

LETTER TO THE EDITOR

Electron correlation effects in the dissociative ionization of H_2

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Abstract. The dissociative and non-dissociative ionization of H_2 by electron impact has been measured up to 1 keV incident energy using a pulsed electron beam and pulsed ion extraction technique in conjunction with a time-of-flight spectrometer and relative flow technique. These data represent the first accurate measurement on the dissociative ionization of H_2 by electron impact over such a large energy range. It has been shown that the ratio, R^* , of the dissociative ionization cross section to non-dissociative ionization cross section in H_2 serves as a useful parameter in probing the electron correlation effects. A comparison of the value of R^* obtained by electron impact with those obtained by proton and antiproton impact shows strong dependence on the sign of the projectile charge.

Various experimental and theoretical studies have been carried out in recent times on the two-electron processes in helium such as double ionization or single ionization leaving the He^+ in the excited state as a function of the projectile charge and energy (McGuire 1982, 1992, Knudsen *et al* 1984, Andersen *et al* 1988, 1987, 1990, Charlton *et al* 1988, Reading and Ford 1987, Ford and Reading 1988, Vegh 1988, Pedersen and Hvelplund 1989, Heber *et al* 1990, Berg *et al* 1990, Bruch *et al* 1993, Ullrich *et al* 1993, Krishnakumar and Rajgara 1993). The most striking result of these studies has been the strong dependence of the ratio of double to single ionization cross sections on the sign of the projectile's charge. It was found that for projectile energies ranging from 0.5 to 5 MeV amu^{-1} this ratio was about a factor of two higher for e^- and p^- projectiles than for e^+ and p^+ projectiles. Starting with McGuire (1982), several authors have concluded that this is due to the interference between the amplitudes of the following two processes responsible for double ionization. One process involves a direct double collision in which the projectile interacts separately with each target electron to produce double ionization. This has been termed as the two-step 2 (TS2) process. In the second process the projectile interacts with only one of the electrons of a target species and knocks it out of the atom. The double ionization may occur as a follow up of this process because of the initial state correlation between the two electrons before the collision or the final state correlation after the collision. The ejection of the second electron due to the initial state correlation has been termed the 'shake-off' (SO) process and that due to correlation in the final state in which the first ejected electron knocks out the second electron on its way out has been termed two-step 1 (TS1) process. The process TS2 is dominant at lower projectile energies and the processes TS1 and SO are dominant at higher energies. At some intermediate energies both processes become comparable to each other and the interference term between them becomes appreciable. The amplitude for the TS2 process gives a q^4 term in the cross section, where q is the projectile charge, and that due to TS1 and SO gives a term proportional to q^2 . The interference term gives a contribution

to the cross section that is proportional to q^3 . This q^3 dependence shows up as a difference in the cross sections for positively and negatively charged projectiles.

Like He, H_2 is an ideal system for carrying out similar studies. It is also of interest to see how the two-centre structure of H_2 modifies the effects due to electron correlations. The double ionization of H_2 by electrons and protons has been studied by Edwards *et al* (1988, 1989) and effects similar to that in helium have been observed by them. Unfortunately, measurements on the double ionization of H_2 are very tedious due to the requirement of making coincident measurements on the two resulting protons. This resulted in some initial controversy as to the exact magnitude of the double ionization cross sections (Edwards *et al* 1988, 1989, Kossman *et al* 1990) which seems to have been resolved (Edwards *et al* 1990). It has been shown by Edwards *et al* (1990) and Andersen *et al* (1990) that the electron correlation effects in H_2 could be probed by merely comparing the dissociative (i.e. $e^- + H_2 \rightarrow H^+ + H + 2e^-$ and $2H^+ + 3e^-$) and non-dissociative (i.e. $e^- + H_2 \rightarrow H_2^+ + 2e^-$) ionization cross sections. This is under the assumption that almost all the dissociative ionization of H_2 is due to two-electron excitations, and, hence should exhibit effects due to electron correlations. However, the dissociative ionization of H_2 has some contribution due to the single electron process leading to the formation of the ground state of $H_2^+(^2\Sigma_g^+)$ in its vibrational continuum. This is because of the Franck-Condon overlap of neutral H_2 with part of the vibrational continuum of the $H_2^+(^2\Sigma_g^+)$ state. But, as shown below, even in the presence of this single electron excitation contribution, it may be possible to look for the effects due to the electron correlation effects by taking the ratio of dissociative ionization to that of non-dissociative ionization.

In the case of the double ionization of helium, interference effects between the shake-off process and TS2 or that between TS1 and TS2 have been considered as the reason for the observed behaviour of the projectile charge dependence of the ratio of double to single ionization cross sections (Andersen *et al* 1987). In the shake-off and TS1 process, the projectile interacts with only one of the electrons through the perturbation $\Omega = -qe^2/r$, whereas the second electron is ejected as a result of electron-electron interaction. The total transition amplitude for these processes may therefore be written as

$$\tilde{a}_I^{fi} = -qa_I^{fi} \quad (1)$$

where i and f refer to initial and final states and a_I^{fi} is independent of the projectile charge q . The transition amplitude for the TS2 process, where the projectile interacts with both target electrons, may equivalently be written as

$$\tilde{a}_{II}^{fi} = q^2 a_{II}^{fi} \quad (2)$$

where a_{II}^{fi} is independent of q .

At high energies where the electron capture cross section is negligible, the cross section for double ionization can be written as:

$$\begin{aligned} \sigma_D &= \sum_f |\tilde{a}_I^{fi} + \tilde{a}_{II}^{fi}|^2 = q^2 \sum_f |a_I^{fi}|^2 + q^4 \sum_f |a_{II}^{fi}|^2 - q^3 \sum_f (a_I^{fi} a_{II}^{fi*} + a_I^{fi*} a_{II}^{fi}) \\ &= q^2 \sigma_I + q^4 \sigma_{II} - 2q^3 \sigma_{int} \end{aligned} \quad (3)$$

where σ_I and σ_{II} are the cross sections for double ionization as a result of one and two interactions of the projectile with the target electrons, respectively. σ_{int} is the contribution

due to the interference between the two processes. Using the expression for the single ionization cross section in the high velocity limit, based on the Born approximation

$$\sigma_S = A \frac{q^2}{v^2} \ln(\alpha v) \quad (4)$$

we may write the ratio of double to single ionization cross section for helium as,

$$R = \frac{\sigma_S}{\sigma_D} = \frac{q^2 \sigma_I + q^4 \sigma_{II} - 2q^3 \sigma_{int}}{Aq^2 \ln(\alpha v)/v^2} = R_I + q^2 R_{II} - 2q R_{int} \quad (5)$$

where A and α are constants and R_I , R_{II} and R_{int} correspond to the contributions to R from σ_I , σ_{II} and σ_{int} respectively.

As discussed earlier, the double ionization of H_2 leads to the formation of two H^+ ions and hence cannot be distinguished without making coincident measurements due to the presence of H^+ resulting from the dissociation of H_2^+ formed in the vibrational continua. However, if we were to consider the ratio, R^* , of the partial ionization cross section for the formation of H^+ to that of H_2^+ , following the case of He, we could write

$$R^* = R_0 + 2R = R_0 + 2(R_I + q^2 R_{II} - 2q R_{int}) \quad (6)$$

where R_0 corresponds to the contribution from the H^+ coming out of the dissociation of the H_2^+ ions formed in the vibrational continua and R is the ratio of double to single ionization cross section. The factor 2 arises because of the formation of two H^+ ions from the doubly charged molecular ion.

As mentioned earlier, it has been observed in the case of He ionization that the value of R has a strong dependence on the projectile charge in the energy range where the shake-off and two-step mechanisms become comparable to each other (McGuire 1992). Such an effect is expected to be seen even in the value of R^* , provided R_0 is small compared to R . However, in the case of H_2 , the cross sections for the formation of H^+ from the H_2^+ states are about a factor of 10 higher than those formed from the H_2^{2+} (Edwards *et al* 1990). Thus, unless the measurements are carried out with extremely high accuracy, the effects due to the electron correlation in double ionization may be masked out.

Now, if we were to consider all two-electron processes (i.e. double ionization and ionization into excited states) and compare them with the one-electron process leading to the formation of H_2^+ in the ground state, it could be seen that measurements on R^* provide information on the dependence of cross sections on the projectile charge. This is because of the fact that all the doubly-excited H_2 as well as the excited states of H_2^+ formed by the projectile interaction invariably dissociate to give H^+ (Edwards *et al* 1990). Also, the contribution to H^+ from the ground state of H_2^+ is very small (Edwards *et al* 1990). Thus if we were to redefine R in terms of the ratio of two-electron excitation + ionization to that of single ionization,

$$R^* = R_0 + R = R_0 + R_I^* + q^2 R_{II}^* - 2q R_{int}^* \quad (7)$$

R_0 would be very small compared to R as the contribution to dissociative ionization through the ground state of H_2^+ is very small. But even with this small contribution from R_0 , R^* should be able to display the interference effects due to R_{int} . It may be noted that unlike in equation (6), the factor 2 does not appear along with R in equation (7), as the contribution

from double ionization to R is considered negligible compared to single ionization into excited states of H_2^+ which dissociate to give H^+ ions.

Edwards *et al* (1990) have measured the cross sections for the formation of H^+ through individual two-electron excited (including ionized) states in H_2 using electron and proton projectiles in the energy range of 0.35–3.5 MeV amu⁻¹. Their measurements were carried out for H^+ ions of energies greater than 1 eV and originating from the H_2 molecules whose axes were oriented at 90° to the projectile direction. The results showed that R^* was about a factor of 2 higher for electrons as compared to that of protons. Andersen *et al* (1990) made measurements on the cross sections for dissociative and non-dissociative ionization of H_2 using antiprotons as projectiles in the energy range of 0.05 to 2 MeV amu⁻¹. These measurements, which were not very accurate, have been repeated very recently in the energy range of 0.013 to 0.503 MeV amu⁻¹ with higher accuracy (Knudsen 1993). Shah and Gilbody (1982) have measured the non-dissociative and dissociative ionization cross sections for H_2 using protons, alphas and positive ions of Li. However, there have not been very accurate measurements for the dissociative ionization cross sections by electron impact. The only reliable electron impact data which existed so far in the high energy region are those by Rapp *et al* (1965) obtained for the formation of H^+ ions with initial kinetic energy greater than 2.5 eV. These measurements were carried out up to an incident energy of 1 keV. There also existed another set of data by Adamczyk *et al* (1966) which are about a factor of 3 smaller than those by Rapp *et al*. This paucity of electron impact data has been due to the problems in collecting and mass analysing all the ions irrespective of their initial kinetic energies and angular distributions without affecting the incident electron beam. Considering this, we have carried out measurements on the dissociative and non-dissociative ionization cross sections for electron impact on H_2 up to an incident energy of 1 keV. The measurements were carried out using a pulsed electron beam and pulsed ion extraction arrangement in conjunction with a time-of-flight mass spectrometer and the relative flow technique (Krishnakumar and Srivastava 1992).

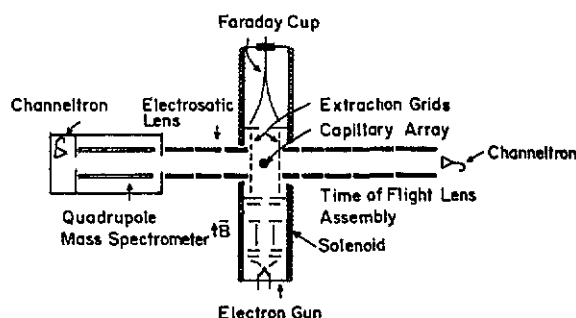


Figure 1. Schematic of the experimental arrangement.

The experimental arrangement is shown in figure 1. The details of the apparatus and method of measurement have been discussed in an earlier paper (Krishnakumar and Srivastava 1992). It consists of a magnetically collimated and pulsed electron gun, a capillary array forming an effusive molecular beam, a pair of extraction grids, a Faraday cup, a quadrupole mass spectrometer and a multi-element time-of-flight (TOF) spectrometer. The measurements reported here were carried out using the TOF spectrometer. Since H^+ ions are produced with kinetic energies up to about 15 eV, extreme care was taken to collect

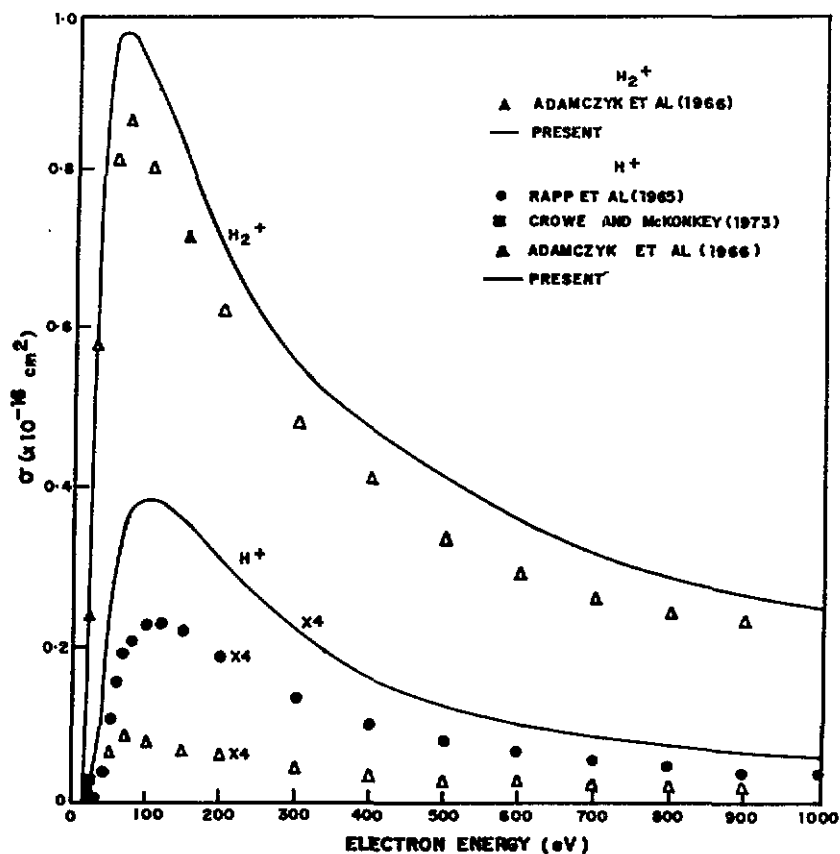


Figure 2. Absolute cross sections for the formation of H^+ and H_2^+ from H_2 .

and detect these ions independent of their initial kinetic energies and angular distributions. For this purpose, it was necessary to have a very high extraction field in the ionization region. In order to prevent this field from adversely affecting the incident electron beam, we used a pulsed electron beam and a pulsed ion extraction method. The pulsing of the two are carried out in such a way that when the electron beam is present in the interaction region, it is at ground potential. Soon after (15–20 ns) the electron beam emerges out of the interaction region, the ion extraction voltages are put on, generating an electric field of 150 V cm^{-1} . The ions thus extracted enter the TOF assembly in the form of a beam with some divergence. The electrostatic lens assembly which constitutes the TOF spectrometer is designed in such a way so as to transport these ions to the channel electron multiplier used as the detector. The TOF spectrum is generated by feeding the amplified detector output and the synchronous pulse from the pulse generator controlling the pulsed electron gun to a time-to-amplitude converter (TAC). The TAC output is fed to a multichannel analyser to obtain the mass spectrum. The excitation function (that is, the intensity of a particular type of ion as a function of the electron energy) is obtained by selecting the particular time range corresponding to that mass peak and storing the ion intensities as a function of the electron energy in a multichannel scaler. This was then normalized by the Faraday cup current to account for any variation in the electron beam current. The normalization of the data to obtain absolute cross sections was carried out using the relative flow technique (Krishnakumar and Srivastava 1988, 1990) using known cross sections for the formation of

singly charged ions from He, Ne, Ar and Kr as the standards.

The uncertainty in our cross section measurement is estimated to be $\pm 15\%$. The major contribution to this is from the uncertainty in the absolute cross section of He^+ from He, which is about 6%, the variation in detection efficiency for H^+ and H_2^+ ions as compared to that of He^+ , and the uncertainties in the flow rate measurements. However, in the case of the ratio of non-dissociative ionization to that of dissociative ionization cross section, the accuracy is expected to be better.

The measured cross sections for the dissociative and non-dissociative ionization are shown in figure 2. As can be seen, our data for H^+ are about 50% higher than those of Rapp *et al* (1965) and about a factor of 4 higher than those of Adamczyk *et al* (1966). The data of Crowe and McConkey (1973) are confined to only the threshold region.

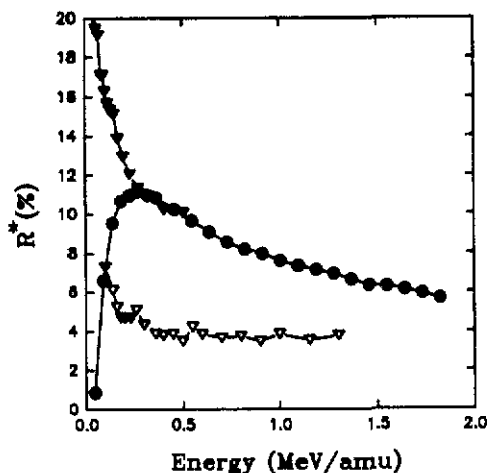


Figure 3. The plot of the ratio, R^* , of dissociative to non-dissociative ionization cross sections for H_2 , plotted against the projectile energy: The full circles represent the present electron impact data, the full inverted triangles represent the antiproton impact data (Knudsen 1993), and the open inverted triangles represent the proton impact data (Shah and Gilbody 1982).

In figure 3 we have plotted the ratio of dissociative to non-dissociative ionization cross sections, R^* , as a function of the incident electron energy in MeV amu^{-1} along with values calculated from the proton impact data by Shah and Gilbody (1982) and the antiproton results by Knudsen (1993). As can be seen, the antiproton data appear to merge very well with the electron impact data, as the projectile energy increases. The most striking behaviour of R^* is that it is a factor of two or more larger for negatively charged projectiles than for positively charged projectiles. This difference seems to be largest at 0.3 MeV amu^{-1} and decreases as the energy rises. This is due to the fact that R^* for proton impact seems to become constant beyond 0.3 MeV amu^{-1} whereas for electron impact it is steadily decreasing. The larger value for R^* for electron impact as compared to proton impact could be explained as due to the interference between the shake-off and two-step processes. This behaviour is similar to that observed in the double ionization of He (Charlton *et al* 1988) as well as that of H_2 (Edwards *et al* 1988). These measurements have also ruled out the possibility that the difference in the electron and proton projectile data is due to the difference in their masses. In the present measurements also we assume that there are no mass dependent

effects. It appears that in the present measurements utilizing electrons we have not been able to reach the high velocity limit where the value of R^* is expected to merge with the proton data. Also, as the interference term is present in both the electron and proton impact cross sections with equal magnitude, one would expect the value of R^* for proton impact to increase and meet that of electron impact midway. However, the presently available proton data are insufficient to test this behaviour. More measurements with various positively and negatively charged particles at higher energies are needed in the future to complete the picture.

Neglecting any contribution to R^* from the dissociation of H_2^+ in its electronic ground state, and using their antiproton data with the proton and alpha particle data of Shah and Gilbody (1982), Andersen *et al* (1990) have calculated R_I^* , R_{II}^* and R_{int}^* at 0.5 MeV amu⁻¹, where R_I^* is the contribution to R^* arising from the shake-off process, R_{II}^* is the term arising from the two-step process and R_{int}^* is that due to the interference term between the two processes. Utilizing the measured values of R^* obtained using e⁻, p⁺ and α particles, it is possible to express R_I^* , R_{II}^* and R_{int}^* , as

$$R_I^* = R_p^* + \frac{1}{3}R_e^* - \frac{1}{3}R_\alpha^* \quad (8)$$

$$R_{II}^* = \frac{1}{6}R_e^* - \frac{1}{2}R_p^* + \frac{1}{3}R_\alpha^* \quad (9)$$

and

$$R_{int}^* = \frac{1}{4}(R_e^* - R_p^*). \quad (10)$$

Using the value of $R_e^* = 0.103$ from the present measurements at 0.5 MeV amu⁻¹ and $R_p^* = 0.0349$ and $R_\alpha^* = 0.068$ obtained from the measurements of Shah and Gilbody (1982), we get $R_I^* = 0.0466$, $R_{II}^* = 0.018$ and $R_{int}^* = 0.017$. This value of R_{int}^* comes to almost 40% of the value calculated by Andersen *et al* (1990). This is very close to the case of ionization excitation of He, thus showing that the interference term in the case of H_2 is almost as important as that in the case of He.

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