross sections for both processes can be obtained, with factors similar to those already described governing the accuracy and energy range of the determination. This is made possible by the fact that the momentum transfer cross section  $q_m$  enters explicitly into the transport integrals whereas the inelastic cross section enters only through its effect on the electron energy distribution function.

The situation is not as favourable when more than one inelastic process is present to control the energy distribution of the swarm. Suppose there are two such processes with cross sections  $q_1(\epsilon)$  and  $q_2(\epsilon)$  and thresholds  $\epsilon_1$  and  $\epsilon_2$  and that  $\epsilon_1 \ll \epsilon_2$ . For the lowest energy swarms an insignificant number of electrons have energy greater than  $\epsilon_2$  and  $q_m(\epsilon)$  and  $q_1(\epsilon)$  can be determined uniquely as described above. On the other hand at higher energies the numbers of inelastic collisions of each type become comparable. However, an electron loses as much energy in a single collision involving the process with threshold  $\epsilon_2$  as it does in making many collisions involving the process with the lower threshold. Consequently collisions in which the energy loss is  $\epsilon_2$  play a dominant role in determining the energy distribution and the threshold behaviour of  $q_2(\epsilon)$  can be determined provided a reasonable extrapolation of  $q_1(\epsilon)$  can be made. We can summarize as follows.

- (1) Above a transition energy somewhat below  $\epsilon_2$ , neither cross section can be uniquely determined from swarm data alone.
- (2)  $q_1(\epsilon)$  can be determined uniquely from threshold to the transition energy. Above this energy, uniqueness in its determination is lost unless  $q_2(\epsilon)$  is accurately known from another source.
- (3)  $q_2(\epsilon)$  can never be uniquely determined unless  $q_1(\epsilon)$  is known. On the other hand, provided the separation between the threshold energies  $\epsilon_1$  and  $\epsilon_2$  is sufficiently large,  $q_2(\epsilon)$  can be determined within comparatively narrow limits even though  $q_1(\epsilon)$  is not accurately known.

Despite the limitations of this method of determining cross sections, important results have followed from its application to molecular gases (Phelps 1968). However, the lack of sufficiently accurate transport coefficient measurements and, more particularly, of any measurements for a gas in which the inelastic thresholds are adequately separated has meant that it has not hitherto been possible to determine any inelastic cross section with an accuracy approaching that already obtained for elastic scattering in monatomic gases.

The experiments with parahydrogen (Crompton and McIntosh 1968) were initiated to overcome these limitations as far as possible. At 77°K the population of the  $J = 0$  state is 99.5%, the remainder of the molecules being in the  $J = 2$  state



(Farkas 1935) since all odd rotational states are absent. The electron concentrations used in the experiments are so small that the change in population of excited levels caused by electron-molecule collisions is negligible. The 0.5% of molecules in the  $J = 2$  state can be involved in  $J = 2 \rightarrow 4$  excitations and in  $J = 2 \rightarrow 0$  superelastic collisions. These effects are discussed in Subsection (b) and are shown to be negligible except for low energy swarms ( $E/N < 0.1 \text{ Td}^*$ ) where the superelastic collisions have considerable influence. Since multilevel excitations such as  $J = 0 \rightarrow 4$  are extremely unlikely (Lane and Geltman 1967), the  $J = 0 \rightarrow 2$  process remains as the only rotational excitation of significance, the threshold of the process being  $0.0439 \text{ eV}^\dagger$ . In the energy range under consideration the only other inelastic processes that need be included are the  $v = 0 \rightarrow 1$  and  $v = 0 \rightarrow 2$  vibrational excitations with thresholds at  $0.51$  and  $1.02 \text{ eV}$ . Thus the excitation energies of the two inelastic processes with the lowest thresholds differ by more than a factor of 10 so that a unique determination of the rotational cross section can be expected over a significant energy range. It is also to be expected that the vibrational cross section could be found with reasonable accuracy near threshold.

### (b) *Method of Analysis*

Two techniques were developed by Frost and Phelps (see also Sherman 1960) for solving equation (1). The complete solution takes account of collisions of the second kind and was obtained by integrating the equation and finding the distribution function  $f(\epsilon)$  that satisfies the resulting set of linear equations. For situations where it is reasonable to neglect collisions of the second kind, a simpler method of solution was developed that requires considerably less computational time. This method relies on the fact that only those values of  $f(\epsilon)$  for  $\epsilon > \epsilon'$  are required to calculate  $f(\epsilon')$ . For  $\epsilon \geq \epsilon_L$ , where  $\epsilon_L$  is an arbitrarily chosen energy very much greater than the highest inelastic threshold,  $f(\epsilon)$  approaches the distribution function that would apply if there were no inelastic processes of any kind, and can therefore be easily calculated. It follows that values of  $f(\epsilon)$  for  $\epsilon \geq \epsilon_L$  can be used to calculate the distribution function at  $\epsilon_L - \delta$ , where  $\delta$  is a small energy interval. Successive applications of this procedure are used to extend the solution to zero energy. Fortunately this method of solution could be used in the present instance with only a small reduction in the energy range over which the analysis could be made and with no significant loss of accuracy in the determination of the rotational cross section.

In addition to the backward prolongation programme (Engelhardt, personal communication), to which some modifications were made which considerably reduced the time to compute  $f(\epsilon)$  at each value of  $E/N$ , a second programme was used which will be described elsewhere (Gibson, in preparation). This programme is based on the suggestion of Lucas (personal communication) of applying the Gauss-Seidel method of solving the integrodifferential equation for  $f(\epsilon)$ . Both methods gave identical results for the transport coefficients calculated from a given set of cross sections.

An examination of the experimental results in parahydrogen shows that over the greater part of the range of  $E/N$  random errors in both  $W$  and  $D/\mu$  amount to

\*  $1 \text{ Townsend (Td)} = 10^{-17} \text{ V cm}^2$  (Huxley, Crompton, and Elford 1966).

† The accuracy of the present analysis warrants the inclusion of second-order terms in the calculation of  $\epsilon_j$  (Herzberg 1950).

less than 1% and usually are considerably less than this. For example the drift velocity results show an experimental scatter of no more than  $\pm 0.15\%$ . For this reason it seemed justified to attempt to fit the experimental data to within  $\pm 1\%$  and adjustments were therefore made to the cross sections until this criterion was satisfied.

It has been indicated earlier that the cross sections are continually improved in an iterate procedure. An attempt was made to find a method of adjusting the cross sections automatically within the computing routine but this was unsuccessful. Nevertheless it was possible to obtain some guidance on how to modify the cross sections using a modification of the procedure devised by Frost and Phelps. Rather than use the parameters  $\nu_m^*$  and  $\nu_u$  of these authors we have used two parameters  $q_m^*$  and  $q_i^*$  that give a rather more direct measure of the elastic and inelastic cross sections.

The first fitting parameter  $q_m^*$  is the effective momentum transfer cross section (Crompton, Elford, and Jory 1967; see also Appendix). Values of  $q_m^*$  were calculated at each value of  $E/N$  from the measured and calculated transport coefficients. If the real and assumed momentum transfer cross sections are independent of energy the fractional difference between the pairs of values of  $q_m^*$  will be nearly equal to the fractional error in the assumed cross section and the necessary adjustment can be made. In the more general case, a comparison of the  $q_m^*$  versus  $D/\mu$  curves gives an estimate of the adjustment to be made to the cross section.

For the second fitting parameter  $q_i^*$  a combination of the transport coefficients was found that gives a greater separation between the effects of the elastic and inelastic cross sections than the parameter  $\nu_u$  used by Frost and Phelps. By using an approximate formula for the power input to *elastic* collisions a relation was derived that can be used to calculate approximately the power input to *inelastic* collisions even when elastic collisions account for a significant fraction of the total energy lost by the swarm. When one inelastic energy loss process is dominant, this relation can be used to derive a formula for an effective cross section  $q_i^*$  analogous to  $q_m^*$  for elastic collisions (see Appendix). A comparison of values of  $q_i^*$  derived from calculated and measured transport coefficients therefore facilitates the adjustment of the cross section for the dominant inelastic process.

The fitting parameters indicate that for a certain value of  $E/N$  either the elastic or inelastic cross section (or both) is in error and they also give an indication of the magnitude of the error, but before the cross sections can be modified some guide is needed as to the energy range over which the modification should be made. The problem is to find the energy at which the cross section has the greatest influence on the behaviour of the swarm. As the action of the collision process is to absorb energy from the electrons it is reasonable to suppose that the energy at which the rate of energy absorption is greatest corresponds to that part of the cross section curve which most affects the swarm in question. For inelastic collisions, the energy transfer at each collision of a given type is constant and so the power absorbed by the process will be proportional to the inelastic collision frequency  $\nu_i$ . At energy  $\epsilon$ ,  $\nu_i$  is proportional to  $\epsilon f(\epsilon) q_i(\epsilon)$ . For a given value of  $E/N$  the energy at which this function maximizes therefore gives the point on the inelastic cross section curve at which an adjustment to the cross section most influences the transport coefficients.

A similar argument holds for elastic collisions, but in this case the energy loss per collision is no longer constant but is approximately proportional to the electron energy. The maximum of the function  $\epsilon^2 f(\epsilon) q_m(\epsilon)$  must therefore be found.

The effects of the 0.5% of molecules in the  $J = 2$  state were examined in two tests carried out during the course of the analysis. First, the transport coefficients were recalculated allowing for the  $J = 2 \rightarrow 4$  excitation of these molecules. Inclusion of this effect caused changes of less than 0.2% in the coefficients. Secondly, energy distribution functions were calculated in which  $J = 2 \rightarrow 0$  superelastic collisions were taken into account. These distribution functions were used to find the power transferred in each collision process. The results, expressed as a percentage of the mean total power ( $eEW$ ) gained by an electron from the electric field, are plotted as a function of  $E/N$  in Figure 1. From the figure it can be seen that at  $E/N = 0.8$  Td the power gained from superelastic collisions is less than 6% of the total power and at  $E/N = 0.2$  Td less than 1%. As expected, the neglect of this small contribution to the energy exchange only slightly affects the calculated transport coefficients.

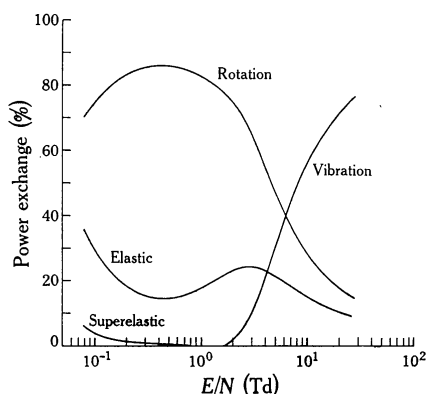


Fig. 1.—Variation with  $E/N$  of the mean power gained by an electron in  $J = 2 \rightarrow 0$  superelastic collisions and lost in elastic collisions and in  $J = 0 \rightarrow 2$  and  $v = 0 \rightarrow 1$  excitations. The power is expressed as a percentage of the mean power  $eEW$  gained from the electric field.

The values of  $W$  and  $D/\mu$  were recalculated for low values of  $E/N$  ( $< 0.6$  Td) using the final cross sections, but including collisions of the second kind; changes of up to 0.4% resulted, but the agreement between calculated and experimental values was still within 1%.

It is also useful to know the value of  $E/N$  above which vibrational excitation begins to be significant. Using a reasonable estimate of the vibrational cross section, the power absorbed by vibrational excitation at  $E/N = 2$  Td was calculated to be only 2% of the total (Fig. 1). Thus the data for  $E/N < 2$  Td can be used to derive a unique rotational cross section.

Although it is possible to use the iterative procedure already described to determine cross sections from swarm data, it is a much simpler procedure to test the validity of a set of cross sections derived from other sources, for example from theory or from a single collision experiment. As the starting point for the analysis, the rotational excitation cross section of Lane and Geltman (1967) and the vibrational cross section of Engelhardt and Phelps (1963) were used to derive a momentum transfer cross section from the parahydrogen data. Because of the separation between the effects of elastic and inelastic collisions already referred to, only minor adjustments to this cross section were required in subsequent tests or iterations. The next step was to test eight other rotational cross sections in the region where vibrational collisions



TABLE 1  
AGREEMENT BETWEEN MEASURED AND CALCULATED VALUES OF  $W$  AND  $D/\mu$  FOR VARIOUS  
THEORETICAL ROTATIONAL CROSS SECTIONS

Reference	Type of Calculation	Maximum Deviation (%)
Gerjuoy and Stein (1955)	Born approximation with quadrupole interactions	17
Dalgarno and Moffett (1963)	As above including nonspherical polarization forces	17
Engelhardt and Phelps (1963)	Dalgarno and Moffett corrected by empirical factor ( $\times 1.5$ )	8
Takayanagi and Geltman (1965)	Distorted wave	9
Dalgarno and Henry (1965)	Born approximation and distorted wave	25
Geltman and Takayanagi (1966)	Distorted wave, including short range nonspherical interaction	11
Lane and Geltman (1967)	Close coupling	8
Henry and Lane (1969)	Close coupling with polarization and exchange	1.4

TABLE 2  
PERCENTAGE DEVIATION BETWEEN OBSERVED AND CALCULATED VALUES OF  $W$  AND  $D/\mu$  FOR THREE  
DIFFERENT CROSS SECTIONS

The effects of  $J = 2 \rightarrow 0$  superelastic collisions have been included in the calculations

$E/N$ (Td)	Lane and Geltman		Henry and Lane		Present Results	
	$\Delta W/W$ (%)	$\Delta(D/\mu)/(D/\mu)$ (%)	$\Delta W/W$ (%)	$\Delta(D/\mu)/(D/\mu)$ (%)	$\Delta W/W$ (%)	$\Delta(D/\mu)/(D/\mu)$ (%)
0.08	1.0	-1.2	0.3	-0.2	0.4	-0.4
0.1	1.5	-1.8	0.8	-0.8	0.9	-1.0
0.2	0.9	-0.9	0.0	0.6	0.4	0.0
0.3	1.0	-1.0	-0.3	1.0	0.3	0.2
0.4	1.6	-1.7	0.0	0.9	0.6	-0.1
0.5	2.2	-2.4	0.2	0.8	0.8	-0.3
0.6	2.2	-2.7	-0.2	1.0	0.5	-0.1
0.7	2.3	-3.3	-0.4	0.9	0.1	0.1
0.8	2.7	-3.5	-0.4	1.2	0.3	0.3
0.9	3.0	-4.1	-0.4	1.1	0.3	0.2
1.0	3.1	-4.3	-0.6	1.4	0.1	0.4
1.2	3.5	-5.2	-0.7	1.3	-0.1	0.3
1.4	3.8	-6.8	-0.9	0.4	-0.2	-0.6
1.6	4.1	-6.4	-1.0	1.4	-0.3	0.4
1.8	4.5	-7.0	-1.0	1.3	-0.4	0.4
2.0	4.9	-7.7	-1.0	1.3	-0.6	0.6

could be neglected. The cross section giving the best agreement was then used as the starting point for the iterative procedure to obtain the rotational cross section consistent with the parahydrogen swarm data and for finding the  $v = 0 \rightarrow 1$  vibrational cross section. Finally a check was made to see whether or not there was agreement

between calculated and experimental values of the transport coefficients when the vibrational cross section determined experimentally by Ehrhardt *et al.* (1968) was used.

#### IV. RESULTS

The maximum difference between the measured transport coefficients and those calculated using various theoretical cross sections are shown in Table 1. The table applies to  $E/N$  values between 0.08 and 2 Td.

TABLE 3

$J = 0 \rightarrow 2$  CROSS SECTION  $q_r$  DERIVED FROM SWARM MEASUREMENTS IN PARAHYDROGEN

Energy (eV)	$q_r$ ( $10^{-16} \text{ cm}^2$ )	Energy (eV)	$q_r$ ( $10^{-16} \text{ cm}^2$ )
0.0439	0.0	0.20	0.120
0.047	0.0185	0.25	0.137
0.050	0.027	0.30	0.160
0.055	0.035	0.35	0.185
0.060	0.042	0.40	0.210
0.065	0.048	0.45	0.236
0.07	0.053	0.50	0.263
0.08	0.060		
0.09	0.068		
0.10	0.074		
0.11	0.079		
0.13	0.089		
0.15	0.099		

TABLE 4

MOMENTUM TRANSFER CROSS SECTION  $q_m$  FOR ELECTRONS IN HYDROGEN

Energy (eV)	$q_m$ ( $10^{-16} \text{ cm}^2$ )	Energy (eV)	$q_m$ ( $10^{-16} \text{ cm}^2$ )
0	6.4	0.15	11.4
0.01	7.3	0.2	12.0
0.02	8.0	0.3	13.0
0.03	8.5	0.4	13.9
0.04	8.96	0.5	14.7
0.05	9.28	0.6	15.6
0.06	9.56	0.7	16.3
0.07	9.85	0.9	17.1
0.08	10.1	1.1	17.7
0.09	10.3	1.4	18.2
0.10	10.5	1.6	18.3
0.11	10.7	1.8	18.2
0.13	11.0	2.0	18.0

The percentage deviations between the experimental values of  $W$  and  $D/\mu$  and the values calculated using the Lane and Geltman and the Henry and Lane cross sections are shown as a function of  $E/N$  in Table 2. Although the cross section calculated by Henry and Lane fits the data very well, it is justifiable to attempt a somewhat better fit since the systematic error in the data is probably less than 1%. The cross section of Henry and Lane was therefore modified in order to reduce the deviations. The results using the cross section so obtained are also shown in Table 2. The cross section itself is shown in Figure 2 and tabulated in Table 3.

As will be shown in the following section, the experimental cross section is far from unambiguous above 0.4 eV. Since our result at this energy is about 3% below that of Henry and Lane our curve was extrapolated to higher energies by using the theoretical curve reduced by 3%. This cross section was then used with the data for  $E/N > 2$  Td to find a vibrational cross section. The result is shown in Figure 3, together with the momentum transfer cross section (Table 4) that is consistent with the experimental data.

The vibrational cross section of Ehrhardt *et al.* (1968) was also tested for compatibility with our data. This vibrational cross section gave poor agreement between calculated and experimental transport coefficients when used with the rotational cross section shown in Figure 3. If this vibrational cross section is taken as

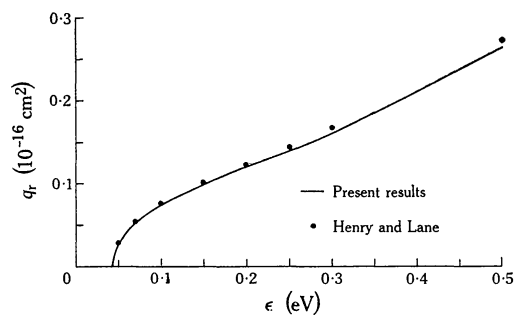


Fig. 2.—The cross section for  $J = 0 \rightarrow 2$  rotational excitation of  $H_2$  derived from swarm data for parahydrogen compared with the theoretical values of Henry and Lane.

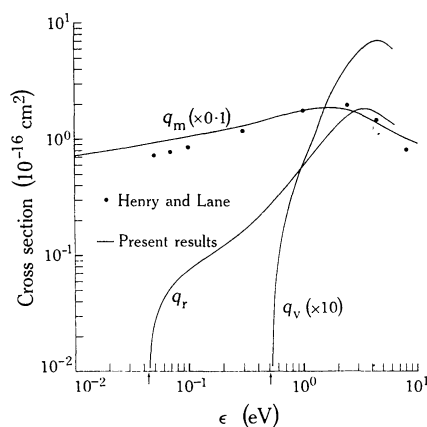


Fig. 3.—Final set of cross sections consistent with the swarm measurements in parahydrogen. The arrows indicate the thresholds for the inelastic processes. Henry and Lane's calculated values of the momentum transfer cross section are shown for comparison. The values of  $q_r$  and  $q_m$  are also shown in Tables 3 and 4 over the region where they are well determined by the experimental data.

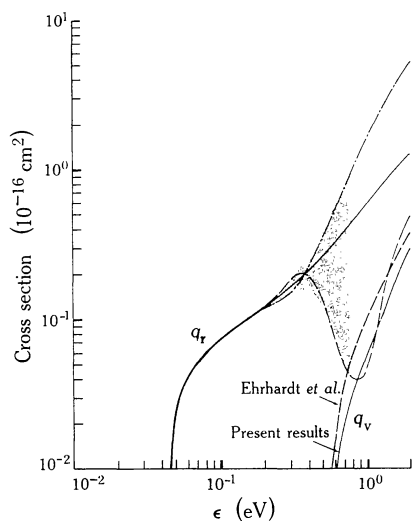


Fig. 4.—Various combinations of  $q_r$  and  $q_v$  that are consistent with swarm data for parahydrogen

- Combination based on an extrapolation of  $q_r$  using Henry and Lane's cross section reduced by 3%.
- $q_r$  curve consistent with the vibrational cross section of Ehrhardt *et al.*
- - -  $q_r$  curve required if  $q_v$  is assumed to be zero everywhere.

The shaded area indicates the rapid loss of uniqueness of  $q_r$ .

correct, then the rotational cross section must be altered as shown in Figure 4 to restore the agreement between the calculated and experimental values of the transport coefficients.

## V. LIMITS OF ERROR

The cross sections given in the previous section are subject to errors arising from the approximations implicit in equations (1), (2), and (3), to errors incurred in matching the calculated data to the experimental results, and to errors that follow directly from systematic errors in the experimental results.

Cavalleri and Sesta (1968) have recently examined an assumption implicit in the derivation of equation (2), namely that there is a negligible variation in electron energy along a free path. Preliminary calculations suggest that errors resulting from this approximation are small (Robertson, personal communication). In applying equations (1), (2), and (3) to molecular gases a further assumption has to be made, namely, that the inelastic collision frequency is small compared with the elastic collision frequency. The effect of this approximation has recently been analysed by Huxley (personal communication). For the present case in which the rotational cross section is of the order of 1% of the momentum transfer cross section, Huxley's analysis suggests that the approximation is not a significant source of error.

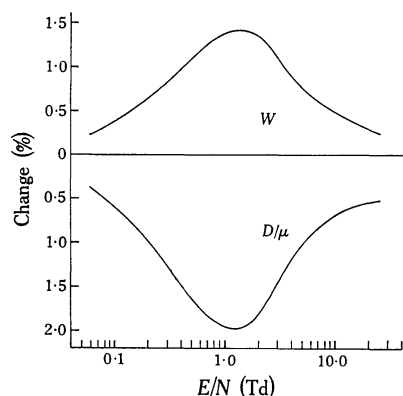


Fig. 5.—The variation with  $E/N$  of the percentage change in  $W$  and  $D/\mu$  caused by a 5% change in  $q_r$ .

Robertson, Elford, and Crompton (in preparation) discuss in some detail the errors that arise in deriving the momentum transfer cross section from swarm data in monatomic gases. In the present case the errors are somewhat larger than in their analysis since the random errors in the parahydrogen data are somewhat higher (but still less than 1%) while the systematic errors may be as large as 2%. Furthermore there is some loss of accuracy resulting from the impossibility of separating completely the effects of elastic and inelastic collisions in molecular gases. These factors suggest an error limit of  $\pm 5\%$  for the momentum transfer cross section.

An estimation of the error in the rotational cross section is less straightforward. It is first necessary to test the sensitivity of the calculated transport coefficients to the assumed rotational cross section in the region where rotational excitation is the dominant energy-loss mechanism. To do this a comparison was made of the values of  $W$  and  $D/\mu$  that were calculated using two cross sections that differed everywhere by 5%. The results of this comparison are shown in Figure 5 from which it can be seen that changes as large as 2% are produced. Since random errors in the data were such that curve fitting to within 1% was justified, this result suggests that, in the region where the results are unaffected by vibrational excitation, a reasonable estimate of the error limit to be placed on the rotational cross section is  $\pm 5\%$ .

In order to estimate the range over which this error limit holds, a rotational cross section was found that accounted for all the inelastic energy loss at all values of  $E/N$ . In this way, by assuming that there was no vibrational excitation, an upper limit to the rotational cross section was found. This upper limit is shown in Figure 4. It is not nearly so simple to obtain the lower limit, for in principle any curve can be used for the vibrational cross section. However, it may be argued that the rotational cross section which corresponds to the vibrational cross section of Ehrhardt *et al.* is an effective lower limit, since the unlikely behaviour of the rotational cross section that results from this analysis suggests that the vibrational cross section of Ehrhardt *et al.* rises too steeply near threshold. The shaded area in Figure 4 therefore indicates the limits of uncertainty for the cross section in the region where uniqueness is first lost through the effect of vibrational excitation. From the figure it can be seen that  $\pm 5\%$  is a reasonable estimate of the limits of error of the cross section for energies less than 0.3 eV but that the limits rise rapidly to about  $\pm 10\%$  at 0.4 eV and  $\pm 30\%$  at 0.5 eV. It is also clear that the availability of an accurate vibrational cross section from an independent experiment would considerably extend the energy range over which an accurate rotational cross section could be obtained by this method.

## VI. DISCUSSION

The only other experimental results with which a comparison can be made are those of Engelhardt and Phelps (1963). Since their work was based on the analysis of data in normal hydrogen a more detailed comparison with their work will be left to a later paper (Gibson, in preparation). It should be noted, however, that the possibility that computational errors were responsible for the differences between their  $J = 0 \rightarrow 2$  cross section and ours was checked by comparing the transport coefficients calculated using their programme with our calculated data when the same input data were used. Excellent agreement was obtained. Thus the lack of agreement in the cross sections is attributable to the use of different experimental data, and it is claimed that the simpler analytical situation in the present instance together with the use of more precise data has established a more accurate cross section.

In the region from threshold to 0.3 eV the agreement between our experimental result and the most recent  $J = 0 \rightarrow 2$  rotational cross section (Henry and Lane 1969) is very satisfactory. Because of the inaccuracies in the representation of the scattering potential, the possible error in the calculated cross section is of the same order as that in the experimental curve. The agreement between the two results is therefore within the combined error limits. The agreement between calculated and measured momentum transfer cross sections (Fig. 3) is not as good but is acceptable (Henry, personal communication).

The error limits that have been assigned to the experimental cross sections are comparatively wide and arise partly from the fundamental limitations of the method and partly from the error limits given to the experimental data. Experience with other transport coefficient measurements suggests that the accuracy of the experimental data could be improved significantly if the determination of a more accurate cross section were justified. Nevertheless the results of Table 1 show that the existing data for parahydrogen are sufficiently accurate to differentiate between the results of the theoretical calculations currently available.



The agreement between theory and experiment for the most recent calculations may be to some extent fortuitously good. Henry (personal communication) has pointed out that the polarization potential used by Henry and Lane (1969) may not be a good representation at short distances so that the accuracy of the cross sections may decrease at higher energies. It is also possible that the low energy results of this calculation, particularly for elastic scattering, may be in error owing to an oversimplification in the treatment of exchange. Notwithstanding these provisos, our results give strong support to the results of their calculations.

No estimate of the accuracy of the vibrational cross section has been made because it depends almost entirely on the accuracy of the theoretical rotational cross section above 0.4 eV. On the other hand, the experimentally determined cross section of Ehrhardt *et al.* (1968) does not appear to be compatible with the results of swarm experiments even though it is not in serious disagreement with our cross section. The two cross sections could be reconciled, in fact, if a small adjustment ( $\sim 0.1$  eV) were made to the energy scale of the cross section of Ehrhardt *et al.* An error of this magnitude may not be unreasonable in view of the difficulty associated with a beam experiment at these energies. Therefore, although we are unable to state confidence limits for our result, it seems not unreasonable to suggest that it is the more accurate result near threshold.

This study of electron swarms in parahydrogen, which is the most easily analysed system involving a diatomic gas, demonstrates clearly both the strengths and weaknesses of this method of determining low energy cross sections. In the first place, much the same arguments apply to the determination of the accuracy of the elastic scattering cross section as apply in the case of monatomic gases. The method therefore represents the best approach at the present time to the problem of determining these cross sections at low energies. Secondly, the two inelastic cross sections (but more particularly the rotational cross section) have been determined accurately near threshold. In view of the very low energies at which the thresholds occur (and also because of the particular advantage that results from the use of high gas pressures in swarm experiments (Crompton, Elford, and Jory 1967)), the accuracy of the results in this energy range is difficult to match with a beam experiment. Finally it should be noted that, for several reasons already discussed, the accuracy of the cross sections becomes poor in the energy range well above threshold. On the other hand, beam experiments become easier to perform, and the results from them become more precise, as the electron energy is increased. The two methods are therefore complementary and the results of both are required to obtain accurate data for inelastic cross sections over the complete energy range.

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## APPENDIX

(a) *Effective Momentum Transfer Cross Section,  $q_m^*$* 

The fitting parameter  $\nu_m$  used by Frost and Phelps (1962) is based on the assumption of a constant collision frequency. In the present case it is more valid to assume that the momentum transfer cross section is constant. We therefore replace  $q_m(\epsilon)$  in equations (2) and (3) by a constant  $q_m$ , obtaining after integration by parts the following expressions

$$W = \frac{e}{3N} \left( \frac{2}{m} \right)^{\frac{1}{2}} \frac{1}{q_m^*} \int_0^\infty f \, d\epsilon, \quad D/\mu = \frac{1}{e} \int_0^\infty \epsilon f \, d\epsilon \bigg/ \int_0^\infty f \, d\epsilon.$$

We can now write

$$W(D/\mu)^{\frac{1}{2}} = \frac{1}{3} \frac{E}{N} \left( \frac{2e}{m} \right)^{\frac{1}{2}} \frac{1}{q_m^*} \left( \int_0^\infty \epsilon f \, d\epsilon \int_0^\infty f \, d\epsilon \right)^{\frac{1}{2}}. \quad (\text{A1})$$

The integrals together form a dimensionless number, the value of which for a Druyvesteyn distribution is 1.18. This number is only slightly modified for other distribution functions and hence may be treated as a constant. We have therefore

$$q_m^* = A(E/N)/W(D/\mu)^{\frac{1}{2}},$$

where  $A$  is a constant (Crompton, Elford, and Jory 1967).

(b) *Effective Inelastic Cross Section,  $q_i^*$*

Assuming that we have only one significant inelastic process we may obtain the following equation expressing the power balance within the swarm by multiplying equation (1) by  $(2/m)^{\frac{1}{2}} \epsilon \, d\epsilon$  and integrating over all energies

$$eEW = N \left\{ \frac{(8m)^{\frac{1}{2}}}{M} \int_0^\infty \epsilon^2 q_m \left( f + kT \frac{df}{d\epsilon} \right) d\epsilon + \left( \frac{2}{m} \right)^{\frac{1}{2}} \epsilon_i \int_0^\infty \epsilon q_i f \, d\epsilon \right\}.$$

If we replace  $q_m(\epsilon)$  and  $q_i(\epsilon)$  by the constant effective values  $q_m^*$  and  $q_i^*$  respectively, rearrangement and integration by parts gives

$$e(E/N)W = \frac{(8m)^{\frac{1}{2}}}{M} q_m^* \left( \int_0^\infty \epsilon^2 f \, d\epsilon - 2kT \int_0^\infty \epsilon f \, d\epsilon \right) + \left( \frac{2}{m} \right)^{\frac{1}{2}} \epsilon_i q_i^* \int_0^\infty \epsilon f \, d\epsilon.$$

Using equation (3) we can express the above integrals in terms of  $De/\mu$  and dimensionless combinations of integrals in the following way

$$\int_0^\infty \epsilon^2 f \, d\epsilon = \left( \frac{De}{\mu} \right)^{3/2} \left( \int_0^\infty f \, d\epsilon \right)^{3/2} \int_0^\infty \epsilon^2 f \, d\epsilon \left( \int_0^\infty \epsilon f \, d\epsilon \right)^{-3/2}$$

and

$$\int_0^\infty \epsilon f \, d\epsilon = \left( \frac{De}{\mu} \right)^{\frac{1}{2}} \left( \int_0^\infty f \, d\epsilon \int_0^\infty \epsilon f \, d\epsilon \right)^{\frac{1}{2}}.$$

Substituting these, as well as  $q_m^*$  obtained from equation (A1), we obtain

$$eW \frac{E}{N} = \frac{e}{m} \frac{E}{N} \frac{1}{W} K_1 \left( \frac{De}{\mu} - kT K_2 \right) + \left( \frac{2e}{m} \right)^{\frac{1}{2}} \epsilon_i q_i^* \left( \frac{D}{\mu} \right)^{\frac{1}{2}} K_3$$

where

$$K_1 = \frac{4}{3} \left( \int_0^\infty f \, d\epsilon \right)^2 \int_0^\infty \epsilon^2 f \, d\epsilon \left( \int_0^\infty \epsilon f \, d\epsilon \right)^{-1},$$

$$K_2 = 2 \left( \int_0^\infty \epsilon f \, d\epsilon \right)^2 \left( \int_0^\infty f \, d\epsilon \int_0^\infty \epsilon^2 f \, d\epsilon \right)^{-1},$$

and

$$K_3 = \left( \int_0^\infty f \, d\epsilon \int_0^\infty \epsilon f \, d\epsilon \right)^{\frac{1}{2}}.$$

Hence we may write

$$q_i^* = \left( \frac{me}{2} \right)^{\frac{1}{2}} \frac{1}{\epsilon_1 K_3} \frac{W E/N}{(D/\mu)^{\frac{1}{2}}} \left( 1 - K_1 \frac{(De/\mu) - K_2 kT}{MW^2} \right).$$

It now remains to find estimates of  $K_1$  and  $K_2$ ;  $K_3$  need not be evaluated as it is a constant of proportionality only. For swarms with energy well above thermal the Druyvesteyn distribution has been found to be a reasonable approximation (e.g. Frost and Phelps 1962). Use of this distribution function yields values of 2.47 for  $K_1$  and 1.27 for  $K_2$ . Also, an empirical estimate of  $K_1$  and  $K_2$  may be obtained from the drift data in helium at low values of  $E/N$  for which  $q_i^*$  must always be zero. Very consistent results for mean energies greater than twice thermal could be obtained if  $K_2$  were given the value of 1.07. It can be seen that this value is a compromise between the Druyvesteyn value of 1.27 and the Maxwell value of 1; because  $De/\mu \rightarrow kT$  as  $E/N \rightarrow 0$  and the distribution approaches the Maxwellian form, one would expect a value weighted towards the Maxwellian value to give the best agreement over the full range of values of  $D/\mu$ . Hence the formula for  $q_i^*$  which was finally adopted was

$$q_i^* = B \frac{W E/N}{(D/\mu)^{\frac{1}{2}}} \left( 1 - 2.47 \frac{(De/\mu) - 1.07 kT}{MW^2} \right),$$

where  $B$  is a constant.