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Vibrational Excitation of H_2 by Low-Energy Electrons

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The $v=0\rightarrow 1$ vibrational cross section for H_2 derived from swarm experiments is shown to be a good approximation to the sum of the cross sections for vibrational transitions that take place with and without simultaneous rotational excitation of the molecule. Experiments are described that prove that this summed cross section does not depend on whether the H_2 molecules are in the $J=0$ or the $J=1$ rotational state, in agreement with a recent theoretical calculation. Reasons are given for the disagreement between the two published swarm-derived vibrational cross sections. However, the discrepancies between the threshold behavior of the cross sections determined by the swarm measurements, beam experiments, and theory have not yet been explained.

I. INTRODUCTION

The publication of the results of three recent experimental determinations of vibrational cross sections in hydrogen[1-3] has failed to clarify a somewhat confused situation. In a review[4] published before these results were available, Phelps had concluded that the results of Schulz's beam experiment[5] (when corrected by a factor of 1.4 to account for nonisotropic scattering[6]), Ramien's multiple-scattering experiment,[7] and his own swarm work with Engelhardt[8] were all reasonably consistent at electron energies above 1.5 eV, but that there were significant differences in the threshold behavior of the cross section as determined by the beam and swarm techniques. Some reconciliation of the results of beam and swarm experiments resulted from Menendez and Holt's work,[9] which confirmed the swarm result that the cross section rises approximately linearly from the threshold at 0.516 eV.

The results of the two recent beam experiments, one by Ehrhardt *et al.* (ELLT)[1] and the other by Burrow and Schulz (BS),[3] also confirm the almost linear rise of the cross section from threshold, and the weight of evidence is therefore against Schulz's previous result[5] that the cross section increases significantly only above about 1 eV. However, the initial slope of ELLT cross section, which covers the energy range from threshold to 10 eV, is only about one-half that measured by Burrow and Schulz whose trapped-electron method restricted measurement to the range between threshold and about 0.1 eV above threshold.

A comparison of the cross section derived by Crompton, Gibson, and McIntosh (CGM)[2] from an analysis of electron-transport data in parahydrogen with the earlier determination by Engelhardt and Phelps (EP)[8] from an analysis of similar data for normal hydrogen presents an equally inconclusive picture. While the shapes of the cross-section curves are generally similar, the initial slope of the EP cross section is approximately twice that of CGM. Thus, in summary, the results from swarm experiments appear to be in poor agreement with each other, as do the results of beam experiments; the result of one beam experiment (ELLT) agrees with one swarm determination (EP), but the initial slope of the ELLT and EP cross sections is one-half that determined by Burrow and Schulz and twice that of the cross section obtained by Crompton *et al.*

Crompton, Gibson, and McIntosh have discussed the apparent incompatibility of the vibrational cross section of ELLT with the results of swarm experiments in parahydrogen at 77 °K. However, there are several possible explanations for this apparent disagreement which have not been discussed previously. In this paper we examine these possible explanations, present some relevant new experimental results, and discuss some implications of our conclusions. One possibility is that swarm experiments could have been previously interpreted incorrectly because no account had been taken of the effects of simultaneous rotational and vibrational transitions. This is examined in Sec. II. An alternative explanation is that the disagreement is due to the presence of different rotational populations in the room-temperature beam experiments and the low-temperature swarm experiments, particularly since parahydrogen was used in one of these experiments. In Sec. III we give the results of drift-velocity experiments which were designed to reveal any dependence of the vibrational cross section in hydrogen on the initial rotational state of the molecule. Section IV contains a detailed comparison of the results of Engelhardt and Phelps with those of Crompton *et al.* and Gibson[10] and an examination of a number of possible explanations for the different results that were obtained from essentially similar experiments and analyses. In Sec. V we discuss our new results, and our conclusions regarding the threshold behavior of the cross section, in relation to other theoretical and experimental work.

II. EFFECT OF SIMULTANEOUS TRANSITIONS ON INTERPRETATION OF SWARM EXPERIMENTS

The recent experiments reported by Linder[11] have shown that simultaneous transitions involving the $J=1\rightarrow 3$ rotational excitation account for approximately 25% of all vibrational excitation in normal hydrogen. It is therefore necessary to examine the effect of such excitation on the usual analysis of electron-transport data. For simplicity, we shall consider the case of parahydrogen at 77 °K.

To calculate the energy distribution functions and transport coefficients rigorously, it is necessary to include two vibrational cross sections, one, the "pure" vibrational cross section $q_{v,00}$ with a threshold of 0.516 eV, and the other, $q_{v,02}$ with a threshold of 0.560 eV for the process in which vibrational excitation is accompanied by a $J=0\rightarrow 2$ rotational excitation.[12] When this procedure is followed, however, it is found that it is possible to construct an infinite set of pairs of cross sections that lead to calculated values of the transport coefficients which match the experimental data adequately, or that, as in all previous analyses, a single cross section with threshold at 0.516 eV can be found to replace the two. The situation here is analogous to the lack of uniqueness that was discussed earlier with respect to the parahydrogen analysis[2] but is accentuated by the close proximity of the thresholds for the pure and simultaneous transitions in this instance. We now examine this point in more detail, particularly since we seek the relation between the single cross section and the pair of cross sections it simulates.

From the equation that describes the power balance for the electron swarm [Eq. (2) of Ref. 8], it can be shown that one would not expect the calculation of the energy distribution function to be seriously affected if a small modification to the threshold of a given inelastic process were accompanied by a corresponding modification to the cross section so as to keep the product of the threshold energy and cross section [that is, $\epsilon_j Q_j(\epsilon)$ in the terminology of Ref. 8] constant. It follows that the cross section for simultaneous excitation can be replaced by a cross section with its threshold at the vibrational threshold provided the cross section is multiplied by (0.560/0.516); that is, the cross section is increased by approximately 8%. Hence, to a good approximation, the cross sections $q_{v,00}$ and $q_{v,02}$ can be replaced in the analysis by a single cross section q_{VS} with its threshold at 0.516 eV, where

$$q_{VS}=q_{v,00}+1.08q_{v,02} \ . \tag{1}$$

The degree to which the relation (1) fulfills the requirement that the predicted transport coefficients remain unchanged by the substitution of q_{VS} for $q_{v,00}$ and $q_{v,02}$ has been checked in a computer calculation in which it was assumed that $q_{v,00}$ and $q_{v,02}$ are approximately equal. This assumption was based on Henry's[13] theoretical calculations of the cross sections and on an argument[14] based on Abram and Herzenberg's[15] theoretical work and Linder's[11] and our own experimental results. The maximum difference between the computed values of the transport coefficients using the q_{VS} of Ref. 2 and the two cross sections $q_{v,00}=\frac{1}{2}q_{VS}$ and $q_{v,02}=\frac{1}{2}(0.516/0.560)q_{VS}$ was found to be less than 0.2% in both the drift velocity W and the diffusion coefficient to mobility ratio D/μ. Thus the interpretation of q_{VS} as the approximate sum of the cross sections for a particular vibrational excitation is justified.

The quantity measured as the vibrational cross section in most beam experiments is the "total" vibrational cross section; in the case of parahydrogen, it would be simply $q_{v,00}+q_{v,02}$. We shall denote this sum by q_{VT}. In the present instance we note that q_{VS} differs from q_{VT} by only 4% so that the accuracy of available experimental data would not enable the difference between the two to be resolved. The same is true for orthohydrogen where the difference is approximately 5%, the larger separation of the threshold energies being largely offset by a smaller ratio of $q_{v,13}$ to $q_{v,11}$.[13] Furthermore it is to be noted that, in general, unless there is a large contribution to the cross section from vibrational excitations accompanied by rotational deexcitation, the swarm cross section should, if anything, be *larger* than the cross section obtained from beam experiments. However, the most important conclusion is that the error made in equating q_{VS} to q_{VT} is at present insignificant compared with experimental error.

III. VIBRATIONAL CROSS SECTIONS FROM SWARM EXPERIMENTS IN HYDROGEN SAMPLES WITH DIFFERENT ROTATIONAL POPULATIONS

The apparent conflict between the data for the vibrational cross section obtained from beam and swarm experiments led to the suggestion that the cross section was dependent on the initial rotational state of the molecule.[16] This suggestion stems from the fact that the rotational populations are different in the room-temperature beam experiment and the low-temperature (77 °K) swarm experiments, and more particularly since parahydrogen was used in some of the swarm experiments. The relative populations are shown in Table I. In order to look for such a dependence, we have performed precise comparative experiments to measure drift velocities under identical conditions in normal and parahydrogen at 77 °K. A further set of measurements was made in normal hydrogen at 293 °K. In this way we have obtained comparable sets of data for which the only significant difference is in the relative populations of the rotational states.

A. Effect of Large Changes in $J=0$ and $J=1$ Populations; Experiments in Normal and Parahydrogen at 77 °K

Before commencing the experiments, it was first necessary to find the range of values of E/N (where E is the electric field strength and N the gas number density) over which the drift velocity is sensitive to the vibrational cross section. For this range of E/N it was then necessary to examine the influence of the different rotational populations on the power absorbed in rotational excitation since this could affect the validity of the conclusions drawn from the comparisons.

The sensitivity of the drift velocity to a change in the vibrational cross section may be determined by comparing the values for parahydrogen calculated by CGM with those calculated when the vibrational cross section is increased by 10%. The percentage change in W is plotted as a function of E/N in Fig. 1. For comparison, the percentage change in D/μ is also plotted in the diagram. Below $E/N = 2$ Td [1 townsend (Td) $= 10^{-17}$ V cm^2] the values are seen to be unaffected. This is to be expected since there is negligible energy loss through vibrational excitation below this value. As E/N is increased, however, there is a rather rapid increase in sensitivity until in the range $6 \lesssim E/N \lesssim 26$ Td, a difference of about 1% is observed.

In order to examine the effect of the different rotational excitations on the transport coefficients in this range of E/N, the fractions of the total power absorbed by rotational and vibrational excitations were calculated for the two forms of hydrogen using the cross sections derived from swarm measurements.[2,10] These fractions are plotted as functions of E/N in Fig. 2. As E/N increases from zero, the power absorbed by rotational excitation increases faster in parahydrogen than in normal hydrogen because of the larger numbers of $J=0$ molecules with low rotational threshold energy (44 meV). The threshold for $J=1\rightarrow 3$ excitation is 73 meV and therefore a higher swarm energy (corresponding to a larger value of E/N) is required before this process can contribute to the absorption of energy. On the other hand, once $J=1\rightarrow 3$ excitations occur they absorb more energy per collision than $J=0\rightarrow 2$ excitations, and therefore the power absorbed in rotational excitation in normal hydrogen might be expected to rise above that in parahydrogen. However, in the case of these two processes, it is found that at energies well above 73 meV the cross sections are inversely proportional to the threshold energies. This relationship had been derived by Chang and Temkin[17] and is confirmed by the theoretical cross sections of Henry and Lane.[18] The consequence is that at sufficiently high E/N the power absorbed by rotational excitation in normal hydrogen becomes equal to that absorbed in parahydrogen. This can be seen in Fig. 2. It follows that any differences in the behavior of electron swarms in the two forms of hydrogen at high values of E/N must be attributed to different vibrational cross sections.

At $E/N = 6$ Td, Crompton and McIntosh[19] found no significant difference between drift velocities W in normal and parahydrogen. However, this value of E/N is the lower limit of the range over

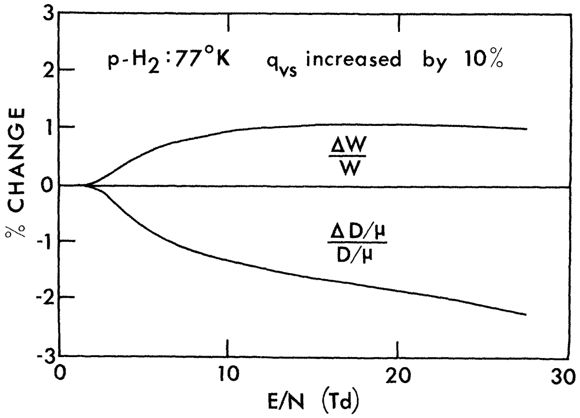

FIG. 1. The sensitivity of the calculated values of W and D/μ in parahydrogen to a 10% change in q_{VS}. The range of values of E/N over which the variations are significant can be clearly seen.

TABLE I. Relative populations for parahydrogen and normal hydrogen at 77 °K, and for normal hydrogen at 293 °K.

	J (°K)	0	1	2	3
		%	%	%	%
p-H$_2$	77	99.3	···	0.7	···
n-H$_2$	77	24.8	75.0	0.2	···
n-H$_2$	293	13.2	66.2	11.6	8.7

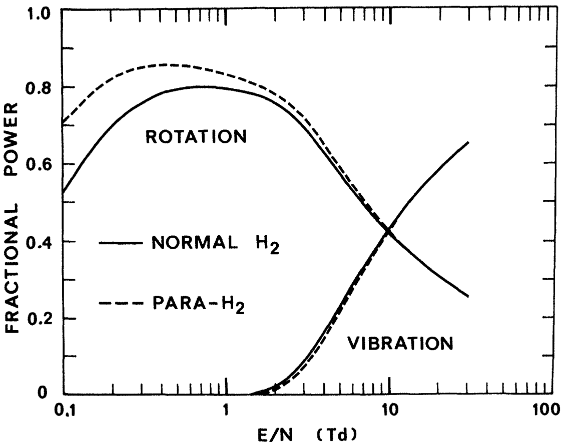

FIG. 2. The power absorbed by rotational and vibrational excitation of normal and parahydrogen calculated as functions of E/N and expressed as fractions of the total power absorbed (eEW). In the case of normal hydrogen the rotational power is the sum of the power absorbed by the $J=0\rightarrow 2$ and the $J=1\rightarrow 3$ excitations.

which the drift velocity is most sensitive to q_{VS}. Using the same apparatus and techniques as used by these authors, we have measured W for $1 \leq E/N \leq 26$ Td in both normal and parahydrogen at 77 °K. The same pressures, temperatures, and field strengths, to within 0.1%, were used in the two sets of measurements. The results are shown in Table II. The relative accuracy of the measurements is considered to be of the order of 0.25%. For $12 \leq E/N \leq 26$ Td there is no significant difference between the drift velocities in the two forms. Below 12 Td there is an increasing difference, amounting to 1% at $E/N = 4$ Td, which we attribute to the increasing influence of the different rotational excitations in each case. From this result it may be concluded that, between threshold and at least 1.5 eV, the "total" vibrational cross section is the same for the $J=0$ and $J=1$ rotational states of hydrogen.

B. Effect of Significant $J=2$ and $J=3$ Populations; Experiments in Normal Hydrogen at 77 and 293 °K

By raising the temperature from 77 to 293 °K, the relative populations of the $J=2$ and $J=3$ states can be increased from less than 1% to 12 and 9%, respectively. It is therefore possible to look for changes in q_{VS} brought about by a significant population of the higher rotational states, although any conclusions must be less definite than for the $J=0$ and 1 states since the populations are still relatively small.

It has already been shown that for sufficiently high values of E/N the power absorbed by rotational excitation in normal and parahydrogen is almost the same. For similar reasons the same is true for normal hydrogen at 77 and 293 °K despite the change in the rotational populations, from which it follows that no significant differences in the transport coefficients at high E/N are to be expected from differences in the rotational energy losses. In this case, however, there is also the possibility that the increased feedback to the swarm at 293 °K, both from collisions of the second kind and from elastic collisions with sufficiently energetic molecules, may still influence the transport coefficients significantly at the higher values of E/N, even though the swarm energy greatly exceeds the thermal value. The over-all effect of the change in rotational excitation and increased feedback was checked by comparing values of W and D/μ calculated for 77 and 293 °K using the cross sections given by Gibson.[10] These comparisons showed that W changed by less than 0.8% and D/μ by less than 1.2% for $E/N > 6$ Td, the corresponding changes being less than 0.3 and 0.5% for $E/N > 15$ Td. It follows, therefore, that any larger differences between the transport coefficients measured at the higher values of E/N at the two temperatures may be reasonably attributed to differences in the vibrational cross sections.

A comparison of the room- and low-temperature data for D/μ in normal hydrogen[20] shows that the values agree to within 2% above 6 Td. A similar comparison of drift velocities using Lowke's[21] data shows agreement to within 2% above $E/N = 3$ Td. In order to extend the comparison of drift velocities to higher E/N and to take advantage of more accurate techniques, thereby making the comparison more significant, a new set of results has been taken in normal hydrogen in the range $1 \leq E/N$

TABLE II. The drift velocities of electrons in parahydrogen and normal hydrogen at 77 °K, and in normal hydrogen at 293 °K, shown as functions of E/N.

E/N (Td)	$W(10^5$ cm sec$^{-1})$ p-H_2(77 °K)	 n-H_2(77 °K)	 n-H_2(293 °K)
1	7.17	6.71	6.24
2	8.93	8.69	8.38
4	11.73	11.62	11.47
6	14.35	14.29	14.15
8	16.72	16.66	16.55
10	18.95	18.86	18.80
12	20.98	20.94	20.82
14	22.89	22.86	22.78
16	24.72	24.68	24.65
18	26.47	26.43	26.43
20	28.16	28.13	28.13
22	29.86	29.83	29.74
24	31.49	31.47	31.44
26	33.14	33.09	33.06

≤26 Td. These results are also shown in Table II. Above $E/N = 6$ Td, the results may be seen to agree to within 1% with even closer correspondence at the highest values of E/N where the sensitivity to the vibrational cross section is maintained but the effects of rotational excitation are diminished. Thus from both the D/μ and the W data there is again no evidence of a significant change in q_{vs} with change in the rotational populations.

From both this and Sec. II we conclude that there is, at least, no strong dependence of the "total" cross section for $v = 0 \rightarrow 1$ excitation on initial rotational state since any change greater than 10% in the slope of the cross section near threshold would have been revealed (Sec. III A). The result is particularly significant in the case of the $J = 0$ and 1 states since the relative populations are altered from 1:3 to 1:0, respectively, in changing from normal to parahydrogen at 77 °K.

IV. COMPARISON OF SWARM DERIVED CROSS SECTIONS IN HYDROGEN

The cross sections for hydrogen that are available from the analysis of swarm experiments are those of Engelhardt and Phelps (EP)[8] and those of Crompton *et al.*[2] and Gibson[10] (CG). Engelhardt and Phelps based their analysis in the energy range of present interest (0–1.5 eV) principally on the 77 and 300 °K normal-hydrogen data of Pack and Phelps,[22] Bradbury and Nielsen,[23] and Warren and Parker.[24] Crompton *et al.* used the 77 °K parahydrogen data of Crompton and McIntosh,[19] while Gibson based his analysis on the results of Crompton *et al.*[2] and the experimental data for normal hydrogen at 77 °K given by Lowke,[21] Crompton *et al.*,[20] and Robertson[25] (Table II). The vibrational cross section of CG, which has not previously been tabulated, is given in Table III.

TABLE III. The $v = 0 \rightarrow 1$ vibrational cross section for hydrogen derived from swarm measurements.

Energy (eV)	Cross section (10^{-16} cm^2)	Energy (eV)	Cross section (10^{-16} cm^2)
0.516	0.0	1.5	0.165
0.7	0.019	1.8	0.26
1.0	0.06	2.4	0.405
1.2	0.095	3.0	0.54

Differences in the cross sections derived from the experimental data can arise from three sources: (a) differences in the numerical analyses used in determining the cross sections; (b) lack of uniqueness in the set of cross sections that are found to be compatible with a given set of transport data; and (c) differences between the sets of experimental results themselves.

The first possibility can be dismissed since it has been shown[2] that the analyses that have been used yield identical calculated values of W and D/μ provided the same input data are used. The second and third alternatives are to some extent interlocked and are therefore best considered together.

We first note that the *vibrational* cross section cannot be derived uniquely from an analysis of electron-transport measurements alone, although it has already been shown[2,10] that the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ *rotational*-excitation cross sections can be so determined near threshold from an analysis of low-temperature parahydrogen data followed by a similar analysis for normal hydrogen. However, provided the validity of a high-energy extrapolation of the $J = 0 \rightarrow 2$ cross section can be established it *is* possible to determine the vibrational cross section uniquely from the parahydrogen data. Alternatively, the normal-hydrogen data can be used if reliable extrapolations of both the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ cross sections are available. In deciding between the vibrational cross sections of EP and CG, therefore, we must look for differences in the experimental data on which the analyses were based in the range of E/N for which vibrational excitation strongly influences the transport properties, i.e., for $E/N > 6$ Td; and (b) explain why the rotational cross sections of the two sets are so different since, as will be shown subsequently, it is this difference that is chiefly responsible for the difference in the vibrational cross sections.

A. Comparison of Experimental Data

In order to determine the magnitude of the discrepancies between the two sets of experimental data that could account for the different vibrational cross sections, we have compared values of W and D/μ in normal hydrogen at 77 °K, calculated using the cross sections of CG with values calculated using the same momentum-transfer and rotational-excitation cross sections but with the vibrational cross section replaced by the cross section of EP. The percentage deviations are plotted in Fig. 3. From the figure it can be seen that if the difference between the two vibrational cross sections results from differences in the experimental data then these differences must occur for E/N greater than about 4 Td and be of the order of 5 to 10%.

A comparison of the transport data used by EP with the data used by CG shows that only a small part of the discrepancy between the vibrational cross sections obtained by these authors can be attributed to differences in the experimental data, although the same is not true for the rotational

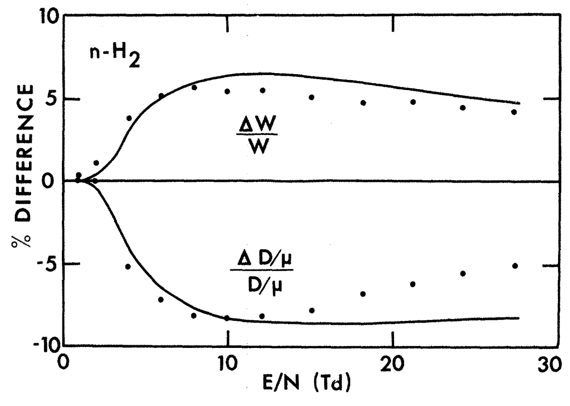

FIG. 3. The effect of using different vibrational cross sections to calculate W and D/μ in normal hydrogen. Full curve shows the effect on the calculations for 77 °K of interchanging the cross sections of EP and CG. Points show percentage differences between values measured at 293 °K and values calculated for this temperature using the q_V of ELLT and Henry' s rotational cross sections.

cross sections. The scatter in the data used by EP makes differences of a few percent hard to estimate but nevertheless the agreement between the D/μ data used by EP and those used by CG appears to be within 2–3% in this range of E/N. Furthermore, the values of D/μ calculated with the EP cross sections agree well with the experimental values. Similarly, the drift-velocity data of Bradbury and Nielsen, on which the EP analysis is based in this region, agree to within about 2% with the data used to derive the CG cross sections, although somewhat inexplicably the values of W calculated using the EP cross sections appear to be as much as 5% higher than the experimental values used by EP in the range of E/N under consideration. However, this disagreement can be largely removed, without significantly disturbing the fit to the D/μ data, by an appropriate adjustment of the momentum-transfer cross section. Such an adjustment reduces the discrepancy between the momentum-transfer cross sections derived by EP and CG.

B. Uniqueness

Although there are small differences in the primary data, computer tests have shown that the major factor leading to the large difference between the vibrational cross sections obtained from the two analyses is the very large difference between the high-energy extrapolations of the rotational cross sections. At 3 eV, for example, the $J = 0 \rightarrow 2$ cross section of CG is a factor of 9 larger than that of EP. When the same momentum-transfer cross section was used but the rotational cross sections of CG were replaced by those of EP, it was found that W changed by approximately 6% and D/μ by 9% in the range $2 \lesssim E/N \lesssim 26$ Td. On the other hand, when all the inelastic cross sections were interchanged, changes of less than 2 and $2\frac{1}{2}$%, respectively, were produced. Thus the much higher vibrational cross section of EP was required to compensate for the low rotational cross sections in the region of overlap in order to produce essentially the same calculated values of the transport coefficients.

C. Evidence in Favor of CG Rotational Cross Sections

Since the validity of the vibrational cross section rests so heavily on the rotational cross sections, we set down below the reasons which, in our view, give overwhelming support for the cross sections of CG.

(a) The low-energy regions of the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ cross sections of CG were determined by analyzing sequentially the transport data in parahydrogen and normal hydrogen. The presence of a single inelastic process at low energies in parahydrogen enabled the $J = 0 \rightarrow 2$ cross section to be determined without reference to other experiments or to theories for the energy dependence of the cross section. The $J = 1 \rightarrow 3$ cross section was then derived by an extension of the procedure to the data for normal hydrogen using the already determined $J = 0 \rightarrow 2$ cross section. Such a procedure could not be used in the analysis of EP since no data for parahydrogen were available. Furthermore, although both the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ cross sections had to be derived by EP before analyzing normal-hydrogen data to obtain the vibrational cross section, only the $J = 0 \rightarrow 2$ cross section was required by CGM to derive the vibrational cross section from the parahydrogen data.

(b) There are significant differences in the transport coefficients for normal hydrogen below $E/N = 2$ Td that were used to derive the rotational cross sections of EP and CG. This may be illustrated by comparing the transport coefficients calculated using the EP cross sections with the experimental data used by CG. Below $E/N = 2$ Td the values of W differ by up to 2.7% and the D/μ values by up to 5.4%. For comparison, the fit to experimental data using the CG cross sections is to within 0.6%. A similar comparison using the $J = 0 \rightarrow 2$ cross sections of CGM and the experimental parahydrogen data has already been described.[2]

(c) The EP cross sections were based everywhere on the energy dependence proposed by Gerjuoy and Stein[26] and modified by Dalgarno and Moffett.[27] The fit to the measured transport coefficients was made by adjusting an arbitrary, energy-independent scaling factor. The high-energy extrapolation of the cross sections, that is, the extrapolation beyond about 0.4 eV, was made on this basis. The CG analysis required a theoretical energy dependence only to obtain the high-energy extrapolation. Furthermore, in making these extrapolations advantage could be taken of recent, more exact, theoretical treatments.[18] This fact is particularly significant since the earlier calculations were subject to considerable error in the high-energy region.[18] Since the experimentally derived rotational cross sections of CG agree so well with Henry and Lane's theoretical cross sections at low energies, where the former could be determined independently of theory, an extrapolation to higher energies using these theoretical cross sections is justified. Further justification is provided by the good agreement between Ehrhardt and Linder's[28] experimental $J=1\rightarrow 3$ cross section and Henry and Lane's theoretical values for energies significantly above threshold.

V. DISCUSSION

A. Comparison of q_V from Beam and Swarm Experiments

The results of ELLT can be tested against the results of swarm experiments by using their vibrational cross section together with Henry and Lane's[18] rotational cross sections to calculate the transport coefficients in normal hydrogen at room temperature. In this way it is possible to show directly the discrepancy between measured and calculated transport coefficients that must be accounted for. Henry and Lane's theoretical cross sections have been used because of the absence of data from beam experiments for some of the cross sections, and because Ehrhardt and Linder's[28] results for the $J=1\rightarrow 3$ transition (which is the dominant rotational-excitation process at this (temperature) are in good agreement with the theoretical calculations. The results of this comparison are shown in Fig. 3. From the figure it can be seen that there is good agreement below $E/N=2$ Td, thus confirming the compatibility of the rotational cross sections with the swarm data, but rather poor agreement above this value where the discrepancies become as large as five times the experimental error. A similar test applied to the Burrow and Schulz[3] data would obviously show still larger discrepancies.

There is now general agreement that the vibrational cross section rises approximately linearly near threshold, but poor agreement on the magnitude of the initial slope of the cross section. We have therefore placed what we believe to be a reasonable upper bound on the slope by using the following argument.

The $J=0\rightarrow 2$ rotational cross section is now known with good accuracy for energies at least up to 0.3 eV,[2,18] while all theoretical and experimental work suggests that the cross section increases monotonically up to at least 3 eV. The maximum q_{VS} derived from the swarm analysis clearly corresponds to the smallest allowable rotational cross section. We have therefore constructed an artificial $J=0\rightarrow 2$ cross section by retaining the cross section of CGM up to 0.5 eV (on the grounds that the cross section is known to ±10% at 0.4 eV and may be extrapolated from 0.4–0.5 eV using Henry and Lane's theory) and thereafter rapidly decreasing the slope of the curve so that the cross section becomes energy independent beyond 0.6 eV (Fig. 4). The vibrational cross section compatible with this rotational cross section was found to have an initial slope only 15% higher than the q_{VS} of CGM, while beyond about 1 eV the cross section had to be increased by approximately 30%.

Figure 4 shows the "upper-bound" cross section together with the q_{VS} of CGM, the q_{VT} of ELLT, and the initial slope of the cross section reported by BS from their trapped-electron method. It should be emphasized that the evidence presented in Sec. IV is heavily against the validity of the artificially constructed rotational cross section used to obtain the upper bound, and that we believe the true cross section lies close to the cross section of CGM. Moreover, we note that the sensitivity of the swarm analysis is such that the variation to the vibrational cross section that is required to accommodate the somewhat improbable high-energy extrapolation of the rotational cross section is not large compared with the discrepancy between the cross section of CGM and those of ELLT and BS.

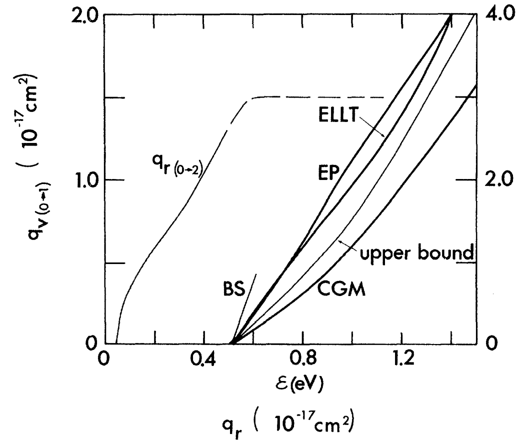

FIG. 4. Comparison of experimentally determined vibrational cross sections in hydrogen from threshold to 1.5 eV. The "upper-bound" cross section was derived from an analysis of transport coefficients using the artificially constructed rotational cross section shown in the figure.

One possible explanation of the disagreement between the results of beam and swarm experiments requires further investigation. The solution of the Boltzmann equation that is used to relate the transport coefficients to the cross sections for the collision processes is developed in terms of a representation of the energy-distribution function by a two-term expansion in spherical harmonics.[29] It is possible that this approximation is inadequate for the present application, even though calculations for the case of helium[30] suggest that the errors are negligible. In the present case the errors will be larger because the inelastic processes cause some of the electrons with energies just above the threshold energies to be brought almost to rest; and it is the class of electrons with smallest speeds that is least well represented by the expansion.[31] Nevertheless, it is likely that the fraction of the swarm for which the approximation is inadequate is sufficiently small for the over-all effect on the calculated transport coefficients to be neglible.

B. Comparison with Theory

Two essentially different theoretical approaches to the problem of calculating the energy dependence of the vibrational cross section in hydrogen have been used, each of which has given results in partial agreement with experiment. Bardsley *et al.*[6] and Abram and Herzenberg[15] have used a model in which the electron is trapped to form a temporary negative ion which decays leaving the molecule in an excited state. In the first paper only the "total" vibrational cross section was calculated since the result corresponded to a sum over all rotational transitions. In the later paper this work was extended to include calculations of the angular dependence of simultaneous rotational-vibrational transitions in order to compare the theory with the recently published data of Ehrhardt and Linder.[28] This model was successful in predicting "total" cross sections for the $v=0\rightarrow 1$ and $v=0\rightarrow 2$ transitions that were in far better agreement with experiment than the earlier calculations using the Born approximation, and particularly successful in accounting qualitatively for Ehrhardt and Linder's results.

Three results of these calculations are of particular importance to the present discussion. In the first place, we note the extreme sensitivity of the results to the shape of the potential-energy curve assumed for the H_2^- ion. Because of the uncertainty of this curve, Bardsley *et al.* did not expect to obtain more than semiquantitative agreement with experiment. A second prediction of the theory is that the ratio $q_{v,02} : q_{v,13}$ is 5 : 3; that is, equal to the ratio of the pure rotational cross sections at energies sufficiently far removed from threshold. This result is in agreement with Henry's later work[13] which is discussed below. The third prediction is that the simultaneous cross section is by no means small compared with the pure vibrational cross section, a result that also agrees with the earlier experimental result of Ehrhardt and Linder.

The alternative approaches, which do not explicitly postulate the formation of a temporary negative ion, are exemplified by the calculations of Carson,[32] Takayanagi,[33] and Henry.[13] Carson and Takayanagi both used the Born approximation, but Takayanagi was able to show that the long-range polarization force is chiefly responsible for vibrational excitation. The inclusion of this force and the use of a distorted-wave approximation led to a calculated cross section in better agreement with experiment than Carson's earlier result which included only short-range interactions and led to results 1 to 2 orders of magnitude too low.

Henry[13] based his calculations on the work of Arthurs and Dalgarno[34] and Ardill and Davison.[35] A close-coupling calculation was made using an interaction potential which accounted for the static field and exchange short-range forces and for the long-range forces arising from polarization and the quadrupole interaction. Henry found that the short-range terms and the long-range polarization term contributed about equally to the pure vibrational-excitation cross section.

From the standpoint of the results presented in this paper the most interesting result of Henry's work is the prediction that the "total" vibrational cross section $q_{v,JJ}+q_{v,J(J+2)}$ is almost the same for $J=0$ and $J=1$. This explains why the results given in Sec. III failed to show any dependence of the cross section on the initial rotational state of the molecule.

A further result of Henry's work is the demonstration that $q_{v,02}/q_{v,13}\approx 1.63$, in agreement with the work of Abram and Herzenberg. If this result is coupled with the two experimental results, (a) that the cross sections for simultaneous excitation are comparable with those for pure vibrational excitation[11] and (b) the result given in Sec. III that q_V is independent of J, then it follows that the cross section for *pure* vibrational excitation must be quite strongly dependent on the initial rotational state. This result is also found theoretically by Henry. As far as we are aware, there is no other experimental evidence for this dependence at the present time.

Although the general agreement between theory and experiment is good, the agreement between the threshold behavior of the "total" vibrational cross section and our swarm-derived result is disappointing. If the rotational and vibrational cross sections derived by Henry and Lane[18] and Henry[13] are used to calculate the transport coefficients, there is good agreement for values of E/N less than 2 Td, but there are discrepancies of up to 8% in W and 14% in D/μ for $2 \leq E/N \leq 26$ Td. For the reason given in Sec. V A, we attribute this to an error in the threshold behavior of the vibrational cross section rather than to errors in the rotational cross sections in this energy range. Furthermore, because of the particular sensitivity of swarm measurements to the threshold behavior of an inelastic cross section, as demonstrated again in this paper, and the ease with which absolute cross sections can be obtained by this technique,[36] it is difficult to believe that the swarm-derived cross section is seriously in error unless the approximations used in solving the Boltzmann equation are very much larger than expected.

VI. CONCLUSION

In this paper, some recently derived vibrational cross sections for hydrogen in the energy range 0–1.5 eV have been discussed. First, it is shown that the rather large discrepancies that exist at present between the results of some beam and swarm experiments cannot be explained as resulting from the effect of simultaneous rotational-vibrational excitation on the interpretation of swarm experiments. It is further shown that the fact that the beam and swarm experiments were performed with samples of hydrogen having different rotational populations also cannot account for the discrepancies, since new drift-velocity measurements made in normal and parahydrogen in the range of E/N most sensitive to vibrational excitation failed to show any variation of the "total" vibrational cross section when large changes were made to the relative populations of the $J=0$ and $J=1$ states. A possible explanation of the difference between the vibrational cross section obtained by Engelhardt and Phelps from their analysis of normal-hydrogen data and the cross section obtained by Crompton, Gibson, and McIntosh from their parahydrogen analysis is thereby removed, although Gibson had in any case shown previously that the same vibrational cross section was compatible with the data from experiments with both normal and parahydrogen.

A reexamination of the experimental data upon which Engelhardt and Phelps based their analysis leads us to the conclusion that their vibrational cross section is in error because of a combination of two factors. In the first place, a small error arose from the use of D/μ data that were a few percent too low and W data that were a few percent too high in the range of E/N sensitive to q_{VS}. However, we believe the principal source of error was the use of incorrect rotational cross sections derived from W and D/μ data that were significantly in error in the region where these coefficients are most sensitive to the rotational cross section (i.e., for $E/N < 2$ Td). Other recent experimental and theoretical work supports this view. The agreement between the EP and ELLT cross sections, therefore, seems to be fortuitous.

Finally, our result that the "total" vibrational cross section in hydrogen is the same for the $J=0$ and $J=1$ rotational states is found to be in agreement with a recent theoretical calculation of these cross sections by Henry. However, the disagreement between the threshold slopes found from beam experiments, from swarm experiments, and from theory requires further investigation since there is a difference of a factor of 4 between the highest and lowest values obtained in the most recent work.

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[1] H. Ehrhardt, L. Langhans, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).

[2] R. W. Crompton, D. K. Gibson, and A. I. McIntosh, Australian J. Phys. 22, 715 (1969).

[3] P. D. Burrow and G. J. Schulz, Phys. Rev. 187, 97 (1969).

[4] A. V. Phelps, Rev. Mod. Phys. 40, 399 (1968).

[5] G. J. Schulz, Phys. Rev. 135, A988 (1964).

[6] J. N. Bardsley, A. Herzenberg, and F. Mandl, Proc. Phys. Soc. (London) 89, 321 (1966).

[7] H. Ramien, Z. Physik 70, 353 (1931).

[8] A. G. Engelhardt and A. V. Phelps, Phys. Rev. 131, 2115 (1963).

[9] M. G. Menendez and H. K. Holt, J. Chem. Phys. 45, 2743 (1966).

[10] D. K. Gibson, Australian J. Phys. 23, 683 (1970).

[11] F. Linder, Abstracts VIICPEAC (MIT Press, Cambridge, Mass., 1969), p. 141.

[12] It is assumed that the effect of the $v=0 \rightarrow 2$ vibrational transition can be ignored in examining the threshold behavior of the $v=0 \rightarrow 1$ transition, an assumption that is justified by the ELLT result for the relative magnitudes of the cross sections. We use the symbol $q_{v,JJ'}$ to represent a $v=0 \rightarrow 1$ vibrational transition in which the initial and final rotational states are J and J', respectively.

[13] R. J. W. Henry, Phys. Rev. A 2, 1349 (1970).

[14] Abram and Herzenberg have shown theoretically that $q_{v,02}/q_{v,13} = \frac{5}{3}$. Linder has shown experimentally that

$q_{v,13}/\sum_J q_{v,JJ} \approx \frac{1}{3}$ and our experimental result (Sec. III) shows that $q_{v,00}+q_{v,02}=q_{v,11}+q_{v,13}$. These results can be combined to show that $q_{v,02}/q_{v,00} \approx 0.7$.

[15] R. A. Abram and A. Herzenberg, Chem. Phys. Letters 3, 187 (1969).

[16] R. J. W. Henry (private communication).

[17] E. S. Chang and A. Temkin, Phys. Rev. Letters 23, 399 (1969).

[18] R. J. W. Henry and N. F. Lane, Phys. Rev. 183, 221 (1969).

[19] R. W. Crompton and A. I. McIntosh, Australian J. Phys. 21, 637 (1968).

[20] R. W. Crompton, M. T. Elford, and A. I. McIntosh, Australian J. Phys. 21, 43 (1968).

[21] J. J. Lowke, Australian J. Phys. 16, 115 (1963).

[22] J. L. Pack and A. V. Phelps, Phys. Rev. 121, 798 (1961).

[23] N. E. Bradbury and R. A. Nielsen, Phys. Rev. 49, 388 (1936).

[24] R. W. Warren and J. H. Parker, Phys. Rev. 128, 2661 (1962).

[25] A. G. Robertson (unpublished).

[26] E. Gerjuoy and S. Stein, Phys. Rev. 98, 1848 (1955).

[27] A. Dalgarno and R. J. Moffett, Proc. Nat. Acad. Sci. India A33, 511 (1963).

[28] H. Ehrhardt and F. Linder, Phys. Rev. Letters 21, 419 (1968).

[29] W. P. Allis, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 383.

[30] R. W. Crompton, M. T. Elford, and A. G. Robertson, Australian J. Phys. 23, 667 (1970).

[31] G. Cavalleri and G. Sesta, Phys. Rev. 170, 286 (1968).

[32] T. R. Carson, Proc. Phys. Soc. (London) A67, 909 (1954).

[33] K. Takayanagi, J. Phys. Soc. Japan 20, 562 (1965).

[34] A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) A256, 540 (1960).

[35] R. W. B. Ardill and W. D. Davison, Proc. Roy. Soc. (London) A304, 465 (1968).

[36] R. W. Crompton, *Advances in Electronics and Electron Physics* (Academic, New York, 1969), Vol. 27, p. 1.

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Auger Electrons from Argon with Energies 150-210 eV Produced by H^+ and H_2^+ Impacts*

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Secondary electrons in the energy range 150–210 eV produced by 125–300-keV H^+ and H_2^+ impacts on argon gas are measured as a function of their energy and angle of emission. Discrete line spectra are due to Auger transitions from L_2 and L_3 vacancy states as well as satellite transitions from multivacancy states. The widths, energies, and branching ratios of the L_2 and L_3 vacancy states are presented. Widths of these states are appreciably greater than those obtained with electron impact excitation. This can be attributed to the recoil velocities of the target atom and to the presence of the proton in the vicinity of the emitting atom. The angular distribution of Auger electrons is found to be nearly isotropic, in marked contrast to electrons in the continuum spectrum. The cross sections for the production of $L_{2,3}$ and L_3 vacancy states are determined as a function of impact energy.

I. INTRODUCTION

When electrons emitted from photon-, electron-, or ion-atom collisions are energy-analyzed with sufficient resolution, structure appears in the spectrum which results from autoionization or Auger transitions in the atom. Earlier work at this laboratory[1] has shown that two of the electron energy regions of interest in argon are 0–15 and 150–210 eV. The low-energy fine structure is associated with excitations of M-shell electrons, while the higher-energy peaks are Auger transitions from single L-shell vacancy states and satellite lines from simultaneous L- and M-shell vacancies.

Using electron impact excitation, Mehlhorn[2] and Mehlhorn and Stahlherm[3] have studied Auger transitions from L_1, and L_2, and L_3 vacancies in argon. Nakamura *et al.*[4] have investigated structure near the L_2 and L_3 edges in argon by absorption of synchrotron light and obtain values for the energies of these edges. Deslattes[5] has deduced new values of the L_2 and L_3 levels from K-series x-ray measurements. Ogurtsov and co-workers[6,7] have studies the production of vacancy states in argon using H^+, Ne^+, and Ar^+ beams up to 20 keV. Cacak[8] has made cross-section measurements at low resolution of the production of argon vacancy states by Ar^+ beams from 50 to 300 keV.

This paper reports on fairly high-resolution measurements of energies and intensities of Auger and satellite lines in the 150–210 eV region of the