Chapter 4

Positron scattering from the isoelectronic molecules N_2, CO and C_2H_2

Total cross section results for positron scattering from the isoelectronic species molecular nitrogen (N_2), carbon monoxide (CO) and acetylene (C_2H_2) are presented in this chapter. The results discussed in this chapter have already been published in Zecca *et al.* (2011d).

4.1 Introduction

Two or more molecules are defined as being isoelectronic with each other when they share the same number of electrons or have an equivalent electronic configuration and the same structure, regardless of the particular chemical elements involved. Chemical species that are isoelectronic with each other in general tend to show similar chemical and physical properties.

Isoelectronic molecules represent a group of rather interesting targets in the field of atomic and molecular collisions, where different trends in scattering cross sections from various molecular species are investigated (Brunger and Buckman, 2002). The most interesting feature to examine is whether or not the common total charge of the compounds in this class of molecules is the main driver of the scattering process, despite possible differences in other relevant molecular physico-chemical properties, like the permanent dipole moment and the dipole polarisability, for instance.

There are a few papers in the literature on electron scattering from isoelectronic molecules, that try addressing this point. In the work by Nickel *et al.* (1988), for example, the elastic differential cross sections for N_2 and CO have been measured over a wide range of energies (20-100 eV) and scattering angles (20-120°). They found that the difference in the cross sections between the two molecules is on average smaller than 5% and amounts to about 20% at most. Since N_2 is non-polar, this suggests that the weak dipole moment of the CO molecule plays little role in the scattering dynamics in this energy range. Gibson *et al.* (1996) and Gote and Ehrhardt (1995) later independently confirmed this result with measurements on CO and N_2, respectively. Another study, although focusing on vibrational excitation (0-1) in these molecules at energies between 20 and 50 eV only, was performed by Middleton *et al.* (1992), they found a similar trend to that observed in the elastic channel. Opposed to these findings, quite significant differences were found in very recent measurements of the electronic-state excitation cross sections for electron scattering from the isoelectronic molecules CO_2 (Kawahara *et al.*, 2008) and N_2O (Kawahara *et al.*, 2009). For instance, at an impact energy of 50 eV, the $c\ ^1\Pi$ integral cross section in N_2O is greater in magnitude by a factor of ~1.5 over that for the $^1\Pi_u$ state in CO_2. Similarly, the $D\ ^1\Sigma^+$ ICS in N_2O is greater than the ICS for the CO_2 $^1\Sigma^+_u$ electronic state by a factor of 3.3. Since N_2O and CO_2 both have a linear triatomic structure and similar dipole polarisabilities, Kawahara *et al.* (2009) noted that the observed discrepancy may reflect the fact that N_2O has a permanent dipole moment, although a rather weak one, while CO_2 does not. In addition, at lower energies where shape resonances play an important role in the scattering dynamics, there is little evidence for any striking similarities in the cross sections of isoelectronic species (Brunger and Buckman, 2002).

As regards positron scattering from isoelectronic molecules, there is only one work in the literature that investigated the scattering process from the respective pairs CO and N_2, and N_2O and CO_2 (Kauppila *et al.*, 2004). In that study, total and quasi-elastic differential cross sections were measured for these species and compared for each of the two pairs. The TCSs for each of the isoelectronic pairs were found to be essentially identical above about 5 eV, to within the overall errors on the measured data, while good agreement was found between the shapes of the angular distributions of the two molecular pairs down to energies as low as about 20 eV.

Since the present knowledge about positron scattering from isoelectronic molecules is so limited, in this chapter we report on results of an extensive series of TCS measurements for positron scattering from the isoelectronic species N_2, CO and C_2H_2. As these molecules share the same number of electrons, we would like to search for discrepancies in the TCSs that may reflect the effect of their different physico-chemical properties on the scattering dynamics.

A schematic diagram for the structure of these molecules is shown in Fig. 4.1, and some of their most important physico-chemical properties are summarised in Table 4.1. Each of the three species possesses 14 electrons, while regarding their structure, all three molecules are linear and each contains a triple bond. However, the structure of the carbon monoxide molecule is a little more complicated, as it actually possesses a double covalent bond and a further dative covalent bond. The bond length in CO is 1.128 Å (Lide, 1995), which is also consistent with it having a "partial" triple bond. The CO molecule has a small permanent dipole moment (see Table 4.1), with its negative end based on the carbon atom, notwithstanding that the oxygen atom is larger in size, has a larger formal charge and a greater electronegativity. The reason for the molecular electron density to be higher close to the carbon atom, rather than to the oxygen atom, is basically that the highest occupied molecular orbital (HOMO) in CO has an energy much closer to that of the *p*-orbitals of atomic carbon. Moreover, the electron cloud turns out to be more diffuse owing to the carbon's lower electronegativity, meaning that CO has a larger dipole polarisability and a greater effective annihilation parameter (Z_{eff}) with respect to N_2, for instance (see again Table 4.1). As we will see later on in this chapter and in the next chapters of this thesis, this is an important point, since the target dipole polarisability often turns out to play a significant role, particularly at the lowest incident positron energies, on the positron-molecule scattering dynamics. In this respect, the higher values of α and Z_{eff} for C_2H_2, over those of N_2 and CO (see Table 4.1), are expected to be significant.

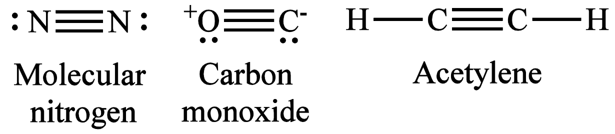

Figure 4.1. Schematic diagram illustrating the Lewis structures for N_2, CO and C_2H_2.

Table 4.1. A selection of the most relevant physico-chemical properties of the isoelectronic molecules N_2, CO and C_2H_2.

Property	**Species**		
	N_2	**CO**	**C_2H_2**
Dipole moment μ (D)		0.122 [a]	
Dipole polarisability α (a.u.)	11.74 [b]	13.09 [c]	22.8 [d,e]
Molecular diameter *D* (Å)	3.75 [f]	3.6 [g]	4.2 [h]
First ionisation potential IP (eV)	15.58	14.01	11.4
Positronium formation energy Ps (eV)	8.78 [i]	7.21 [i]	4.6 [j]
Structure	Linear diatomic	Linear diatomic	Linear polyatomic
Annihilation parameter Z_{eff}	30.5 [k]	38.5 [k]	3160 [k]
Total number of electrons *Z*	14	14	14

References: [a] Muenter (1975), [b] Sun *et al.* (1995), [c] Parker and Pack (1976), [d] Nakagawa (1995), [e] Spackman (1989), [f] Khakoo *et al.* (2008), [g] Skowronek and Alayli (1979), [h] Preining (1998), [i] Marler and Surko (2005), [j] Nishimura and Gianturco (2004), [k] Surko *et al.* (2005).

4.2 Experimental details

The experiments on these three isoelectronic molecules were performed with the positron spectrometer at the University of Trento, by following the procedure described in Section 2.1. Only high-purity N_2 (>99.9%), CO (99.9%) and C_2H_2 (99%) samples were used (BOC Gases) in the respective measurements. We note that the C_2H_2 sample contains a very small amount (< 1%) of acetone contaminant in order to prevent the dissociation of C_2H_2. However, previous independent TCS measurements for positron scattering from acetone, conducted with the same apparatus (Zecca *et al.*, 2010b), indicate that the effect of such a small contaminant on the C_2H_2 TCS will be insignificant.

Readings of the pressure inside the scattering cell for the three isoelectronic molecules ranged between 6×10^{-4} Torr and 3×10^{-3} Torr and were achieved with two different manometers: the 628B model was used for the N_2 measurements, whereas the 627B model was employed for both the CO and C_2H_2 experiments. The two manometers operated at 100 °C and 45 °C, respectively, whereas the scattering chamber was at room temperature (~24 ± 2 °C) during the three experiments. To calculate the thermal transpiration correction to the pressures measured by the two manometers we used the following molecular diameter values in Eqs. (2.18-2.20): 3.75 Å for N_2 (Khakoo *et al.*, 2008), 3.6 Å for CO (Skowronek and Alayli, 1979) and 4.2 Å for C_2H_2 (Preining, 1998). For the N_2 measurements this correction is a maximum of +10%, while for CO and C_2H_2 it amounts to at most +3% of the cross section magnitudes.

The magnitude of the axial magnetic field was ~10 G during the entire N_2 experiment. In the measurements on CO and C_2H_2, the intensity of the magnetic field was enhanced to ~12 G for energy values up to ~40 eV, while it was reduced to ~5 G for measurements above that energy. The correction for the increased effective positron path length L is +5% for the N_2 measurements, while for the CO and C_2H_2 experiments the increase in L was typically 6% below ~40 eV and +2.5% above that energy.

The N_2 measurements were conducted with a 1 μm-thick tungsten moderator, while the CO and C_2H_2 experiments employed a 2 μm-thick nickel moderator. The activity of the radioactive source was nearly 3.9 mCi at the time of the N_2 experiments, while it had decreased to 2.2 mCi when the measurements on CO and C_2H_2 were performed. The energy width of the positron beam with the nickel moderator was ~0.1 eV, and ~0.3 eV when using the tungsten moderator. So, this means that at positron energies below ~0.5 eV the measured TCSs we report are actually a convolution over these finite energy resolutions. This means that our lowest energy TCSs should actually be somewhat higher in magnitude than what we present here, once they were corrected for this effect (see Section 2.1.2.2).

4.3 Results and discussion

The TCS results for the present experiments on N_2, CO and C_2H_2 are listed in Tables 4.2-4.4, respectively. The positron energy range of the present measurements is ~0.1-40 eV for the N_2 experiment, ~0.15-40 eV for the CO work and ~0.15-50 eV for the C_2H_2 study. Tables 4.2-4.4 report also the statistical components of the overall error bars on the TCS data, which are estimated as one standard deviation of the average of the results obtained with many runs performed at the same energy. The statistical errors on the present measurements are usually in the range 1-6% and are about 4% on average for the three experiments. The overall uncertainties on the total cross sections typically span 5-10%.

The present TCS results for N_2, CO and C_2H_2 are also plotted in Figs. 4.2-4.4, respectively, as a function of the incident positron energy. Comparisons with previous experimental investigations and existing theoretical calculations for these molecular targets are also provided in Figs. 4.2-4.4. Finally, in Fig. 4.5 we show the present N_2, CO and C_2H_2 TCS data together in one plot, in order to seek for any differences and similarities in the trends of the cross sections for these isoelectronic species.

4.3.1 Molecular nitrogen

N_2 represents perhaps the prototypical system for investigating the dynamics of lepton scattering from molecules, since it is a quite small and relatively simple molecule, it occurs in nature as an inert gas and it is the most abundant element in the Earth's atmosphere. This is particularly true in the case of electron scattering, as there is now a good number of papers in the literature reporting on cross section data for this species, originating both from experiments and calculations (Brunger and Buckman, 2002). These results are in pretty good agreement with each other, even for the various discrete inelastic scattering channels (Brunger and Buckman, 2002), like electronic excitation (Khakoo *et al.*, 2005; Johnson *et al.*, 2005; Kato *et al.*, 2010b). In these papers very accurate cross section measurements are available, against which results of scattering models may be compared. An important application of the electron-N_2 TCS data is to check for its consistency with the sum of the various partial cross sections for the individual scattering channels that are open. It is therefore fairly reasonable to assume that N_2 might represent a good model for positron collisions as well, particularly with the advent of Penning-Malmberg traps (Surko *et al.*, 2005) for use in scattering experiments.

There are indeed many models in the literature aiming at describing the dynamics of positron scattering from N_2. Calculations are available at both the total (Darewych, 1982; Gillespie and Thompson, 1975; Elza *et al.*, 1989; Danby and Tennyson, 1991) and elastic integral cross section (Armour and Plummer, 1991; Gianturco and Mukherjee, 1997; de Carvalho *et al.*, 2000; Del Valle *et al.*, 2005) level (Fig. 4.2a). Theoretical calculations have then been extended to consider also electronic excited states (Chandhuri *et al.*, 2004; Arretche *et al.*, 2006) and direct ionisation (Campeanu *et al.*, 2004), as relatively new experimental data have become available more recently (Sullivan *et al.*, 2001a; 2001b; Marler and Surko, 2005).

In Fig. 4.2(a) we show the present TCSs for positron scattering from N_2, together with a selection of the theoretical results available in the literature (Darewych, 1982; Gillespie and Thompson, 1975; Elza *et al.*, 1989; Danby and Tennyson, 1991; Gianturco and Mukherjee, 1997; de Carvalho *et al.*, 2000; Del Valle *et al.*, 2005). The numerical values of the present TCSs are reported in Table 4.2, where the statistical uncertainties ($\pm 1\sigma$) are also given. Statistical errors in the N_2 data set are 3.6% on average, and typically lower than about 6.5% throughout the entire energy range of measurements.

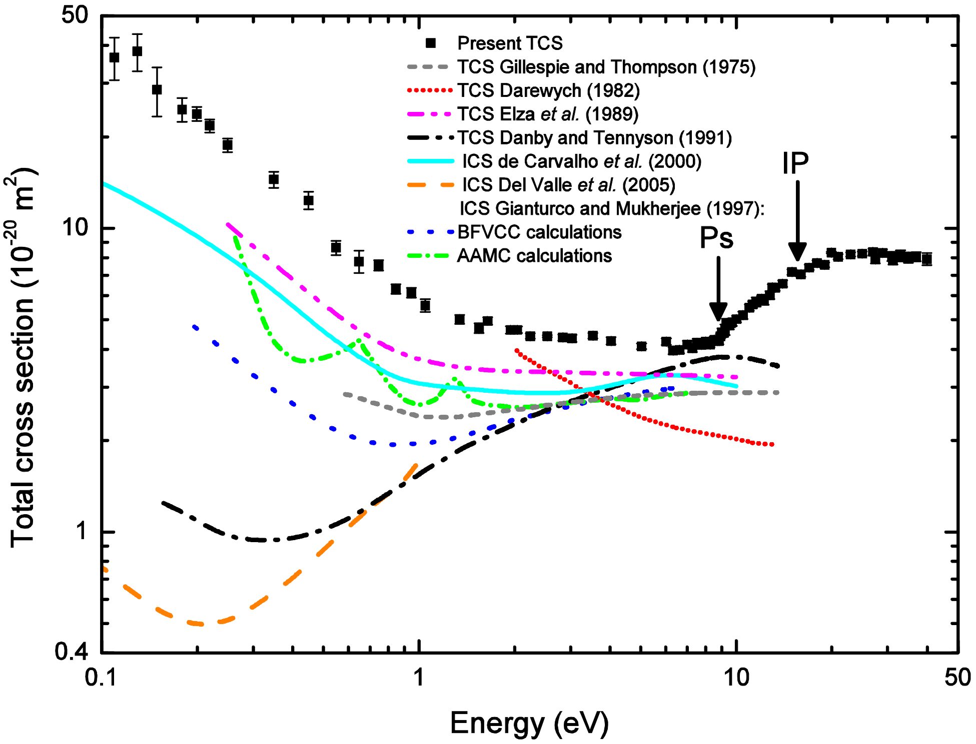

Figure 4.2. (a) The present total cross sections for positron scattering from N_2, compared against theoretical results at the total cross section (TCS) and elastic integral cross section (ICS) level. The errors represent the statistical component only of the total uncertainties on the present TCSs. The thresholds corresponding to the positronium formation energy and the first ionisation potential are indicated by black arrows labelled "Ps" and "IP" respectively.

We clearly note in Fig. 4.2(a) that the level of agreement between the existing theories at the total, but also elastic integral cross section level, is only quite marginal. As none of the theories take into account positronium formation in their model, a fair comparison with the present experimental data can only be made at energies below 8.78 eV (see Table 4.1). Nonetheless, there is a lack of agreement between the magnitude of the present TCSs and those predicted by theoretical calculations even below that energy threshold. If we limit our attention to the shape (i.e. energy dependence) of the cross sections, however, the TCS calculation of Elza *et al.* (1989) and the elastic ICS computation by de Carvalho *et al.* (2000) seem to do a good job at reproducing the trend of the present experimental TCS data below the positronium formation threshold. As we noted in Chapter 3 for positron-H_2 scattering, the level of agreement between theory and experiment generally improves as the quality of the theoretical description of the target-state becomes more physically realistic and accurate. If we pursue this idea, then we may interpret the poor agreement we find in Fig. 4.2(a), between the various computations and our experimental TCSs, as being due to the relatively approximate nature of the respective N_2 target descriptions employed in these earlier calculations.

Table 4.2. The present total cross sections for positron scattering from N_2. The errors represents the statistical components (±1σ) of the overall uncertainties on the total cross sections.

Energy	**TCS (10^{-20} m^2)**		**Energy**	**TCS (10^{-20} m^2)**	
(eV)	**Average**	**Error**	**(eV)**	**Average**	**Error**
0.11	36.85	5.90	8.85	4.29	0.12
0.13	38.56	5.40	8.95	4.44	0.08
0.15	28.84	5.30	9.05	4.57	0.15
0.18	24.79	2.20	9.15	4.55	0.13
0.20	23.98	1.26	9.25	4.67	0.19
0.22	21.90	1.09	9.35	4.87	0.20
0.25	18.92	0.96	9.55	4.87	0.19
0.35	14.59	0.89	9.65	4.91	0.04
0.45	12.45	0.82	9.75	4.94	0.13
0.55	8.70	0.48	10.05	5.06	0.12
0.65	7.83	0.65	10.55	5.21	0.15
0.75	7.62	0.30	11.05	5.52	0.14
0.85	6.36	0.22	11.30	5.65	0.15
0.95	6.18	0.23	11.60	5.76	0.20
1.05	5.61	0.27	12.05	5.91	0.13
1.35	5.06	0.17	12.30	5.83	0.19
1.55	4.73	0.17	12.80	6.06	0.18
1.65	4.99	0.14	13.05	6.44	0.15
1.95	4.66	0.13	13.30	6.43	0.16
2.05	4.66	0.12	14.05	6.62	0.16
2.25	4.45	0.09	15.05	7.23	0.14
2.55	4.44	0.04	16.05	7.10	0.13
2.85	4.40	0.10	17.05	7.48	0.15
3.05	4.37	0.12	18.05	7.75	0.14
3.55	4.47	0.09	19.05	7.63	0.13
4.05	4.29	0.12	20.05	8.37	0.05
5.05	4.11	0.09	21.05	8.10	0.15
6.05	4.26	0.10	23.05	8.25	0.12
6.35	3.99	0.11	25.05	8.30	0.15
6.65	4.01	0.11	27.05	8.42	0.20
7.05	4.17	0.12	27.55	7.96	0.23
7.30	4.06	0.12	29.05	8.36	0.22
7.55	4.23	0.13	31.05	8.14	0.29
7.80	4.16	0.09	31.30	7.94	0.30
8.05	4.27	0.08	33.05	8.16	0.34
8.30	4.18	0.10	35.05	8.07	0.32
8.35	4.27	0.09	37.05	8.11	0.28
8.55	4.32	0.11	40.05	7.99	0.36
8.75	4.29	0.10			

The first measurements of positron scattering from N_2 aimed at measuring the TCS (Sullivan *et al.*, 2001a; Hoffman *et al.*, 1982; Charlton *et al.*, 1983; Sueoka and Hamada, 1993). The differential cross section data by Przybyla *et al.* (1999) represent an exception in this sense. It is only in more recent times that ICS for positronium formation (Marler and Surko, 2005; Leslie *et al.*, 2002), electronic excitation states (Sullivan *et al.*, 2001a; 2001b; Marler and Surko, 2005) and direct ionisation (Marler and Surko, 2005) have been reported (Surko *et al.*, 2005). The agreement between the TCSs measured in the experiments performed so far (Sullivan *et al.*, 2001a; Hoffman *et al.*, 1982; Charlton *et al.*, 1983; Sueoka and Hamada, 1993) is only fair, so that in general the agreement between experimental data and theoretical calculations for positron scattering from N_2 is not particularly satisfactory (see Figs. 4.2a, 4.2b).

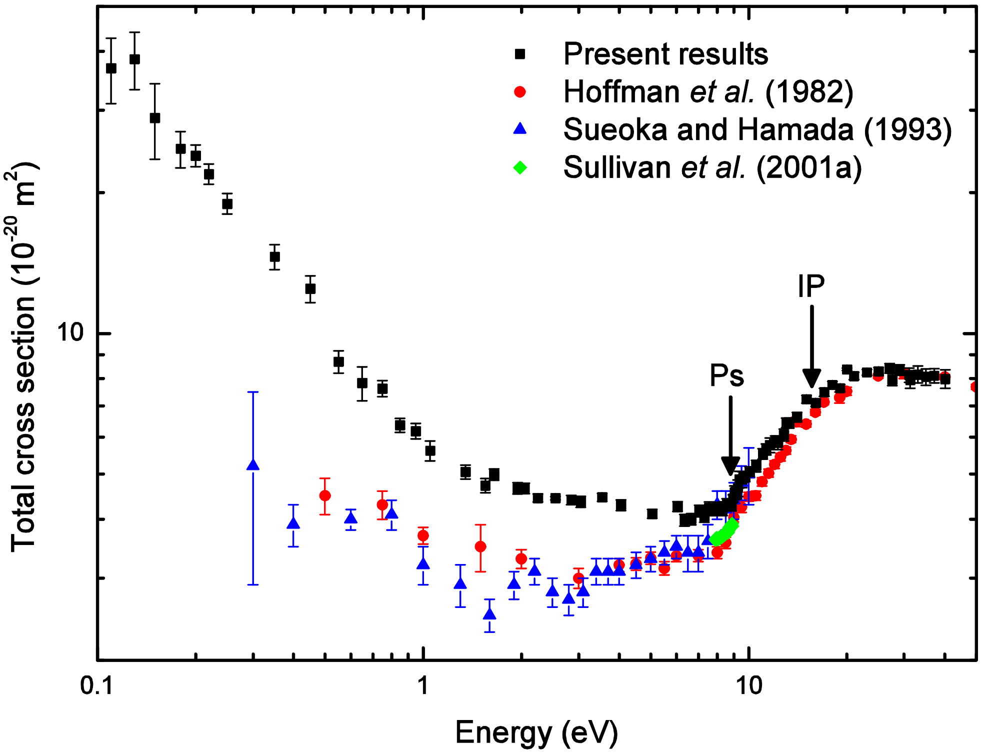

Figure 4.2. (b) The present total cross sections for positron scattering from N_2, compared against previous experimental results. The shown uncertainties are at the statistical level only (±1σ). The black arrows labelled "Ps" and "IP" indicate the threshold energies of the positronium formation energy and the first ionisation potential, respectively.

Fig. 4.2(b) shows a comparison between the present N_2 TCSs and the previous experimental investigations (Sullivan *et al.*, 2001a; Hoffman *et al.*, 1982; Sueoka and Hamada, 1993). Note that the data from Sullivan *et al.* (2001a) are available in a very narrow energy range of a few eV only. We can see that, for energies higher than ~9 eV (i.e. above the positronium formation energy of N_2), the present data are in very good agreement with the previous experimental results, both in terms of the shape and magnitude of the TCS, to within the combined total errors on the various data sets.

Below that energy threshold, however, the agreement with Hoffman *et al.* (1982) and Sueoka and Hamada (1993) vanishes and the discrepancy becomes progressively worse at lower energies. We think that the origin of this divergence can be traced back to the different angular discriminations of the apparatus used for the respective measurements. The present apparatus has, in fact, a superior angular resolution compared to that of both Sueoka and Hamada (1993) and Hoffman *et al.* (1982). The angular acceptance of the Trento apparatus, in fact, is $\Delta\theta \sim 4°$ (see Section 2.1.3.4), while those of the Yamaguchi and Detroit spectrometers are ≈7° (Makochekanwa, 2010, private communication) and ≈16° (Kauppila *et al.*, 1981), respectively. Note also that the angular discrimination effect is energy dependent (again see Section 2.1.3.4) and that it is noticeably higher at lower energies (below ~10 eV) with respect to higher energies (above ~10 eV) (see Table 2.5). This means that the forward angle scattering correction to the measured TCSs will possibly be larger in those earlier studies, compared to the present one, and greater at the lower energies.

Finally, if we closely compare the present data with that of Hoffman *et al.* (1982) in the energy region above 10 eV, there is a suggestion of a slight error in the energy calibration in the experiment of Hoffman *et al.* (1982). This assertion is based on the observation that if their TCS data are shifted by about -1 eV, then they seem to agree better with the present data.

4.3.2 Carbon monoxide

Positron collisions with CO have been quite extensively studied, both from an experimental as well as a theoretical perspective. Previous experimental investigations of the scattering TCS (Fig. 4.3), include the linear transmission measurements of Kwan *et al.* (1983), Sueoka and Mori (1984) and Sueoka and Hamada (1993), and those of Sullivan *et al.* (2001b) obtained with a Penning-Malmberg trap-based apparatus.

There are also quite a few computations for the positron-CO system (Fig. 4.3). However, all of them are restricted to the elastic ICS level, and they generally cover the energy range below the positronium formation threshold only. These include the model-potential calculations reported by Jain (1986; 1990a) and Gianturco *et al.* (1997), while an R-matrix computation was performed by Tennyson and Morgan (1987). The most recent theoretical results available in the literature are due to Arretche *et al.* (2008), who employed the iterative Schwinger variational method in their calculations.

The present TCS results are plotted in Fig. 4.3, together with all earlier experimental measurements and a selection of the scattering model results. The numerical data of the present TCSs are reported in Table 4.3, together with the statistical deviation (±1σ) from the average. The TCS data for CO have a statistical uncertainty which is usually smaller than 5.8% and is about 4% on average.

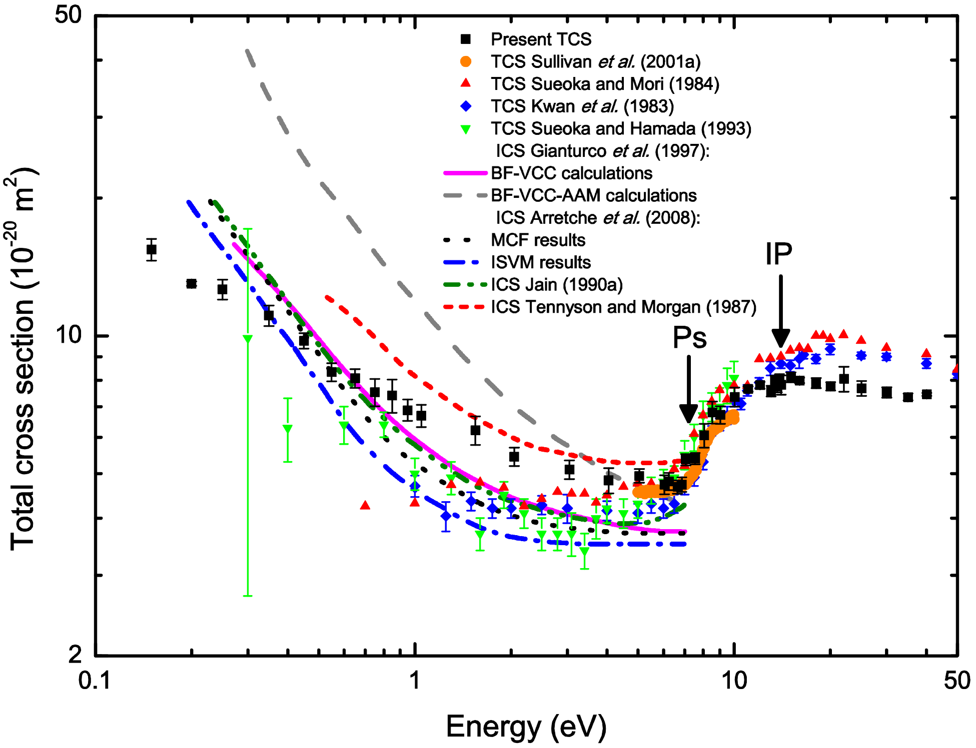

Figure 4.3. The present total cross sections for positron scattering from CO compared against previous experimental results and available computations. Shown are only the statistical uncertainties on the present TCSs at the one standard deviation level. The threshold energies corresponding to the positronium formation energy and the first ionisation potential are indicated by black arrows labelled "Ps" and "IP" respectively.

If we have a closer look at the experimental results reported in Fig. 4.3, we note a similar pattern to that previously discussed for N_2 (see Section 4.3.1. and Fig. 4.2b). That is, we find a good quantitative agreement between all the measurements above some energy value, about 4 eV in this case, to within the combined statistical uncertainties on the data. The present data are in particularly good accord with those by Sullivan *et al.* (2001a), though the latter cover the energy range from 5 to 10 eV only. While the present TCSs seem to be systematically a little lower in magnitude than those of Kwan *et al.* (1983) and Sueoka and Mori (1984), particularly above ~15 eV, in reality they are still in agreement with them if we account for the overall rather than statistical uncertainty of each data set. Below about 4 eV, however, the present TCS data are higher in magnitude than those of Kwan *et al.* (1983), Sueoka and Mori (1984) and Sueoka and Hamada (1993) and lie outside the combined error bars of the respective data sets. This may be again due to the different forward angular scattering effects affecting the various experiments, such that the correction for it is not as severe in this case compared to the others (Kwan *et al.*, 1983; Sueoka and Mori, 1984; Sueoka and Hamada, 1993). In fact, as we noted for the N_2 measurements, the present apparatus has a superior angular discrimination compared to that of the other experiments (Kwan *et al.*, 1983; Sueoka and Mori, 1984;

Sueoka and Hamada, 1993). Nevertheless, all the measurements available below ~4 eV appear to exhibit at least a similar energy trend.

Table 4.3. The present positron-CO total cross sections together with the corresponding statistical errors at the one standard deviation level.

Energy	TCS (10^{-20} m^2)		Energy	TCS (10^{-20} m^2)	
(eV)	Average	Error	(eV)	Average	Error
0.15	15.43	0.83	7.55	5.39	0.15
0.20	12.99	0.14	8.05	6.06	0.36
0.25	12.64	0.62	8.55	6.80	0.37
0.35	11.07	0.57	9.05	6.72	0.30
0.45	9.76	0.38	10.05	7.36	0.35
0.55	8.33	0.38	11.05	7.65	0.11
0.65	8.07	0.38	12.05	7.80	0.14
0.75	7.53	0.52	13.05	7.57	0.21
0.85	7.40	0.62	13.45	7.98	0.21
0.95	6.88	0.37	13.65	7.75	0.23
1.05	6.69	0.37	13.85	8.05	0.19
1.55	6.22	0.45	14.05	7.81	0.38
2.05	5.45	0.25	15.05	8.11	0.20
3.05	5.10	0.24	16.05	7.98	0.11
4.05	4.84	0.31	18.05	7.88	0.20
5.05	4.94	0.17	20.05	7.76	0.16
6.05	4.73	0.23	22.05	8.05	0.50
6.25	4.81	0.21	25.05	7.68	0.28
6.65	4.68	0.16	30.05	7.52	0.19
6.85	4.73	0.17	35.05	7.35	0.13
7.05	5.36	0.15	40.05	7.45	0.05

When looking at the theoretical results for the positron-CO system in Fig. 4.3, it appears somewhat astonishing that almost all the elastic ICS calculations (Jain, 1986; 1990a; Gianturco *et al.*, 1997; Tennyson and Morgan, 1987; Arretche *et al.*, 2008) are able to reproduce fairly well the available experimental data. In effect, the computations appear to be giving a much more physical description of the positron scattering process from CO, as compared to N_2 (Fig. 4.2a), even if we do not really comprehend the theoretical rationale for this to be the case. Below the positronium formation threshold of CO (see Table 4.1), all theories exhibit a similar energy trend, which is also in fair qualitative accord with the experimental data. Among the available models, perhaps the elastic ICS calculations of Tennyson and Morgan (1987) quantitatively best describe the present TCS energy dependence. Note that the elastic ICS of Tennyson and Morgan (1987) and the BFVCC-AAM model of Gianturco *et al.* (1997) are higher in magnitude than the present TCS, which is clearly unphysical. Nevertheless, if we recall that our TCSs are not corrected for forward angle scattering effects and that they are actually convoluted over the finite energy resolution of our positron beam, then the present measured TCS should increase in magnitude once accounting for these effects. Both corrections are expected to be important particularly at the lowest energies. If the present TCS were corrected for these effects, the level of agreement with at least the R-matrix results might then become rather good. Nonetheless, it is clear that further theoretical improvements for this scattering system are still required, both above the positronium threshold, in order to produce also TCS results, and at energies below that threshold.

4.3.3 Acetylene

In Table 4.4 we list the present TCSs for positron scattering from acetylene. The statistical uncertainties on the data are also provided in Table 4.4 and are estimated as ±1 standard deviation of the average. The C_2H_2 TCS results show statistical errors that amount to 3.8% on average and are generally lower than 6%. These data are also plotted in Fig. 4.4, along with the only previous experimental determination from Sueoka and Mori (1989) and the computations by Occhigrossi and Gianturco (2003), de Carvalho *et al.* (2003), Franz *et al.* (2008) and Zhang *et al.* (2011b). We note, however, that none of these theories include a model for positronium formation, so that they cover only the energy range below ~5 eV (see Table 4.1) and are limited to the elastic ICS level.

It is clear from Fig. 4.4 that the present data are in quite good agreement with those from Sueoka and Mori (1989) over the common energy range, except perhaps near the positronium formation threshold, where the present TCS suggests a rather more marked opening of that channel than found by Sueoka and Mori (1989). This difference is possibly due to the poorer energy resolution of the apparatus used in the experiment of Sueoka and Mori (1989) compared to the Trento spectrometer. This observation suggests that measurements by the ANU group (Makochekanwa *et al.*, 2009) or the San Diego group (Surko *et al.*, 2005), who can directly measure the positronium formation cross section and with better energy resolution, might be very useful in the case of acetylene.

The available elastic ICS calculations by de Carvalho *et al.* (2003) and Franz *et al.* (2008) do quite a good job in reproducing the magnitude and energy trend of both experimental TCSs, at least for energies down to about 1 eV (see Fig. 4.4). Below that energy the present TCS turns out to be somewhat lower in magnitude than the elastic ICS predicted by those models. As for CO, this apparent physical inconsistency is likely due to the present TCS data being uncorrected for forward angle scattering (see Section 2.1.3.4) and also being convoluted over the finite energy resolution of the positron beam (see Section 2.1.2.2). As we noted above, this physically means that the present TCSs should somewhat increase in magnitude, once they are corrected for these effects, especially at the lowest energies. Nonetheless, this discrepancy might also reflect limitations in those scattering models. The elastic ICS results by Occhigrossi and Gianturco (2003) and Zhang *et al.* (2011b) are, instead, lower in magnitude than the experimental data and appear to reproduce the present TCS only qualitatively, i.e. in shape. However, these two calculations tend to become higher in magnitude compared to our data below 0.5 eV and 0.2 eV, respectively, similar to the other aforementioned models.

Table 4.4. The present total cross sections for positron scattering from C_2H_2. The statistical uncertainties (±1σ) are also given.

Energy	**TCS (10^{-20} m^2)**		**Energy**	**TCS (10^{-20} m^2)**	
(eV)	**Average**	**Error**	**(eV)**	**Average**	**Error**
0.15	81.92	2.07	11.05	17.12	0.87
0.25	67.43	2.43	11.45	16.22	0.53
0.35	58.83	1.47	11.65	15.96	0.19
0.45	51.53	1.41	11.85	16.50	0.49
0.55	46.81	0.30	11.95	17.25	0.70
0.65	45.67	0.35	12.05	16.56	0.79
0.75	41.28	2.80	12.55	16.54	0.67
0.85	39.45	1.38	13.05	15.70	0.64
0.95	36.88	1.44	14.05	16.45	0.43
1.05	35.81	0.51	15.05	15.97	0.47
1.25	34.54	1.01	16.05	16.28	0.23
1.45	29.64	1.95	17.05	15.30	0.44
1.95	24.58	1.30	18.05	15.10	0.17
2.05	24.21	0.40	19.05	15.46	0.54
3.05	19.76	1.10	20.05	15.14	0.21
4.05	18.59	1.13	22.05	15.16	0.11
4.55	20.75	0.08	25.05	15.08	0.80
4.65	22.36	1.50	26.05	14.22	0.55
4.85	22.20	1.68	27.05	14.14	0.77
5.05	18.58	1.31	28.05	14.44	0.18
5.55	21.64	1.10	29.05	13.97	0.07
6.05	19.26	1.32	30.05	14.13	0.41
7.05	18.50	1.99	31.05	13.36	0.66
8.05	17.40	1.01	33.05	13.83	0.63
9.05	16.45	0.51	34.05	13.24	0.26
9.35	16.00	0.35	34.95	13.08	0.83
9.65	17.20	0.59	37.05	13.21	0.67
10.05	16.72	0.72	40.05	13.50	0.78
10.25	17.14	0.80	50.05	12.53	0.80
10.45	16.65	0.23			

Among the various models, we note that the Density Functional Theory (DFT) computation employed by Franz *et al.* (2008) matches very well with both their own scaled R-matrix results and the Schwinger method calculation of de Carvalho *et al.* (2003). Ignoring the question as to whether or not DFT functionals are a physical representation for “orbitals”, there is ample evidence from electron momentum spectroscopy literature (Brunger and Adcock, 2002) suggesting that DFT-based computations provide a very accurate description for the measured triple differential cross sections and, at the same time, allow a saving of CPU-time. Thus the extension of this approach, as done by Franz *et al.* (2008), to electron and positron elastic and discrete excitation scattering processes represents a notable theoretical advancement.

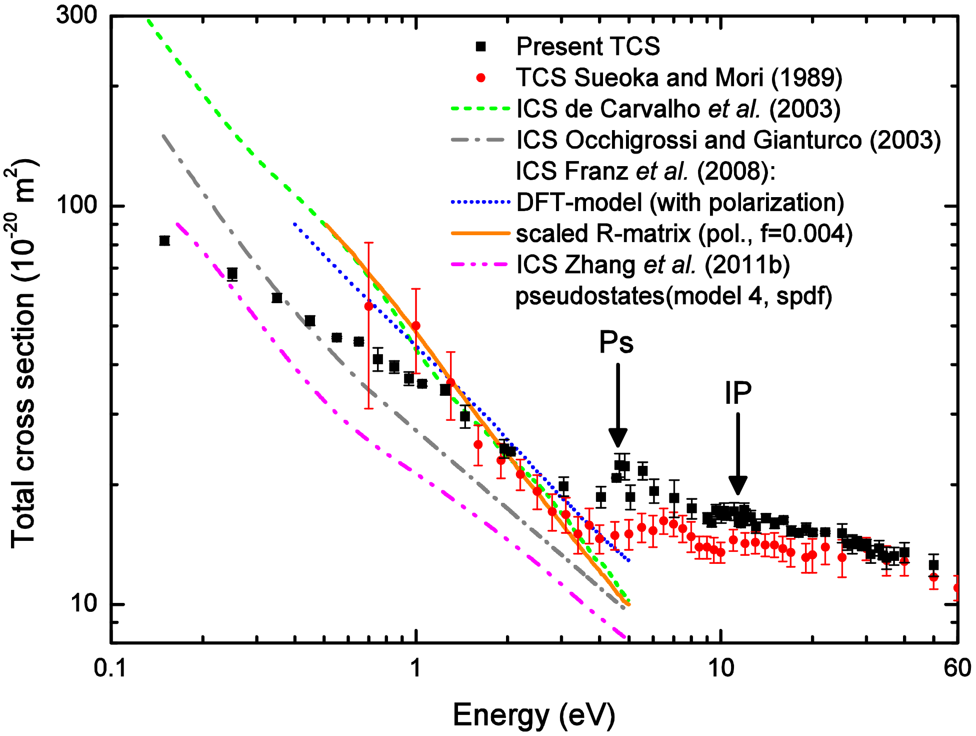

Figure 4.4. The present total cross sections for positron scattering from C_2H_2 compared against previous experimental results and theoretical elastic integral cross sections. The uncertainties shown here are only at the statistical level (±1σ). Black arrows labelled “Ps” and “IP” appear in correspondence to the positronium formation threshold energy and the first ionisation potential, respectively.

4.4 Comparison of the isoelectronic molecules

In Fig. 4.5 we finally compare the TCSs for each of the isoelectronic molecules N_2, CO and C_2H_2. It is clear from this picture that, given a number of electrons Z, it is the nature of the molecular bonding in the species that ultimately determines the extent of the scattering interaction. The magnitude of the TCS for C_2H_2 is visibly larger than that of both N_2 and CO throughout the entire energy range of the present measurements. This can be interpreted as a result of C_2H_2 having a more diffuse electron cloud, which is supported by its relatively larger values of α and Z_{eff} (see Table 4.1).

Although the bonding in the CO and N_2 molecules is quite similar, their TCS only tends to almost the same value at just above ~20 eV. Note that this result is consistent with the observation made previously by Kauppila *et al.* (2004). Below ~20 eV, however, their TCSs are very different, with the positronium formation inception being more marked in the case of CO relative to N_2. Opposite to what one might expect from N_2 having a smaller dipole polarisability than CO and N_2 being non-polar (see Table 4.1), the magnitude of the TCS for N_2 is larger than that of CO at very low energies (less than ~0.6 eV). However, this observation may simply be an artefact of the CO TCSs needing a relatively larger correction to account for the forward angle scattering effect, as compared to N_2 (Sullivan *et al.*, 2011). This would be the case, for instance, if the angular distribution of CO was more peaked at low scattering angles compared to N_2 in the very low energy range, as the TCS data for the two molecules were measured with the same apparatus (i.e. the angular discrimination is essentially equal for both measurements). However DCSs for the two molecules are not available, so that this assertion cannot be checked yet.

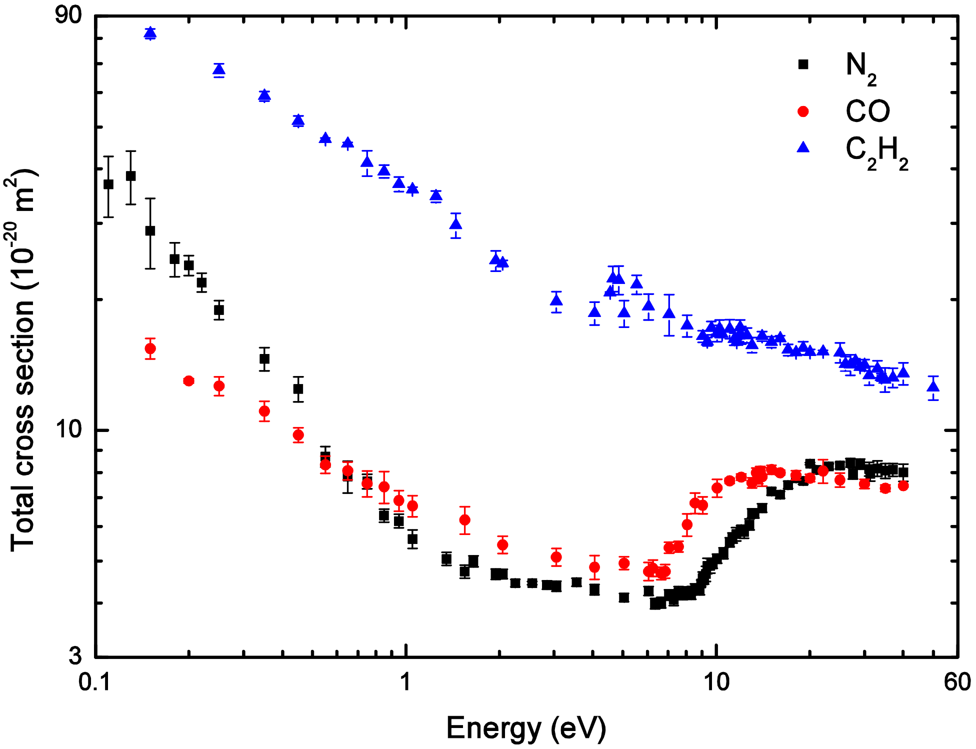

Figure 4.5. The present total cross sections for positron scattering from the isoelectronic molecules N_2, CO and C_2H_2. The errors include the statistical uncertainty components (±1σ) of the overall error only.

The final comparative observation we make is that below the positronium formation threshold for C_2H_2, the energy trend of the TCS for C_2H_2 and CO are almost identical. This suggests to us that the common element in these two molecules, namely the carbon atom, might also be playing some role in those respective scattering processes.

4.5 Summary and conclusions

In this chapter we have reported on a comprehensive series of TCS measurements for positron scattering from the isoelectronic species N_2, CO and C_2H_2. In each case, the present measurements were compared against the corresponding results from previous experimental studies and theoretical investigations. For N_2 and CO the agreement with previous data was found to be limited to relatively higher positron impact energies, while for C_2H_2 good agreement with the only other available results was observed across almost the entire common energy range. We believe that the low-energy disagreement between the various data sets is likely to stem from the different corrections required to account for forward angle scattering effects. With respect to theory, the accord with the present data is in general marginal and only qualitative (i.e. in shape). Further progress toward the explicit inclusion of the positronium formation channel into the calculations, for instance, would certainly help improving the accord. Finally, the present work clearly indicates the key role played by the nature of the bonding in the target species, in the scattering process. Indeed, in this respect, the positron appears to be a more sensitive probe than the electron.