

# THE CROSS SECTIONS FOR ROTATIONAL EXCITATION OF H<sub>2</sub> AND D<sub>2</sub> BY LOW ENERGY ELECTRONS

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## Abstract

The  $J = 1 \rightarrow 3$  rotational cross section for H<sub>2</sub> has been derived from an analysis of electron transport coefficients. A new technique is described for calculating the energy distribution functions taking into account superelastic collisions, since these must be included for an analysis of low energy transport data in D<sub>2</sub>. Unique rotational cross sections cannot be obtained for this gas from the experimental data available, but two sets of cross sections have been derived which are compatible with the existing data and are also in accord with recent theoretical calculations. Evidence is also presented to show that there is probably a small difference between the momentum transfer cross sections in H<sub>2</sub> and D<sub>2</sub>.

## I. INTRODUCTION

The  $J = 0 \rightarrow 2$  rotational cross section for hydrogen has already been obtained from an analysis of electron transport coefficients in parahydrogen by Crompton, Gibson, and McIntosh (1969; hereafter referred to as CGM). One obvious extension of this work is the derivation of the  $J = 1 \rightarrow 3$  cross section from swarm data in normal hydrogen; another is a similar analysis of deuterium data. Engelhardt and Phelps (1963) have already considered these gases, but a new analysis would benefit from the transport data for parahydrogen, the more recent and accurate data for normal hydrogen and deuterium, and the recent cross section calculations of Henry and Lane (1969). For these reasons it seems well worth while to re-examine the situation in hydrogen and deuterium.

The technique for deriving inelastic cross section data from measurements of transport coefficients was originally described by Frost and Phelps (1962) and has been reviewed in CGM. In CGM the method was used to analyse electron drift data in parahydrogen gas at 77°K, which is a special case since there is only one significant inelastic process for low  $E/N$  (where  $E$  is the electric field strength and  $N$  the gas number density, the ratio  $E/N$  being expressed in townsend†). The present paper describes the application of a similar procedure to normal hydrogen and deuterium at 77°K.

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† 1 townsend (Td) =  $10^{-17}$  V cm<sup>2</sup>.

The room temperature equilibrium composition of hydrogen consists of three parts orthohydrogen and one part parahydrogen. Unless a catalyst is present this ratio will be preserved for a very long time at 77°K. The cross sections relevant to parahydrogen are already known from CGM. As orthohydrogen may be assumed to have the same momentum transfer and vibrational cross sections, an assumption which is justified in Section III, there remains only one unknown cross section in this case, that for  $J = 1 \rightarrow 3$  rotational excitation. Hence this cross section can be found uniquely by applying the analytical techniques already described.

In deuterium the energies of the rotational levels are approximately half the equivalent energies in hydrogen. Consequently at 77°K the  $J = 0$  and 2 states of orthodeuterium\* would be populated in the ratio of 84·8% to 15·2%. Thus in order to gain the great advantage of having almost all molecules in one rotational state, as in parahydrogen at 77°K, it is necessary to work at much lower temperatures. For this reason swarm measurements have not yet been made in orthodeuterium.

Normal deuterium consists of orthodeuterium and paradeuterium in the ratio 2 : 1 and at 77°K the rotational states are populated as:

$$J = 0, \quad 56\cdot5\%; \quad J = 1, \quad 33\cdot0\%; \quad J = 2, \quad 10\cdot1\%; \quad J = 3, \quad 0\cdot3\%.$$

The rotational cross sections needed to calculate the distribution functions are listed below (with their threshold energies):

$$J = 0 \rightarrow 2 \quad (0\cdot0222 \text{ eV}), \quad J = 1 \rightarrow 3 \quad (0\cdot0369 \text{ eV}), \quad J = 2 \rightarrow 4 \quad (0\cdot0514 \text{ eV}),$$

the  $J = 3 \rightarrow 5$  cross section being omitted because it was found in the course of the analysis that this process absorbed a negligible fraction of the total power. For the higher values of  $E/N$  the vibrational cross section with threshold 0·36 eV must also be included. As the three rotational cross sections cannot be distinguished by their effects on the transport coefficients, it is clear that without additional information from theory or another experiment only a composite, or effective, cross section can be derived. Fortunately such information is available from the recent calculations of Henry (personal communication).

Because of the comparatively large population of the  $J = 2$  rotational state in deuterium, any calculation of the energy distribution function must take the  $J = 2 \rightarrow 0$  superelastic collisions into account. Also, for very low  $E/N$  the  $J = 3 \rightarrow 1$  process accounts for about 1·5% of the total power. Therefore, before the analysis of deuterium could be commenced a technique was needed for calculating distribution functions which included the effects of superelastic collisions. One such technique has been described briefly by Frost and Phelps (1962). An alternative method was used for the present work. Although it has not been compared in detail with that described by Frost and Phelps, it has some obvious advantages. The method and its relationship to other methods are described in the following section.

\* In  $D_2$  the relation between the para and ortho states and the odd and even rotational states is the reverse of that in  $H_2$ ; this is a consequence of the different nuclear spins of the two isotopes.

## II. SOLUTION OF THE BOLTZMANN EQUATION

The energy equilibrium of the electron swarm is expressed in the following simplified form of the Boltzmann equation (Frost and Phelps 1962)

$$\begin{aligned} \frac{E^2}{3N} \frac{d}{d\epsilon} \left( \frac{\epsilon}{q_m(\epsilon)} \frac{df}{d\epsilon} \right) + \frac{2mNkT}{M} \frac{d}{d\epsilon} \left( \epsilon^2 q_m(\epsilon) \frac{df}{d\epsilon} \right) + \frac{2mN}{M} \frac{d}{d\epsilon} \left( \epsilon^2 q_m(\epsilon) f(\epsilon) \right) \\ + \sum_{j,k} N_j \{ (\epsilon + \epsilon_{jk}) f(\epsilon + \epsilon_{jk}) q_{jk}(\epsilon + \epsilon_{jk}) - \epsilon f(\epsilon) q_{jk}(\epsilon) \} \\ + \sum_{k,j} N_k \{ (\epsilon - \epsilon_{jk}) f(\epsilon - \epsilon_{jk}) q_{kj}(\epsilon - \epsilon_{jk}) - \epsilon f(\epsilon) q_{kj}(\epsilon) \} = 0, \end{aligned} \quad (1)$$

where  $\epsilon$  is the electron energy (in eV),  $m$  the electron mass,  $M$  the molecular mass,  $E$  the electric field strength,  $N$  the gas number density,  $k$  the Boltzmann constant (in eV degK<sup>-1</sup>),  $T$  the absolute temperature of the gas,  $q_m(\epsilon)$  the momentum transfer cross section,  $N_j$  the number density of molecules in the  $j$ th state,  $\epsilon_{jk}$  the difference in internal energy between the  $j$ th and  $k$ th molecular states,  $q_{jk}(\epsilon)$  the cross section for the excitation from the  $j$ th to the  $k$ th state,  $q_{kj}(\epsilon)$  the cross section for the super-elastic transition from the  $k$ th to the  $j$ th state, and  $f(\epsilon)$  the energy distribution function normalized such that

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

By making use of the principle of detailed balancing at thermal equilibrium it can be shown that

$$N_k = (n_k/n_j) N_j v_{jk}, \quad (2)$$

where  $v_{jk} = \exp(-\epsilon_{jk}/kT)$  and  $n_j$  and  $n_k$  are the numbers of available states corresponding to the  $j$ th and  $k$ th energy levels; furthermore

$$q_{kj}(\epsilon - \epsilon_{jk}) = \frac{n_j}{n_k} \frac{\epsilon}{\epsilon - \epsilon_{jk}} q_{jk}(\epsilon). \quad (3)$$

Now equation (1) may be integrated from 0 to  $u$  and, after simplification, expressions (2) and (3) substituted to yield

$$a(u) f(u) + b(u) df/du + c(f, u) = 0, \quad (4)$$

where

$$a(u) = (2m/M) u^2 q_m(u),$$

$$b(u) = \frac{1}{3} (E/N)^2 u / q_m(u) + kT a(u),$$

and

$$c(f, u) = \sum_{j,k} N_j \int_u^{u+\epsilon_{jk}} \epsilon q_{jk}(\epsilon) \{ f(\epsilon) - v_{jk} f(\epsilon - \epsilon_{jk}) \} d\epsilon. \quad (5)$$

The formal solution of (4) is (Murphy 1960)

$$f(u) = g(u) \left( C - \int_0^u \{ c(f, u) / b(u) g(u) \} du \right), \quad (6)$$

where

$$g(u) = \exp\left(-\int_0^u \{a(u)/b(u)\} du\right).$$

In the Appendix it is shown that

$$c(f, u)/a(u) f(u) \rightarrow 0 \quad \text{as } u \rightarrow \infty$$

and hence as  $u \rightarrow \infty$  equation (4) becomes

$$df/du = \{a(u)/b(u)\} f(u)$$

with the solution  $f(u) = g(u)$ . Therefore the integration constant in (6) must have the value

$$C = 1 + \int_0^\infty \{c(f, u)/b(u)g(u)\} du,$$

whereupon (6) becomes

$$f(u) = g(u) \left(1 + \int_u^\infty \{c(f, u)/b(u)g(u)\} du\right).$$

If the infinite integral is truncated at a large energy  $u_m$  and the expression (5) substituted, the equation becomes

$$f(u) = g(u) \left\{1 + \int_u^{u_m} \frac{1}{b(u)g(u)} \sum_{j,k} N_j \left( \int_u^{u+\epsilon_{jk}} \epsilon q_{jk}(\epsilon) \{f(\epsilon) - v_{jk} f(\epsilon - \epsilon_{jk})\} d\epsilon \right) du \right\}. \quad (7)$$

For further progress this equation must be expressed in a form suitable for numerical treatment. The energy range  $u_m$  is divided into a number ( $m$ ) of equal intervals ( $\delta$ ), the subdivision being fine enough to permit the integrals to be expressed as the sums of trapeziums to within the required accuracy. Equation (7) can then be written as a system of  $m$  simultaneous equations in  $f(1), \dots, f(m)$ . Values of  $f(n)$  for  $n > m$  are known, being taken as either zero or equal to  $g(n)$ . The  $i$ th equation of the set will be of the form

$$f(i) = I_i^i f(i) + \dots + I_m^i f(m) + S_0^i f(0) + \dots + S_m^i f(m), \quad (8)$$

where the  $I$  and  $S$  coefficients denote the parts of (7) which can be attributed to inelastic and superelastic collisions respectively.

The most obvious way of solving the system of equations is to calculate all the coefficients and then solve the equations by the standard technique of elimination. This technique has been used by Frost and Phelps (1962). The sorting out of the coefficients was facilitated by reversing the order of the integration in (7). A disadvantage of the technique was the very large number of coefficients that had to be stored in the computer at one time (the number is  $m^2$  where typically  $m = 300$ ). It also seems that the computational time was rather long.

Another technique for solving simultaneous equations is that of Gauss-Seidel iteration. This method has been used by Lucas (1969) for evaluating distribution

functions for cases where superelastic collisions could be neglected. It has the advantage that the sorting out and storing of the coefficients is avoided. For the present work an attempt was made to apply this iterative technique to equation (7), that is, to extend the technique to include superelastic collisions. An initial form of the distribution function  $f(\epsilon)$  was assumed (e.g. Maxwellian) and new values  $f(u)$  were calculated using equation (7). These values of  $f(u)$  were then used for  $f(\epsilon)$  in equation (7) to obtain a further set of values for  $f(u)$ . This process was continued until the distribution function did not change significantly on further iteration.

This technique was found to work well, provided that the superelastic terms were very small. Examination of equation (8) shows the reason for this proviso. If the  $S$  coefficients are much smaller than the  $I$ 's the requirement of dominant diagonal terms which is necessary for the convergence of the Gauss-Seidel method is fulfilled. However, the criterion is not fulfilled when the superelastic collisions have an appreciable influence on the swarm and further investigation was necessary to find a satisfactory method for solving equation (7).

If the superelastic terms are negligible, clearly the  $m$ th equation contains  $f(m)$  as the only unknown, the  $(m-1)$ th equation contains  $f(m-1)$  and  $f(m)$ , and so on. Hence  $f(m)$  can be found immediately from the  $m$ th equation and it may then be used in the preceding equation to yield  $f(m-1)$ . By proceeding in this way, from the high energy to the low, all values of  $f$  can be found. This technique, developed by Sherman (1960), has the name "backward prolongation" and is suitable for fast computation.

A technique which could handle large superelastic terms was developed by combining the methods of Gauss-Seidel iteration and backward prolongation. The equations were solved in order, starting from the highest energy, as in backward prolongation. In order to calculate the superelastic terms the unknown values of  $f$  at lower energies were required. They were estimated by matching a known distribution function to the one being calculated at the energy point last calculated. Initially a Maxwellian distribution was used to extend the calculated distribution function to low energies. In order to reduce the computation time, the Maxwellian distribution was chosen to have its mean energy appropriate to the value of  $E/N$  being considered. Then, as in the iterative method, the calculation was repeated a number of times, using each time the previously calculated distribution function to extend the newly calculated points to lower energies. Only three to five iterations were found to be necessary for convergence to a distribution function that remained essentially unaltered on further iteration. This technique was the one used for the calculations for deuterium, and also for hydrogen at low  $E/N$  where the  $J = 2 \rightarrow 0$  process has some effect on the transport coefficients.\*

### III. RESULTS AND DISCUSSION

For both H<sub>2</sub> and D<sub>2</sub> the experimental values of  $D/\mu$  were taken from Crompton, Elford, and McIntosh (1968). The drift velocities were measured by Robertson (to be published).

\* A copy of the calculated energy distribution functions may be obtained on application to the author.

(a) *Hydrogen*

The results of calculations with four different sets of cross sections are compared with the experimental values in Table 1. For the first comparison (set A) the  $J = 1 \rightarrow 3$  rotational cross section of Henry and Lane (1969) was used together with the momentum transfer cross section, the  $J = 0 \rightarrow 2$  cross section, and the vibrational cross section derived from parahydrogen data by CGM. Systematic discrepancies of up to 1.7% indicate that the calculated  $J = 1 \rightarrow 3$  cross section is somewhat too

TABLE 1  
DIFFERENCES BETWEEN OBSERVED AND CALCULATED VALUES OF  $W$  AND  $D/\mu$  IN HYDROGEN FOR  
FOUR DIFFERENT SETS OF CROSS SECTIONS

$E$ $N$ (Td)	Set A*		Set B†		Set C‡		Set D§	
	$\frac{\Delta W}{W}$ (%)	$\frac{\Delta(D/\mu)}{D/\mu}$ (%)						
0.08	0.6	-1.5	0.5	-1.2	0.4	-1.0	-0.3	4.1
0.10	0.7	-1.6	0.4	-1.1	0.4	-1.1	-0.8	4.1
0.12	0.8	-1.6	0.3	-0.9	0.5	-1.0	-1.2	4.4
0.14	0.9	-1.3	0.3	-0.4	0.6	-0.8	-1.4	4.8
0.16	1.0	-1.5	0.3	-0.4	0.7	-1.0	-1.6	4.7
0.18	1.1	-1.7	0.2	-0.4	0.7	-1.2	-1.8	4.6
0.2	1.1	-1.4	0.1	0.0	0.7	-0.9	-2.0	5.0
0.25	1.0	-1.6	-0.1	-0.1	0.8	-1.3	-2.3	4.8
0.3	1.1	-1.6	-0.2	0.2	0.8	-1.2	-2.5	5.0
0.35	1.1	-1.7	-0.2	0.2	0.8	-1.2	-2.6	5.1
0.4	1.0	-1.4	-0.3	0.5	0.8	-1.0	-2.7	5.3
0.5	0.9	-1.2	-0.4	0.6	0.6	-0.8	-2.7	5.4
0.6	0.8	-1.1	-0.4	0.6	0.5	-0.7	-2.4	5.2
0.8	0.5	-1.1	-0.5	0.2	0.2	-0.7	-1.6	4.1
1.0	0.2	-0.7	-0.5	0.2	0.0	-0.4	0.0	3.0
2.0	-0.6	-0.1	-0.7	0.1	-0.8	0.3	3.6	-2.4
4.0	-0.7	0.3	-0.7	0.2	-0.8	0.5	0.4	0.6
6.0	-0.2	0.2	-0.3	0.3	-0.4	0.4	-2.8	2.6
8.0	-0.1	0.0	-0.1	0.1	-0.1	0.1	-3.8	3.2
10.0	0.2	-0.3	0.1	-0.2	0.1	-0.2	-4.6	3.1

\* Values of  $q_{J(0 \rightarrow 2)}$  from CGM and  $q_{J(1 \rightarrow 3)}$  from Henry and Lane (1969).

† Values of  $q_{J(0 \rightarrow 2)}$  from CGM and  $q_{J(1 \rightarrow 3)}$  adjusted to minimize the deviations.

‡ Both rotational cross sections from Henry and Lane (1969).

§ All cross sections from Engelhardt and Phelps (1963).

small. This contrasts with the case of parahydrogen where the theoretical  $J = 0 \rightarrow 2$  cross section was found to be too large. The difference could arise from the fact that the spherically symmetric and anisotropic parts of the interaction potential are weighted differently in the calculations for  $J = 0 \rightarrow 2$  and  $J = 1 \rightarrow 3$  cross sections.

The agreement between calculated and measured transport coefficients could be improved by making appropriate adjustments to the  $J = 1 \rightarrow 3$  cross section. The second comparison (set B of Table 1) shows the results of the optimum adjustment of the cross section. The validity of the cross section obtained in this way

depends entirely on the swarm data in normal hydrogen and parahydrogen. This swarm-derived cross section is up to 14% higher near threshold than that of Henry and Lane; it is shown in Table 2 and Figure 1. At low values of  $E/N$  discrepancies of 1.2% still exist, and these cannot be eliminated except by adding a rather sharp peak at the threshold of the  $J = 1 \rightarrow 3$  cross section. However, a consideration of the possible errors in this region shows that the addition of a peak would be unjustified, since at low  $E/N$  the accuracy of  $D/\mu$  falls off and also errors in the  $J = 0 \rightarrow 2$  cross section would have a large effect.

The fractional power absorbed by the different processes has been calculated using the swarm-derived cross section and it is plotted as a function of  $E/N$  in Figure 2. The mean energy  $\bar{\epsilon}$  and mean momentum transfer collision frequency  $\bar{\nu}_m$  of the electrons were also calculated and are shown in Table 3.

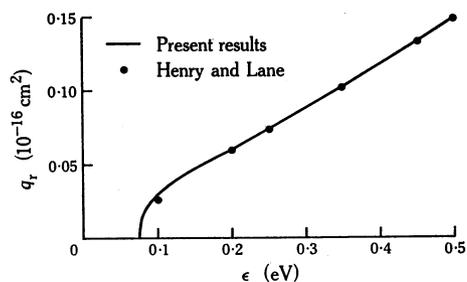


Fig. 1.—Cross section for  $J = 1 \rightarrow 3$  rotational excitation of H<sub>2</sub> derived from swarm data for parahydrogen compared with the theoretical values of Henry and Lane (1969).

TABLE 2  
 $J = 1 \rightarrow 3$  CROSS SECTION  $q_r$  DERIVED FROM SWARM MEASUREMENTS IN HYDROGEN

$\epsilon$ (eV)	$q_r$ ( $10^{-16}$ cm <sup>2</sup> )	$\epsilon$ (eV)	$q_r$ ( $10^{-16}$ cm <sup>2</sup> )
0.0727	0.0	0.13	0.041
0.0750	0.01	0.15	0.047
0.08	0.017	0.20	0.060
0.085	0.0215	0.25	0.074
0.09	0.025	0.30	0.088
0.095	0.0275	0.35	0.102
0.1	0.0295	0.40	0.118
0.11	0.0335	0.45	0.133
0.12	0.0380	0.50	0.149

The error limits placed on the transport data are  $\pm 2\%$  (Crompton, Elford, and McIntosh 1968). From this it could be argued that the Henry and Lane cross section was within the experimental error. However, the  $\pm 2\%$  limit allows for a random error of  $\pm 1\%$  and an equal systematic error. Inspection of the results in set A shows that over a large range of  $E/N$  there is a systematic tendency for the calculated values of  $W$  to be too small and those of  $D/\mu$  to be too large, each by more than 1%. Here it must be remembered that the two transport coefficients are determined in quite separate experiments. Therefore, even allowing for the uncertainty in the  $J = 0 \rightarrow 2$  cross section, it seems that the deviation from the theoretical values is just significant. This deviation ( $\sim 14\%$ ) gives a measure of the accuracy of the determination of the  $J = 1 \rightarrow 3$  cross section, and shows that larger errors arise from the increased complexity of the analysis compared with that of parahydrogen.

For the third comparison (set C of Table 1) both the  $J = 0 \rightarrow 2$  and  $J = 1 \rightarrow 3$  cross sections of Henry and Lane were used. The agreement is nearly as good as for set B. Thus it appears that the overestimated  $J = 0 \rightarrow 2$  cross section and the underestimated  $J = 1 \rightarrow 3$  cross section compensate each other. The additional

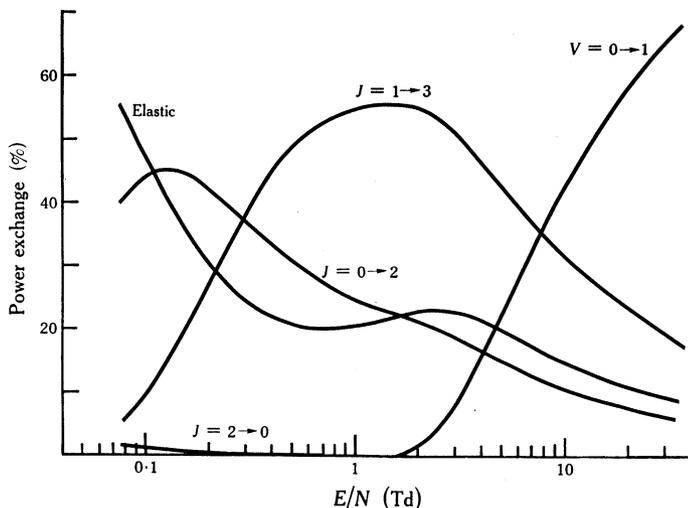


Fig. 2.—Variation with  $E/N$  of the mean power gained by an electron in  $J = 2 \rightarrow 0$  superelastic collisions and lost in elastic collisions and in  $J = 0 \rightarrow 2$ ,  $J = 1 \rightarrow 3$ , and  $V = 0 \rightarrow 1$  excitations in  $H_2$ . The powers are expressed as percentages of the mean power  $eEW$  gained from the electric field.

TABLE 3

VALUES OF MEAN ELECTRON ENERGY  $\bar{\epsilon}$  AND MEAN MOMENTUM TRANSFER COLLISION FREQUENCY  $\bar{\nu}_m/N$  FOR ELECTRON SWARMS IN HYDROGEN

$E/N$ (Td)	$\bar{\epsilon}$ (eV)	$\bar{\nu}_m/N$ ( $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ )	$E/N$ (Td)	$\bar{\epsilon}$ (eV)	$\bar{\nu}_m/N$ ( $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ )
0.08	0.0242	0.730	2.0	0.199	3.050
0.10	0.0268	0.780	3.0	0.274	3.844
0.12	0.0291	0.823	4.0	0.335	4.461
0.16	0.0332	0.899	5.0	0.388	4.975
0.20	0.0370	0.966	6.0	0.437	5.425
0.30	0.0459	1.114	8.0	0.525	6.204
0.40	0.0547	1.252	10.0	0.606	6.874
0.50	0.0635	1.384	12.0	0.683	7.466
0.60	0.0725	1.514	16.0	0.829	8.490
0.80	0.0909	1.766	18.0	0.901	8.943
1.0	0.110	2.006	20.0	0.972	9.366
1.2	0.128	2.236	30.0	1.355	11.16
1.6	0.165	2.664			

information gained from the parahydrogen data is immediately apparent. The analysis of the swarm data for the two forms of hydrogen also shows that the momentum transfer cross section and the vibrational cross section are independent of the rotational state of the  $H_2$  molecule, for the lowest two rotational states at least. This aspect of the vibrational cross section is treated more fully by Crompton, Gibson, and Robertson (1970).

It is also worth while pointing out that the momentum transfer cross section determined by swarm methods is almost certainly in good agreement with the total collision cross section measured by Golden, Bandel, and Salerno (1966). As there are not yet any comprehensive measurements of the angular distributions of the scattered electrons the two cross sections cannot be directly linked by experiment. However, Henry and Lane (1969) have in effect linked the two results by means of their calculated angular distributions and shown them to be in accord with each other. The momentum transfer cross section is considerable larger than the elastic scattering cross section at low energies, due to the high proportion of back scattering.

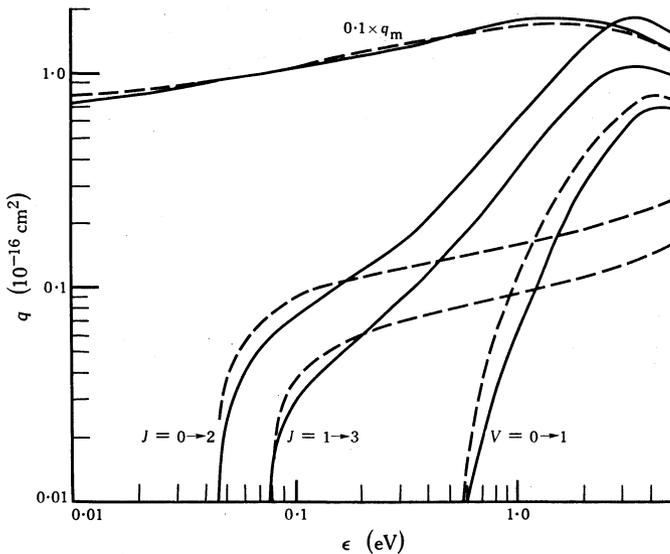


Fig. 3.—Comparison of the H<sub>2</sub> cross sections found in the present work and CGM (full curves) with those of Engelhardt and Phelps (dashed curves).

Of the existing calculations of the rotational cross section the ones which would be expected to be valid in the energy range from threshold to 0.5 eV are those employing the close coupling or the distorted wave methods. It has been shown in CGM that the recent close coupling calculation of Henry and Lane (1969) gave the best fit with swarm data; the theoretical  $J = 1 \rightarrow 3$  cross section of these authors is therefore compared with the experimental cross section in Figure 1. The only other experimental determination of the H<sub>2</sub> rotational cross sections in this energy range is that of Engelhardt and Phelps (1963). Their results are compared with the present ones in Figure 3. The discrepancies between the two sets of cross sections are rather large. It must be emphasized that these differences do not arise from the method of analysis,\* but from differences in the primary data. This point is demonstrated clearly in set D of Table 1, where the transport coefficients calculated with the cross

\* The author is indebted to Dr. A. V. Phelps for supplying tabulations of his input data and calculated transport coefficients. With this input data the computer program used in the present work yielded transport coefficients which agreed to within 0.25% with those supplied.

sections of Engelhardt and Phelps are compared with the present experimental data. The results of the present analysis differ from those of Engelhardt and Phelps not only because of differences in the experimental data, but also because of the increased accuracy of the new data. Because of this second point a much better fit between calculation and measurement can be demanded, and hence the constraints on the cross sections are more stringent. Furthermore, as has already been pointed out, in the present analysis the data for parahydrogen enable the two rotational cross sections to be uniquely determined.

TABLE 4

DIFFERENCES BETWEEN OBSERVED AND CALCULATED VALUES OF  $W$  AND  $D/\mu$  IN DEUTERIUM FOR FOUR DIFFERENT SETS OF CROSS SECTIONS

$E$ $N$ (Td)	Set A*		Set B†		Set C‡		Set D§	
	$\frac{\Delta W}{W}$ (%)	$\frac{\Delta(D/\mu)}{D/\mu}$ (%)						
0.04	0.5	0.0	0.7	-0.1	0.6	-0.1	0.6	-0.1
0.06	0.4	0.4	0.6	0.1	0.5	0.1	0.5	0.2
0.08	0.2	0.5	0.6	0.1	0.5	0.1	0.4	0.3
0.10	0.0	0.7	0.5	0.0	0.4	0.0	0.2	0.3
0.12	-0.1	1.0	0.5	0.2	0.4	0.2	0.2	0.6
0.16	-0.3	1.0	0.5	0.1	0.4	0.0	0.1	0.5
0.2	-0.2	1.5	0.6	0.3	0.5	0.3	0.2	0.8
0.3	-0.1	1.8	1.0	0.3	0.8	0.2	0.5	0.7
0.4	-0.3	2.4	1.0	0.7	0.9	0.6	0.6	1.0
0.5	-1.1	2.1	0.5	0.2	0.3	0.1	0.0	0.5
0.6	-1.2	2.3	0.5	0.2	0.3	0.1	0.0	0.5
0.8	-1.5	3.0	0.5	0.6	0.2	0.5	-0.1	0.9
1.0	-2.0	3.0	0.2	0.6	-0.2	0.4	-0.4	0.8
2.0			0.4	0.7	-0.4	0.6	-0.7	1.0
4.0			1.3	0.6	-0.1	0.5	-0.3	0.8
6.0			1.9	0.2	0.0	0.1	-0.2	0.4
8.0			1.9	0.1	-0.4	0.0	-0.6	0.2
10.0			1.8	0.3	-1.0	0.1	-1.1	0.4

\* Values of  $q_{J(0 \rightarrow 2)}$ ,  $q_{J(1 \rightarrow 3)}$ , and  $q_{J(2 \rightarrow 4)}$  from Henry (personal communication);  $q_m$  from CGM.

† Values of  $q_{J(0 \rightarrow 2)}$  reduced to minimize the deviations.

‡ Values of  $q_m$  reduced to minimize the deviations.

§ Rotational cross sections of Henry all modified by the same energy-dependent factor.

### (b) Deuterium

Theoretical  $J = 0 \rightarrow 2$ ,  $1 \rightarrow 3$ , and  $2 \rightarrow 4$  rotational cross sections provided by Henry (personal communication) were used together with the momentum transfer cross section derived for hydrogen. The calculations were carried out for  $E/N$  up to 1 Td, permitting vibrational excitation to be ignored. It can be seen from set A of Table 4 that these cross sections lead to an overestimation of the power absorbed by inelastic collisions. In the Introduction it was pointed out that the rotational

cross sections in D<sub>2</sub> cannot be uniquely determined from the swarm data now available. Therefore, at this point the procedure for modifying the cross sections must be decided rather arbitrarily. It was decided to modify only the  $J = 0 \rightarrow 2$  cross section for the following reasons:

- (1) In the case of H<sub>2</sub> the  $J = 0 \rightarrow 2$  cross section calculated by Henry and Lane has been shown in CGM to be slightly too large; the same tendency might be expected to apply in the case of D<sub>2</sub>.
- (2) Calculations show that in this range of  $E/N$  between 45% and 80% of the power is absorbed by  $J = 0 \rightarrow 2$  excitations; hence the results are more sensitive to changes in this cross section than in any other.

It was necessary to lower the  $J = 0 \rightarrow 2$  cross section by up to 17% to obtain the agreement with experiment shown in set B of Table 4. The cross sections themselves are shown in Figure 4 (full curves).

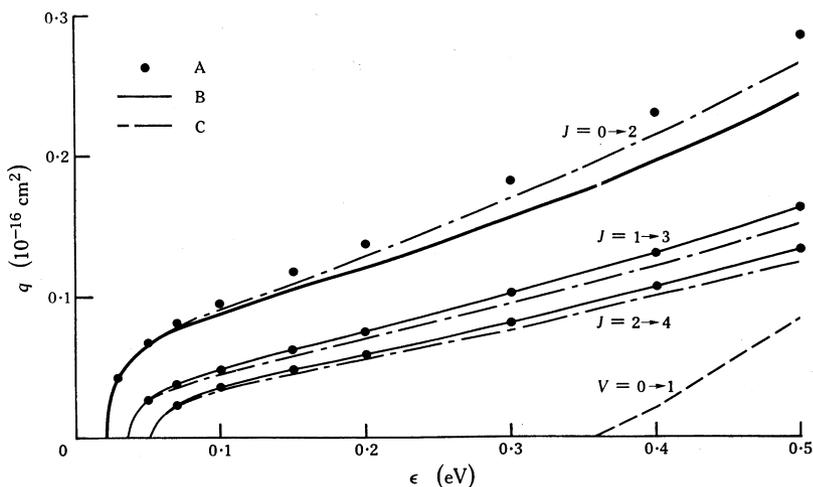


Fig. 4.—Inelastic cross sections for deuterium: A, theoretical rotational cross sections from Henry (personal communication); B, rotational cross sections derived from Henry's calculations by modifying the  $J = 0 \rightarrow 2$  cross section only; C, rotational cross sections found by modifying all three calculated cross sections by the same energy-dependent factor.

Using the theoretical  $J = 0 \rightarrow 2$  cross section as a guide, the modified cross section was extrapolated to energies of several eV. With these fixed rotational cross sections it was possible to use the data for  $E/N > 1$  Td to derive a vibrational cross section, which is also shown in Figure 4.

It will be noticed in set B of Table 4 that the experimental values of both  $W$  and  $D/\mu$  are consistently larger than those calculated. It is impossible to correct this tendency by modifying any inelastic cross section since any such modification always produces opposite effects on  $W$  and  $D/\mu$ . Therefore the evidence is that the momentum transfer cross section in D<sub>2</sub> is smaller than that in H<sub>2</sub>. Gerjuoy and Stein (1955) have shown theoretically that any differences between the two cross

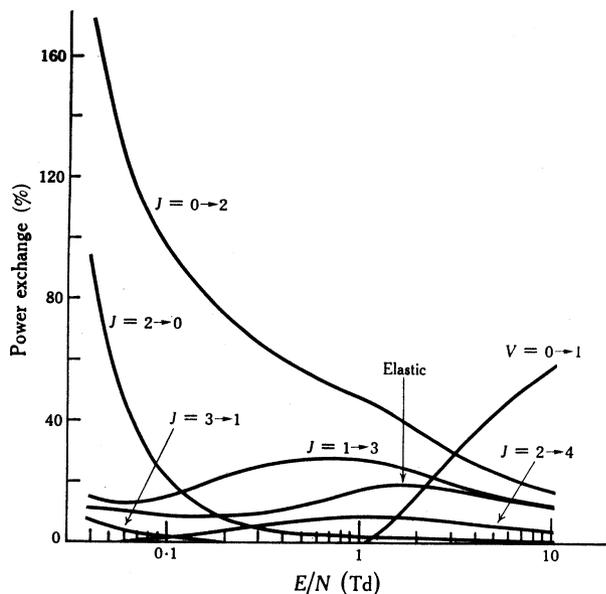


Fig. 5.—Variation with  $E/N$  of the mean power gained by an electron in  $J = 2 \rightarrow 0$  and  $J = 3 \rightarrow 1$  superelastic collisions and lost in elastic collisions and in  $J = 0 \rightarrow 2$ ,  $J = 1 \rightarrow 3$ ,  $J = 2 \rightarrow 4$ , and  $V = 0 \rightarrow 1$  excitations in  $D_2$ . The powers are expressed as percentages of the mean power  $eEW$  gained from the electric field.

TABLE 5

VALUES OF MEAN ELECTRON ENERGY  $\bar{\epsilon}$  AND MEAN MOMENTUM TRANSFER COLLISION FREQUENCY  $\bar{\nu}_m/N$  FOR ELECTRON SWARMS IN DEUTERIUM

$E/N$ (Td)	$\bar{\epsilon}$ (eV)	$\bar{\nu}_m/N$ ( $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ )	$E/N$ (Td)	$\bar{\epsilon}$ (eV)	$\bar{\nu}_m/N$ ( $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ )
0.04	0.0139	0.507	0.6	0.0818	1.63
0.05	0.0148	0.529	0.8	0.109	1.99
0.06	0.0158	0.552	1.0	0.136	2.32
0.08	0.0178	0.595	1.2	0.161	2.61
0.10	0.0198	0.637	1.6	0.206	3.10
0.12	0.0218	0.679	2.0	0.245	3.51
0.16	0.0261	0.762	3.0	0.326	4.32
0.20	0.0305	0.844	4.0	0.396	4.98
0.30	0.0423	1.05	5.0	0.461	5.55
0.40	0.0550	1.25	6.0	0.521	6.05
0.50	0.0682	1.44	8.0	0.634	6.93
			10.0	0.740	7.67

sections should be small. Engelhardt and Phelps (1963) could find no evidence for a difference from their analysis of the then available swarm data, but these data were subject to too much scatter to reveal such a small effect. The deviations in set B, however, were larger than the expected error, and therefore the momentum transfer

cross section was modified to reduce the discrepancies. An improvement in the agreement, shown in set C of Table 4, was obtained by lowering the momentum transfer cross section by an amount proportional to the electron energy, the rate of reduction being 3% per electron-volt. From Table 4 the evidence for a small difference in the momentum transfer cross sections of H<sub>2</sub> and D<sub>2</sub> can be seen to be quite strong.

The fact that the rotational cross sections in D<sub>2</sub> cannot be uniquely determined from swarm experiments may be illustrated by fitting the data in a different way. It could be argued that the ratios of the theoretical cross sections might be more accurate than their absolute values. At energies well above threshold this idea is supported by arguments based on the adiabatic approximation (Chang and Temkin 1969). A set of cross sections may be obtained by multiplying each of the three rotational cross sections of Henry by the same energy-dependent factor. The function was found which minimized the deviations between the calculated and measured transport coefficients (set D, Table 4). The resulting rotational cross sections are compared with the other set in Figure 4 (dashed curves).

The swarm-derived cross sections of set C were used to calculate the distribution of power exchange (Fig. 5) and also  $\bar{\epsilon}$  and  $\bar{v}_m$  (Table 5). The D<sub>2</sub> cross sections, as for H<sub>2</sub>, have been compared with the theoretical cross sections of Henry in Figure 4. As the statistical weights of the rotational states in D<sub>2</sub> used by Engelhardt and Phelps (1963) were incorrect their results are not included in the figure.

The results presented here are the only experimental rotational cross sections for D<sub>2</sub> that are currently available. If there were any reason to believe that further investigation would be profitable, the lack of uniqueness could be removed, as has been done for H<sub>2</sub>. But the present indications are that the rotational cross sections for D<sub>2</sub> are analogous to those for H<sub>2</sub>, and that the cross sections in both cases can be calculated with considerable accuracy by the theoretical methods developed by Henry and Lane.

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## APPENDIX

From the definitions of  $a(u)$  and  $c(f, u)$  we have

$$\frac{c(f, u)}{a(u) f(u)} = \frac{M}{2mu^2 q_m(u) f(u)} \sum_{j,k} N_j \left( \int_u^{u+\epsilon_{jk}} \epsilon q_{jk}(\epsilon) \{f(\epsilon) - v_{jk} f(\epsilon - \epsilon_{jk})\} d\epsilon \right).$$

As the cross sections must always be finite we may write  $q'_m$  for the *minimum* value of  $q_m(u)$  and  $q'_{jk}$  for the *maximum* values of the  $q_{jk}(u)$ . Then

$$\begin{aligned} \frac{c(f, u)}{a(u) f(u)} &< \frac{M}{2mq'_m u^2 f(u)} \sum_{j,k} N_j q'_{jk} f(u) \int_u^{u+\epsilon_{jk}} \epsilon d\epsilon \\ &< \sum_{j,k} N_j \frac{M}{2mq'_m} \frac{q'_{jk} u \epsilon_{jk} + \frac{1}{2} \epsilon_{jk}^2}{u^2}. \end{aligned}$$

Since the right-hand side of the inequality tends to zero as  $u$  tends to infinity, and the left-hand side can never be negative, we have proved that

$$c(f, u)/a(u) f(u) \rightarrow 0 \quad \text{as } u \rightarrow \infty.$$