Chapter 3

Positron scattering from H_2

In this chapter we introduce and discuss the total cross section measurements on molecular hydrogen (H_2). The work presented here was originally published in Zecca *et al.* (2009b).

3.1 Introduction

Hydrogen is the lightest and most abundant chemical element in the whole Universe. It is present in water and in all organic compounds and living organisms. It is also the main constituent of stars in the main sequence. However, in its most elemental state hydrogen exists in the form of the diatomic molecule H_2, which is a gas at atmospheric pressure and room temperature.

Hydrogen is the simplest atom in nature, so it has often been used as a reference for theoretical models. In quantum mechanics, for instance, the Schrödinger equation has an analytical solution in the case of the hydrogen atom. Molecular hydrogen, as well, is a good target for validation of theory, especially in the field of atomic and molecular collisions. It represents, in many respects, the prototypical species for studying the physical dynamics of lepton diffusion from matter. It contains nearly all the elements that one must address when dealing with the complexities of multicentred targets in scattering computations. Moreover, H_2 has only two bound electrons, so that, at least in principle, its structure may be calculated to relatively high accuracy with present computational resources. Therefore, this particular molecular target, should enable theoreticians to relatively easily test the performance, for example, of the model that they employ in their calculation of the interaction potential. Note that H_2 is a homonuclear diatomic species, which means it is a non-polar molecule. The absence of a permanent dipole moment should noticeably simplify the understanding of the scattering process. In effect, scattering models usually become much more complicated when one tries to incorporate also the lepton interaction with the molecular dipole moment.

Furthermore, understanding low-energy positron and electron scattering from H_2 is the first step towards a deeper understanding of matter and matter-antimatter chemistry, as these are the simplest chemical reactions

involving molecules. High precision experimental data might thus provide new standards for future experimental investigations and be used as a benchmark for theoretical calculations.

Existing TCS measurements of the positron-H_2 system are now quite dated, except for that by Sullivan *et al.* (2001a), which, however, spans a very short interval of positron energies only. As we will see more in detail in Section 3.3, the scatter in the very low energy range between those earlier data (Hoffman *et al.*, 1982; Charlton *et al.*, 1983; Zhou *et al.*, 1997; Deuring *et al.*, 1983) is found to be quite large (see Fig. 3.1). In this chapter we thus present precise TCS measurements for positron scattering from H_2 in the energy range from 0.1 to about 50 eV. At the best of our knowledge, the present data below 1 eV are the very first experimental results for the positron-H_2 system in that energy range. Extending the available TCS data to very low energy might help theoretical colleagues in the development of their models at those very low energies.

3.2 Experimental details

The measurements were performed with the positron spectrometer at University of Trento described in Section 2.1 and by following the standard experimental procedures described in that Section. A high-purity sample of molecular hydrogen (≥99%, Air Liquide) was used for this experiment.

The pressure within the scattering cell, with the H_2 gas routed to it, was in the range 7×10^{-4} - 5×10^{-3} Torr and the readings were performed with the Model 627B capacitance manometer operated at 45 °C. The scattering chamber instead was at room temperature (~24 ± 2 °C). For the calculation of the thermal transpiration correction to the measured pressures a value of 2.9 Å for the H_2 molecular diameter (Dresselhaus *et al.*, 1999) was used in Eqs. (2.18-2.20). The correction to account for this effect was found to be on the order of +2% of the magnitude of the cross section throughout the entire range of the investigated energies.

The magnitude of the axial magnetic field was set to ~11 G during these measurements, except at the three highest energies, when the magnetic field was reduced to ~6 G. The correction for the increased effective positron path length was, therefore, less than +5% and +2.5%, respectively.

A 2 μm-thick nickel moderator was employed in conjunction with the radioactive ^{22}Na isotope, whose activity was nearly 2.3 mCi at the time of these measurements. As a result, the energy resolution of the positron beam in this experiment was ~0.12 eV. Note that the measured TCSs are somewhat smaller in magnitude than the real TCSs owing to the convolution over this finite energy resolution of the beam. Because of the relatively small energy resolution, this effect is expected to be negligible at the higher investigated energies and become important only at the lowest energies, where the energy of the beam is comparable to its energy width.

3.3 Results and discussion

In Table 3.1 we report the present TCSs for positron scattering from H_2 at different energy values in the range from 0.1 to 49.95 eV. The statistical uncertainties of the data are also given in Table 3.1 and are at the ±1 standard deviation level. Those errors are typically smaller than ~5% throughout the entire energy range and amount to ~2.3% on average. We estimate the overall uncertainties on our data to be generally smaller than ~8%, with the largest errors normally being found at the lowest energies.

Table 3.1. The present total cross sections for positron scattering from H_2. The uncertainties represent the statistical components of the overall errors only and are at the one standard deviation level.

Energy	TCS (10^{-20} m^2)		Energy	TCS (10^{-20} m^2)	
(eV)	Average	Error	(eV)	Average	Error
0.10	7.32	0.19	8.95	1.43	0.01
0.15	6.29	0.01	9.45	1.42	0.01
0.20	6.21	0.61	9.95	1.61	0.01
0.25	5.22	0.34	10.45	1.87	0.01
0.35	4.14	0.01	10.95	2.19	0.01
0.45	3.71	0.18	11.95	2.44	0.01
0.55	3.50	0.02	12.95	2.87	0.03
0.65	3.30	0.19	13.95	3.43	0.02
0.75	2.93	0.11	14.95	3.89	0.42
0.85	2.79	0.05	15.95	3.99	0.18
0.95	2.52	0.05	16.95	4.44	0.09
1.05	2.17	0.01	17.95	4.54	0.01
1.25	2.06	0.07	18.95	4.54	0.18
1.45	1.96	0.12	19.95	4.93	0.22
1.85	1.76	0.01	20.95	5.29	0.01
1.95	1.87	0.02	21.95	4.97	0.05
2.05	1.64	0.01	22.95	4.82	0.01
2.25	1.61	0.01	23.95	5.03	0.25
2.45	1.55	0.01	24.95	5.17	0.21
2.95	1.46	0.04	25.95	5.16	0.01
3.95	1.48	0.01	26.85	4.66	0.53
4.95	1.38	0.01	29.95	5.02	0.01
5.95	1.36	0.05	31.95	4.59	0.01
6.95	1.25	0.01	34.85	4.62	0.01
7.95	1.33	0.09	39.95	4.45	0.01
8.25	1.26	0.01	44.95	3.78	0.01
8.65	1.31	0.02	49.95	4.14	0.01

The present TCSs are also plotted in Figs. 3.1 and 3.2, where they are compared with previous experimental measurements and a selection of the theoretical calculations available within the literature, respectively. We

observe in Fig. 3.1 and 3.2 that the present TCS data qualitatively exhibit two distinct trends depending on the incident positron energy. In the energy range between 0.1 and about 9 eV, the magnitude of the TCS decreases monotonically with increasing energy. We noted in Section 3.1 that H_2 is a homonuclear diatomic molecule and, as such, it possesses no permanent dipole moment. This means that the observed general behaviour of the TCS in this first energy region is likely to be due mainly to its small but not insignificant dipole polarisability α = 6.74 a.u. (Cafiero and Adamowicz, 2002).

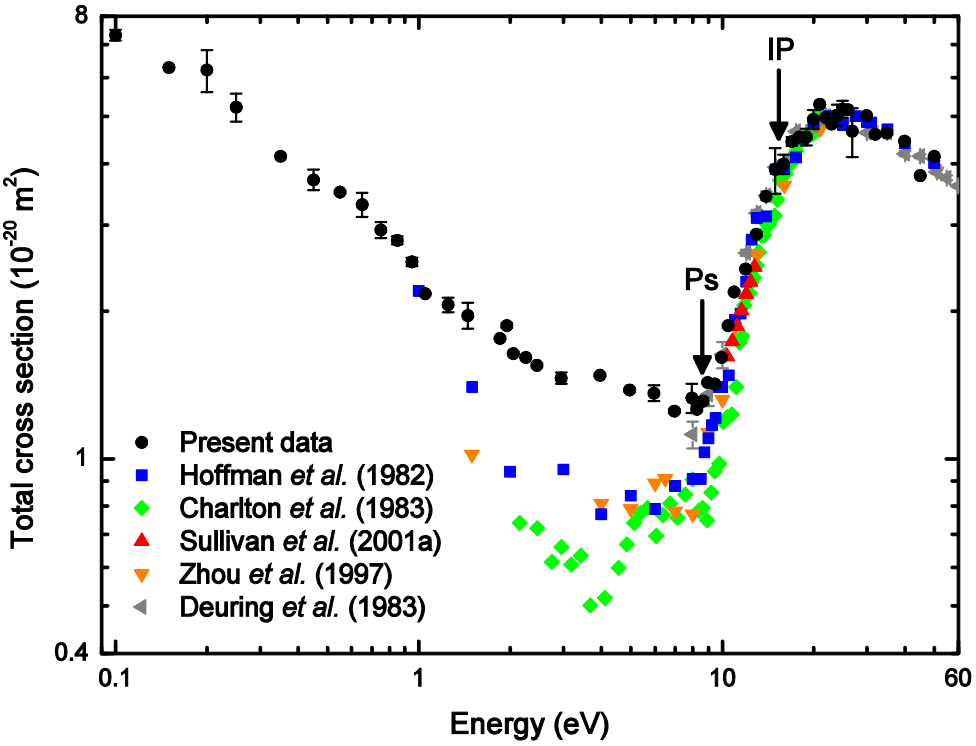

Figure 3.1. The present total cross sections for positron scattering from H_2 are compared with previous experimental measurements. Note that only a fraction of the points from Sullivan *et al.* (2001a) have been included for clarity. Errors bars are marked at each point and represent the statistical components only of the total uncertainties; where the error bars are not visible, they are smaller than the symbol size. The thresholds corresponding to the positronium formation energy and the first ionisation potential are indicated by black arrows labelled "Ps" and "IP" respectively.

There is also a suspicion for some very small structure in our TCS data between about 0.5 and 0.9 eV, probably owing to the opening of the lower-lying vibrational sublevels of the ground electronic state ($v' = 0 \rightarrow 1, 2$). The threshold energy of the first vibrational level in H_2 is about 0.52 eV and owing to the harmonic nature of this system, each higher level, to first order, opens at energies that are integer multiples of that value. However, this

effect on the TCS is rather small here, so that we cannot establish the origin of this small bump in lack of any theoretical support.

At around ~9 eV the TCS starts increasing markedly until it reaches a maximum at around 25 eV, before once again falling in magnitude as the energy increases further. This initial sharp rise in the value of the TCS is associated with the opening of the positronium formation channel followed by the that of the singlet electronic states in H_2 (e.g., the $B^1\Sigma_u$ and $C^1\Pi_u$ states) and finally by the direct ionisation channel at progressively higher energies.

The magnitude of the TCS for H_2 is quite low compared to that of the other molecules previously measured with the same spectrometer (Zecca *et al.*, 2005; 2006a; 2006b; 2007) and also the atomic and molecular species presented in Section 2.1.4 and in the following chapters of this thesis. This is possibly due to one or more of the following reasons. First, H_2 is a non-polar molecule, whereas most of the other targets have a permanent dipole moment. Second, the dipole polarisability of H_2 is smaller than that of all the other targets considered here. Finally, from a semiclassical point of view, molecular hydrogen is by far the smallest species among all the molecules investigated at the University of Trento, including those presented later in this thesis.

The present TCS results can also be used to determine the positronium formation threshold energy (Ps), by seeking at about what energy value the monotonic decrease of the TCS changes slope. From Fig. 3.1 or 3.2 the best estimate for this threshold energy turns out to be 8.4 ± 0.2 eV. As a general rule (Surko *et al.*, 2005), the positronium formation threshold for a given species is given by:

$$\mathrm{Ps} = \mathrm{IP} - 6.8\ \mathrm{eV}, \tag{3.1}$$

where IP is the first ionisation potential. For H_2 we know that IP = 15.4 eV (Herzberg, 1969) and, therefore, Eq. (3.1) provides Ps = 8.6 eV. This value is consistent with the positronium threshold energy we have extracted from the present TCS data.

In Fig. 3.1 the present TCS are also compared to the results from previous experiments. Among previous experimental investigations, the most recent results are the ones by Sullivan *et al*. (2001a), however their measurements were performed only over a very narrow energy range (~2 eV). The measurements by the Bielefeld group (Deuring *et al.*, 1983) focussed only on the high energy region, basically above the positronium formation threshold (8-400 eV). Other available TCS data sets include that of Zhou *et al*. (1997), spanning from 1.5 to 300 eV, the one measured by Charlton *et al*. (1983) over the range from about 2 to 20 eV, and that covering the much larger interval of 1-500 eV by Hoffman *et al*. (1982). Note that the measurements of Zhou *et al*. (1997) and Hoffman *et al*. (1982) both originate from the same group in Detroit. Hence we conclude that the current TCSs include the first very low-energy measurements of positron scattering from H_2, namely for energies below 1 eV.

The agreement of the present data with the earlier experimental measurements is typically very good at energies above 10 eV, i.e. just above the positronium formation threshold, but becomes progressively worse towards the lower energies. There, the TCSs of the different groups exhibit a rather high degree of scatter in their respective magnitudes. This is possibly due to the fact that in the last two decades or so the understanding of the techniques needed to produce stable low-energy positron beams has grown significantly and, in addition, technology developments, such as the availability of higher activity sources, have aided us in realizing these techniques and to put them into practice. The data measured at Detroit by Hoffman *et al*. (1982), together with those at University College by Charlton *et al*. (1983), were among the first measurements of the modern positron scattering era, where measurement difficulties were of increasing importance when going toward low energies. Hence, there is no surprise in finding that the lowest-energy cross sections in that era were measured only down to ~1 eV.

The discrepancy between the present TCSs and the earlier data in the 1-10 eV energy range may be explained, at least in part, in terms of the better experimental reliability of the current measurements performed with the Trento apparatus and because of the need for only relatively small corrections to the measured data due to thermal transpiration and the effective positron path length. The angular discrimination correction is also possibly smaller in the configuration of the Trento spectrometer compared to earlier experimental setups. We know, for instance, that the angular acceptance of the Detroit apparatus is $\Delta\theta \sim 16°$ (Kauppila *et al.*, 1981), while the one of the Trento apparatus is $\Delta\theta \sim 4°$ (see Section 2.1.3.4). So, a large fraction of the observed discrepancy in the TCSs between the present results and the previous data in the 1-10 eV energy region is possibly due to the superior angular discrimination of the apparatus used to gather the present results relative to those employed earlier. Further details on this effect can be found in Sullivan *et al.* (2011).

The four long-range experimental data sets mentioned above (Hoffman *et al*., 1982; Charlton *et al*., 1983; Zhou *et al*., 1997; Deuring *et al.*, 1983) have served as reference for various theoretical models over the years (Armour *et al.*, 1990; Arretche *et al.*, 2006; Danby and Tennyson, 1990; Gibson, 1992; Mukherjee and Sarkar, 2008; Reid *et al.*, 2004; Zhang *et al.*, 2011a). Figure 3.2 shows the present TCSs compared with calculations from the various models aiming at describing the physical process of positron scattering from H_2. The interaction between positrons and matter involves a positive static potential (repulsive short range interaction between the positron and the atomic nucleus) and a negative polarization potential (attractive long range interaction between the positron and the atomic electron cloud) which, to some extent, can be thought of as counter-balancing one another. Comparison of theoretical TCSs with reliable experimental results enables a good evaluation of the quality of the polarization potential that is used in the model. Most of the published theoretical results are available in the energy range from ~0.1 eV to nearly the positronium formation threshold. These include the *R*-matrix calculation

of Danby and Tennyson (1990), the Kohn variational method (KVM) calculation of Armour *et al*. (1990), the distributed positron model (DPM) by Gibson (1992), aiming at treating short-range correlation effects, and the calculation by Reid *et al.* (2004), who employ GAUSSIAN to generate the molecular electronic charge density and use a complex model potential to describe the scattering dynamics. More recently, another calculation at the TCS level using the R-matrix but, this time, incorporating the pseudo-states method has been published by Zhang *et al.* (2011a). Also shown in Fig. 3.2 are the integral elastic cross sections by Arretche *et al.* (2006), using the Schwinger multichannel method (SMC), and those of Mukherjee and Sarkar (2008), which include the rotational and vibrational motion of the target nuclei.

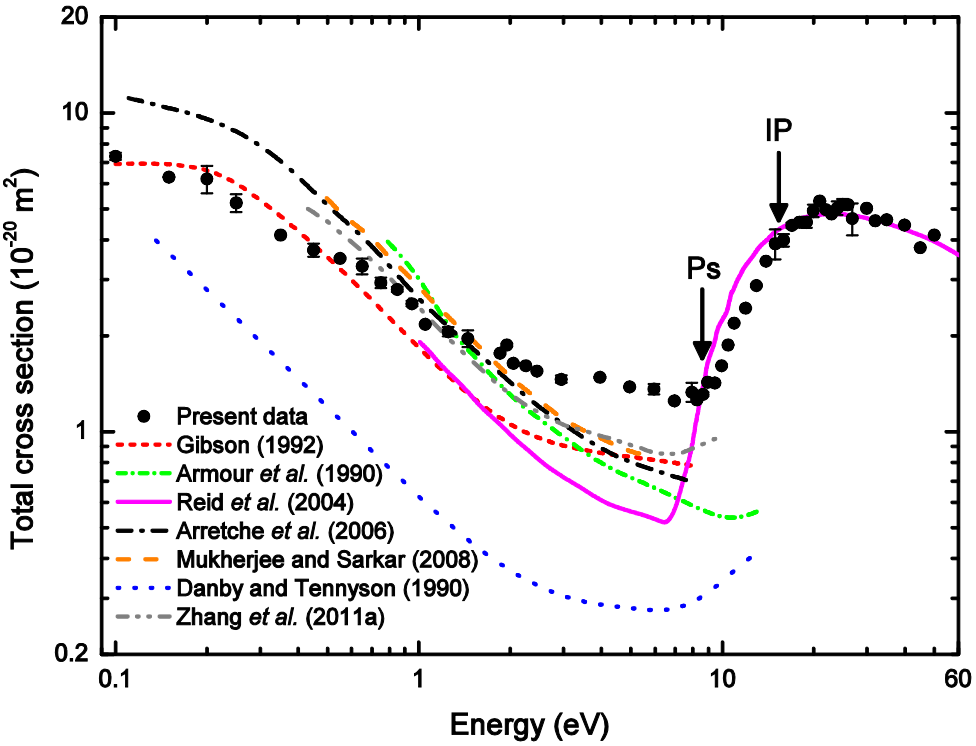

Figure 3.2. The present total cross sections for positron scattering from H_2 are compared with results from theoretical models. Error bars are marked at each point and represent the statistical component of the overall error only; where the error bars are not visible, they are smaller than the symbol size. The black arrows labelled "Ps" and "IP" indicate the thresholds corresponding to the positronium formation energy and the first ionisation potential, respectively.

It is quite clear from Fig. 3.2 that while none of the present theories are able to quantitatively reproduce our TCSs over the entire energy range of the measurements, most at least qualitatively agree with the trend in the measured data at energies below the positronium formation threshold. We note, however, that the computation by Reid *et al.* (2004) is doing a very

good job in reproducing our TCSs, at least above about 10 eV, where it is the only calculation currently available in the literature. It is also clear that further improvements in the present models are still needed to understand and properly model the positron-H_2 collision process, before a good level of quantitative accord between calculation and measurement might be achieved. In this respect, we note the recent theoretical work from Cooper *et al.* (2008), who demonstrated the importance of using an accurate target wave function in variational calculations for positron-H_2 scattering.

Finally, we address criticism made in Zhang *et al.* (2009) of our measurements. Specifically, they noted that our experimental cross section (published in Zecca *et al.*, 2009b) at 0.1 eV was "absolutely incompatible with the present scattering length". This statement failed to account for two very important experimental caveats in our measurements. Firstly, they did not heed our note that the present TCS are uncorrected for forward angle scattering effects which would only increase the TCS magnitudes. Secondly, they did not appreciate that at these low energies the TCSs are actually a convolution over the experimental energy resolution of the positron beam. Again, if corrected for, this would increase the TCS magnitude. It also appears that Zhang *et al.* (2009), in their analysis, did not further appreciate the effect that the uncertainty in the experimental energy calibration would have on the conclusions they drew above. As a consequence, we are confident their view is erroneous and can be ignored.

3.4 Summary and conclusions

We have reported experimental TCS results for positron scattering from H_2, that have been obtained with the apparatus at University of Trento in the energy range between 0.1 and ~50 eV and with an energy resolution of ~0.12 eV. It is the first time that TCSs for this species have been obtained in the lowest energy range (i.e. below ~1 eV), so that a comparison with the theoretical results already available in the literature in that energy range is now feasible. This comparison shows that a further improvement in the positron-H_2 models is required at all energies investigated in the present work. There is agreement, to within the combined error bars, between the present data and previous experimental measurements at energies above ~10 eV. At lower energies, however, the present results tend to be higher in magnitude compared to the earlier data, suggesting that the measurements carried out with the Trento apparatus need to be corrected for a smaller forward angle scattering effect compared to those obtained with the other experimental apparatus.