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Collisions between electrons and H_2^+ ions
II. Measurements of cross sections for dissociative excitation

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Abstract. Cross sections for the dissociative excitation of H_2^+ by electrons have been measured for interaction energies between 25·4 and 715 eV. A source was used which produced H_2^+ ions under clearly defined conditions. Over the whole energy range, the measurements agree very closely with values obtained by averaging the theoretical cross sections of Peek in 1967 and Peek and Green in 1969 over a vibrational population given by Franck–Condon factors between hydrogen and H_2^+.

1. Introduction

The H_2^+ ion is the simplest molecule and it is the only one which can, within the framework of the Born–Oppenheimer approximation, be represented by exact wavefunctions. It is also a common constituent of thermonuclear plasmas.

This is the second of a series of papers which will discuss collisions between electrons and H_2^+. Three dissociative inelastic processes are possible, namely

$$
\mathrm{e} + \mathrm{H_2^+}(1s\sigma_g) \rightarrow \begin{cases} \mathrm{H^+ + H^+ + 2e} \\ \mathrm{H^+ + H + e} \\ \mathrm{H + H.} \end{cases}
$$

In the two latter reactions the hydrogen atoms can be produced in states which may or may not be excited. These processes are respectively called dissociative ionization, excitation and recombination, and their cross sections will be denoted by σ_i, σ_e, and σ_r.

Crossed-beam experiments have been performed by Dunn *et al* (1965), Dunn and Van Zyl (1967) and Dance *et al* (1967) to measure cross sections σ_p for proton production. These authors measured the proton currents with an electrometer and it follows that $\sigma_p = \sigma_e + 2\sigma_i$ because dissociative ionization results in the formation of two protons. A previous communication (Peart and Dolder 1971 to be referred to as I) described a slightly different experiment in which the protons were detected by a particle multiplier and counted. Since the two protons due to dissociative ionization arrived simultaneously at the multiplier they were recorded as single events and a cross section, $\sigma_p' = \sigma_e + \sigma_i$ was obtained. The differences between σ_p and σ_p' should not, however, be large because a classical calculation of σ_i (Alsmiller 1962) gives a value which is typically an order of magnitude smaller than σ_e. When these results were plotted as $\sigma_p' E$ against $\lg E$ (E represents the interaction energy) it was found that they merged with the linear relation predicted by Peek (1967) when $E \gtrsim 200\,\mathrm{eV}$. This asymptotic behaviour was not displayed by the measurements of σ_p by Dance *et al* and Dunn and Van Zyl. It was therefore suggested in I that these discrepancies may have arisen from the imperfect exclusion of slow secondary electrons from the region in which the beams collided in the earlier experiments.

2. Cross section measurement

The present paper describes the first measurements of σ_e. These were made by the coincident detection of protons and hydrogen atoms formed by dissociative excitation. It was of paramount importance to specify the initial excitation of the H_2^+ beam because Peek and Green (1969) and others (see I) have predicted that σ_e differs by three orders of magnitude for the various vibrational states of H_2^+. Paper I includes a description of a novel ion source which was designed to fulfil criteria suggested by Dunn and Van Zyl. These authors argued that if cold hydrogen is ionized by fast electrons and the ensuing H_2^+ ions are removed quickly without further collisions, then ions should be produced with a distribution of vibrational states given by the appropriate Franck–Condon factors. Subsequent measurements of the photodissociation of H_2^+ by von Busch and Dunn (private communication) indicated that ions produced in this way had somewhat less vibrational excitation, but when calculated values of σ_e, σ_p and σ_p' are averaged over the two distributions, the results differ by only 4% at high energies. The effects of vibrational excitation will be discussed further in § 3.

The apparatus was the same as that represented by figures 2 and 3 of I, except that an additional particle detector was placed in line with the path taken by H_2^+ ions through the interaction region. This detector, which responded to fast hydrogen atoms, was identical with that used for protons (labelled D in I). The efficiencies of both detectors were measured for protons with energies ranging from 7 to 10 keV and it was assumed that the efficiency for fast hydrogen atoms ($\simeq 90\%$) was the same as that measured for protons of the same energy. Support for this assumption was given by a previous experiment (Peart *et al* 1970) in which it was demonstrated that a similar detector had virtually the same efficiency for fast H^+ and H^- ions.

In the present experiment the output of both detectors, after amplification and pulse shaping, entered a fast coincidence unit from which the output was fed to the counting system mentioned in I. Details of this system and of the beam modulation which was necessary to separate signals from background are illustrated by figure 5.2.8 of a review by Dolder (1969).

The cross section was related to measurable quantities by

$$\sigma_e = \frac{R_c}{IJ}\frac{vV}{(v^2+V^2)^{1/2}}\frac{e^2F'}{\Omega_1\Omega_2}$$

where R_c represents the rate of coincidence counts (corrected for dead time) due to electron–ion collisions and $\Omega_1\Omega_2$ is the product of the two counter efficiencies. The other symbols were defined in I which also described procedures used to deduce cross sections from the experimental data. The following values are typical for the present experiment: $R_c \simeq 10\,\mathrm{s^{-1}}$, $R_T \simeq 10^3\,\mathrm{s^{-1}}$, $J = 5\times10^{-4}\,\mathrm{A}$, $I = 2\times10^{-10}\,\mathrm{A}$, $p = 5\times10^{-10}$ Torr, $E = 20\,\mathrm{keV}$, $\Omega_1 \simeq \Omega_2 \simeq 90\%$.

3. Results and discussion

Table 1 summarizes the measurements of σ_e and the estimates of systematic and random errors, which were assessed as described in I. The random errors are 90% confidence limits at each energy.

Table 1.

Interaction energy (eV)	Cross section (πa_0^2)	Random error ($\pm$ %)	Systematic error ($\pm$ %)
25·4	4·85	6	8
33·4	4·17	5	8
48·4	3·29	8	6
63·4	2·89	4	6
103	2·13	4	6
153	1·50	6	6
203	1·23	7	6
303	0·90	3	6
403	0·71	4	6
503	0·61	4	6
715	0·46	6	6

Figure 1 illustrates these results and compares them with theoretical values obtained from the work of Peek (1967), and Peek and Green (1969). The latter paper gives cross sections for the transition $1s\sigma_g$–$2p\sigma_u$ in the form $8/v^2(A \ln v + B)$, where v represents the interaction velocity (au) and the constants A and B are given for each of the 20 vibrational states of H_2^+. Peek (private communication) subsequently averaged these cross sections over the vibrational populations deduced from Franck–Condon factors and from the experiments of von Busch and Dunn. For the former distribution he obtained $\bar{A} = 0{\cdot}622$ and $\bar{B} = 0{\cdot}869$ whilst in the latter case $\bar{A} = 0{\cdot}587$ and $\bar{B} = 0{\cdot}756$. The Franck–Condon factors were taken from unpublished work by Peek but they are essentially identical to those presented by Villarejo (1968). When averaging over the von Busch–Dunn distribution it was necessary to guess the contribution from the $v = 19$ state because its population had not been predicted. However, this contribution is probably so small ($\ll 1$ %) that any error can be neglected.

The transition $1s\sigma_g$–$2p\pi_u$ is much less sensitive to the vibrational excitation of H_2^+ so that the less rigorous calculation of Peek (1967) will suffice to predict this cross section. Following the procedure outlined above, Peek obtained $\bar{A} = 0{\cdot}400$ and $\bar{B} = 0{\cdot}0249$ for the average over the Franck–Condon distribution and $\bar{A} = 0{\cdot}395$ and $\bar{B} = 0{\cdot}0222$ for the von Busch–Dunn distribution.

We have assumed that states other than $2p\pi_u$ and $2p\sigma_u$ make a negligible contribution to excitation so that σ_e is given by adding the two cross sections. This was done for both vibrational populations and the results are illustrated by the curves in figure 1. The inset of this figure shows the same results plotted as $\sigma_e E$ against lg E.

These results have some surprising features. In particular, theory is seen to be accurate to remarkably low energies. This is clearly shown by the inset which illustrates that the measurements follow the linear relation associated with Bethe's approximation even at energies below 30 eV. It is also surprising that there is better agreement when theory is averaged over the Franck–Condon distribution than over the von Busch–Dunn

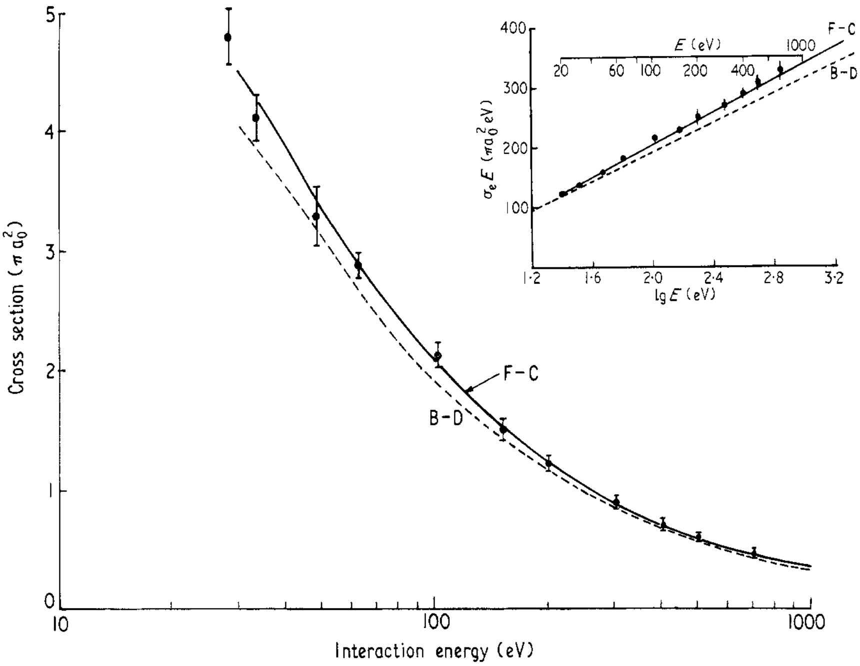

Figure 1. Cross sections for dissociative excitation of H_2^+. The present experimental points, which are plotted against the interaction energy, are compared with theoretical estimates based on the work of Peek, and Peek and Green (see text). The broken line assumes vibrational excitation of H_2^+ given by Franck–Condon factors whilst the continuous line assumes a distribution deduced from experiments by von Busch and Dunn. The brackets show 90% confidence limits of random error at each energy.

distribution. It should, however, be remembered that the differences between the two theoretical curves may not exceed the magnitudes of other experimental and theoretical uncertainties.

At first sight, the agreement with the Bethe–Born approximation at low energies appears to conflict with the measurements of σ_p' presented in I. It will be remembered that $\sigma_p' E$ was only linearly related to lg E at energies greater than about 200 eV. However, calculations of σ_p' naturally include a contribution from ionization (remember $\sigma_p' = \sigma_e + \sigma_i$) and since the ionization threshold is about 25 eV one would not expect the Bethe–Born approximation to be valid for ionization until the interaction energy was an order of magnitude larger. Dissociative excitation, on the other hand, has much lower thresholds and this may partly explain the observed linearity between $\sigma_e E$ and lg E. There are of course numerous complications in the theory of molecular dissociation and other more subtle considerations may also influence this functional dependence.

It is particularly interesting to plot measurements of σ_p (Dunn and Van Zyl 1967), σ_p' (paper I) and the present results for σ_e against energy. Since $\sigma_p = \sigma_e + 2\sigma_i$ and $\sigma_p' = \sigma_e + \sigma_i$ it follows that when E exceeds the ionization threshold $\sigma_p > \sigma_p' > \sigma_e$. Moreover, the differences $(\sigma_p - \sigma_p')$ and $(\sigma_p' - \sigma_e)$ should give two estimates of σ_i. In view of the fact that σ_i is probably an order of magnitude smaller than σ_e, and the three experiments claim accuracies of only about 10%, one cannot approach these estimates of σ_i with much optimism. Nevertheless, figure 2 illustrates measurement of σ_p, σ_p' and σ_e and it is immediately apparent that there is excellent consistency between the results.

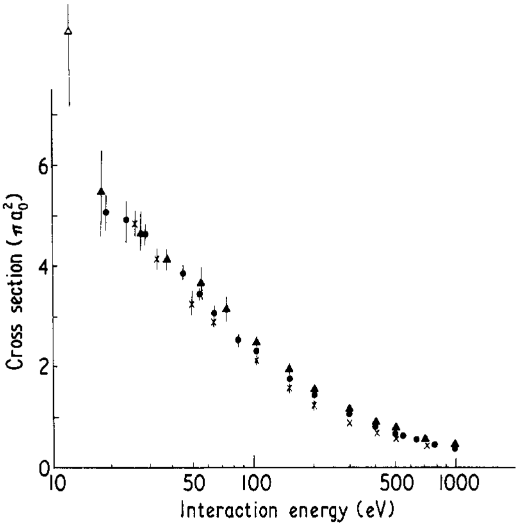

Figure 2. Measured cross sections σ_p, σ'_p and σ_e (defined in text) plotted against interaction energy. The symbols ▲, ● and × respectively represent results for σ_p (Dunn and Van Zyl), σ'_p (paper I) and the present measurements of σ_e.

Moreover, the differences $(\sigma_p - \sigma'_p)$ and $(\sigma'_p - \sigma_e)$ are in reasonable accord with Alsmiller's classical calculation of σ_i and, when $E \lesssim 30$ eV, the three measured cross sections show the expected agreement. Although there must be some fortuitous element in such close agreement figure 2 illustrates, what others have previously noted, that measurements of ionization by crossed electron–ion beams can be surprisingly accurate. In spite of the complex apparatus required for this type of measurement, the record of agreement between different laboratories compares favourably with results for electron–atom collisions obtained by long-established methods.

The very close agreement with the results of Dunn and Van Zyl is particularly noteworthy because it implies that the vibrational excitation of the H_2^+ beams produced in the two laboratories must be remarkably similar. It will be remembered that both groups used ion sources designed to fulfil the same criteria. By contrast, the measurements of σ_p by Dance *et al* fall below the results in figure 2 at low energies but this is not surprising because these authors used a plasma-type ion source which probably tended to depopulate the higher vibrational levels of H_2^+

4. Conclusions and future experiments

The measurements of σ_e agree closely with theory over the complete range of energies (25·4 to 715 eV) investigated in these experiments. The agreement was particularly good when theory was averaged over the vibrational population given by Franck–Condon factors. The agreement, even at low energies, with the measurements of σ_p by Dunn and Van Zyl suggests that the initial excitation of beams of H_2^+ produced in the two laboratories was virtually the same.

It is inevitable that there is some energy below which theory will fail. It is, therefore, proposed in future experiments to employ the technique of inclined beams (Walton *et al* 1971) to make a detailed investigation of low energy collisions between electrons and H_2^+.

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