

Chapter 5

Positron scattering from the primary alcohols methanol and ethanol

In this chapter we report on the present total cross section results for positron scattering from two primary alcohols, methanol and ethanol. The data presented in this chapter have been published in Zecca *et al.* (2008b) and Brunger *et al.* (2009).

5.1 Introduction

The study of lepton scattering from primary alcohols has recently gained some attention in the research area of atomic and molecular collisions (Brunger *et al.*, 2009). This is primarily due to a growing interest within the scientific community in investigating electron and positron collisions with biological molecules. The paper by Surdutovich *et al.*, 2008 provides a very good description of the main reasons for examining positron scattering from biomolecules and we return to this theme more in detail in the next chapter. However, the interest of the scientific community is not restricted to biological molecules only, but also to other molecules that are still relevant from a biological perspective, although cannot be strictly considered as biomolecules. This is the case, for instance, of the primary alcohols, like methanol and ethanol. In fact, the primary alcohol group $-\text{CH}_2\text{-OH}$ is contained in the ribose and deoxyribose sugars, which can bind to the nucleobases to form nucleosides. Through the chemical reactions that take place in the cell, nucleosides can then eventually turn into nucleotides, which are the molecular building-blocks of the nucleic acids DNA and RNA.

In addition, for the further development of positron-molecule scattering theory, cross sections for smaller molecules, that are now computationally treatable, are required to better test the validity of the approximations in those calculations. Two smaller but polar species, like methanol and ethanol, thus represent prototypes towards achieving that goal.

In chemistry, methanol and ethanol are both classified as primary alcohols (Tarendash, 2001). A primary alcohol is an organic compound with a hydroxyl radical ($-\text{OH}$) connected to a carbon atom (i.e. an alcohol), which, in turn, is bound to at least two hydrogen atoms (i.e. a primary carbon). In other words, it is a molecule containing a “ $-\text{CH}_2\text{OH}$ ” group (Tarendash, 2001). The molecular formula of methanol is CH_3OH (see Fig. 5.1). In this species a hydroxyl functional ($-\text{OH}$) is attached to a methyl group ($-\text{CH}_3$) through a single bond between the oxygen and the carbon atom of the respective groups. Hence, methanol represents the simplest alcohol. At room temperature it is a polar but volatile liquid (see Table 5.1). The most common alcohol, though, is ethanol. Its molecular formula is $\text{C}_2\text{H}_5\text{OH}$ and its structure is a straight chain (see Fig. 5.1): the carbon atom of the methyl functional ($-\text{CH}_3$) is bound to the carbon of the methylene group ($-\text{CH}_2-$), which, in turn, is attached to the oxygen atom of the hydroxyl radical ($-\text{OH}$). The physico-chemical properties of ethanol (see Table 5.1) are mainly due to its hydroxyl group, being able to participate in hydrogen bonding. In effect, many of the chemical reactions concerning ethanol involve the hydroxyl group of the molecule. Ethanol is a light and volatile liquid at room temperature.

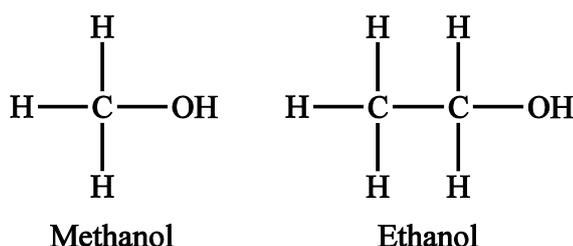


Figure 5.1. Schematic diagrams of the structures of the primary alcohols methanol and ethanol.

Table 5.1. A selection of the most important physico-chemical properties of the primary alcohols methanol and ethanol.

Property	Methanol	Ethanol
Molecular diameter D (Å)	4.1 ^a	5.2 ^a
Dipole moment μ (D)	1.70 ^b	1.69 ^c
Dipole polarisability α (a.u.)	22.13 ^d	35.50 ^d
First ionization potential IP (eV)	10.84 ± 0.10 ^c	10.48 ± 0.10 ^c
Positronium formation energy Ps (eV)	4.04 ± 0.10	3.68 ± 0.10

References: ^a Van der Bruggen *et al.* (1999), ^b NIST, ^c Weast (1977), ^d Lima and Bettega (2008, private communication).

In the present context of scattering of charged particles from molecules, it is important to note that, in general, it is the hydroxyl group of the alcohol species that makes the molecule polar. Both methanol and ethanol, indeed, have a large permanent dipole moment and a significant dipole

polarisability (see Table 5.1). Therefore in the physical dynamics of the positron-methanol and positron-ethanol collisions, we expect the long-range dipole interaction to dominate over the short-range static interaction between the projectile and the target.

In the remainder of this chapter we present TCS results for low-energy positron scattering from the primary alcohols methanol and ethanol. These species have been extensively investigated both from a theoretical and experimental perspective with low energy (1-100 eV) electrons as probes. Khakoo *et al.*, 2008 reports an overview of the extensive series of measurements and calculations for elastic electron scattering from methanol and ethanol. When using positrons as probes, however, the situation is rather different. There appears to be only one experimental work on methanol presently available in the literature (Kimura *et al.*, 2000), while, to the best of our knowledge, the present positron-ethanol measurements are original. There are currently no existing theoretical results against which we can compare the present TCSs for both methanol and ethanol.

5.2 Experimental details

The experiments on methanol and ethanol were conducted with the positron spectrometer at the University of Trento by following the practices described in Section 2.1. All the data were initially gathered for methanol and, after the sample source was changed, corresponding data for ethanol were recorded. High-purity (99.9% in each case, Aldrich) methanol and ethanol target samples were used throughout our studies. We note that, since methanol and ethanol are polar gases, they may stick on the surfaces of the gas handling sections of the apparatus, scattering cell and vacuum chamber (Khakoo *et al.*, 2008). Nevertheless, this matter was not found to be a problem during the measurements on both species.

The pressure measurements inside the scattering cell were taken with the 627B model barometer (operating temperature 45 °C) and were typically between 5×10^{-4} Torr and 1×10^{-3} Torr. The temperature of the target gas in the scattering cell was nearly the same as that of the room in which the measurements were undertaken ($\sim 25 \pm 2$ °C). To calculate the thermal transpiration correction to the pressure readings with Eq. (2.15), we used the following estimates of the molecular hard sphere diameters: 4.1 Å for methanol and 5.2 Å for ethanol (Van der Bruggen *et al.*, 1999). This correction turned out to be less than $\sim +2\%$ on the magnitude of the cross sections on both methanol and ethanol.

Throughout the whole time of the measurements on the two primary alcohols, the magnitude of the focussing axial magnetic field present in the scattering region was kept at ~ 8 -10 G. The correction for the effective positron path increase caused by the gyration of the positrons in the scattering cell was typically $\sim 5\%$ or less.

Finally, we note that the measurements on the primary alcohols were undertaken by employing a 1 μm -thick tungsten moderator and were performed at a time when the radioactive source activity was approximately

3.8 mCi. The energy width of the moderated positron beam was ~ 0.3 eV for both experiments. We remind the reader that this implies that at positron energies below ~ 0.5 eV the measured TCSs are actually a convolution over this energy resolution. This physically means that the present TCSs at very low energy should somewhat increase in magnitude, if corrected for this effect (see Section 2.1.2.2).

5.3 Results and discussion

In Tables 5.2 and 5.3 we report the data sets of the present TCSs for positron scattering from the two primary alcohols methanol and ethanol, respectively. The energy range of the measurements on both alcohols is 0.1-40 eV. Note that the statistical errors on the data are calculated as ± 1 standard deviation of the average of the results of many measurements made at the same energy. The statistical component of the total error is generally found to range between about 0.5% and 6.5% throughout the energy range of the measurements on both methanol and ethanol, with an average value of 3.5%. The absolute TCS errors are estimated as the root of the quadratic sum of the contributing errors. On both our methanol and ethanol data these are typically in the range 5-9% with the larger errors occurring only at the lowest energies.

Table 5.2. The present total cross sections for positron scattering from methanol. The uncertainties represent the statistical components of the overall errors only and are at the one standard deviation level.

Energy (eV)	TCS (10^{-20} m ²)		Energy (eV)	TCS (10^{-20} m ²)	
	Average	Error		Average	Error
0.10	184.03	12.30	7.00	17.09	0.23
0.15	152.01	21.23	8.00	15.83	0.24
0.20	129.03	15.15	9.00	15.56	0.32
0.25	119.76	4.11	9.50	15.42	0.22
0.30	112.08	6.20	10.50	15.13	0.37
0.40	86.91	4.66	12.00	14.78	0.69
0.50	75.82	3.24	13.00	14.51	0.30
0.60	74.24	4.86	14.00	14.34	0.40
0.70	69.87	3.05	15.00	14.00	0.37
0.80	61.97	4.47	16.00	14.25	0.06
0.90	60.39	2.67	17.00	14.17	0.66
1.00	57.01	1.37	18.50	14.34	0.10
1.30	45.39	0.15	20.00	13.73	0.77
1.60	38.73	2.38	22.50	14.00	0.57
2.00	32.39	1.02	25.00	14.19	0.43
2.50	28.50	0.30	27.50	13.24	0.29
3.00	24.16	0.30	30.00	13.44	0.19
4.00	20.48	0.66	35.00	13.32	0.48
5.00	18.75	1.52	40.00	12.84	0.05
6.00	17.34	0.05			

Table 5.3. The present total cross sections for positron scattering from ethanol. The statistical uncertainties ($\pm 1\sigma$) of the TCSs are also provided.

Energy (eV)	TCS (10^{-20} m^2)		Energy (eV)	TCS (10^{-20} m^2)	
	Average	Error		Average	Error
0.10	218.70	14.35	7.00	23.84	0.44
0.15	189.38	19.51	8.00	23.14	0.48
0.20	146.36	12.12	9.00	22.99	0.41
0.25	142.94	2.55	10.50	21.73	0.68
0.30	134.32	15.74	11.00	20.42	0.09
0.40	108.03	6.13	12.00	20.25	0.35
0.50	95.09	2.49	13.00	20.42	0.41
0.60	81.03	0.53	14.00	19.42	0.32
0.70	81.96	5.66	15.00	19.96	0.81
0.80	74.27	3.37	16.00	19.58	0.57
0.90	69.22	4.00	17.00	18.85	1.63
1.00	70.60	0.85	18.50	19.91	0.61
1.30	57.96	1.57	20.00	19.91	0.18
1.60	45.12	1.24	22.50	19.58	0.25
2.00	39.82	1.40	25.00	18.85	0.02
2.50	35.29	3.01	27.50	19.31	0.13
3.00	31.12	0.04	30.00	18.85	0.13
4.00	27.73	1.39	35.00	18.66	0.98
5.00	25.73	0.38	40.00	17.60	0.10
6.00	23.92	0.14			

We compare in Fig. 5.2 the current TCS results for methanol and ethanol. Both TCSs increase significantly with decreasing positron energy and we interpret this behaviour as the effect of the significant permanent dipole moments and dipole polarisabilities of the target species, dominating the scattering dynamics at low energy. In effect we have already observed in our previous investigations on H_2 (Chapter 3) and the isoelectronic molecules N_2 , CO , C_2H_2 (Chapter 4), that below the positronium formation energy the dipole polarisability of the molecule in question plays a major role in the scattering process. In addition, in the previous studies on tetrahydrofuran (Zecca *et al.*, 2005) and water (Zecca *et al.*, 2006a), performed with this same apparatus, and in the measurements on the biomolecules 3-hydroxy-tetrahydrofuran and formic acid that will be presented in Chapter 6, the low energy scattering also seems to be significantly affected by the permanent dipole moment of the molecule in question, with an important contribution from the dipole polarisability of the species.

In this particular case, it is interesting to note that the dipole moments of the two alcohols are very similar, whereas the dipole polarisability of ethanol is larger than that of methanol (see Table 5.1). This latter discrepancy in the dipole polarisability of the two alcohols may explain the apparent outcome in Fig. 5.2, that the low energy ethanol TCSs are uniformly larger in magnitude than the corresponding methanol data.

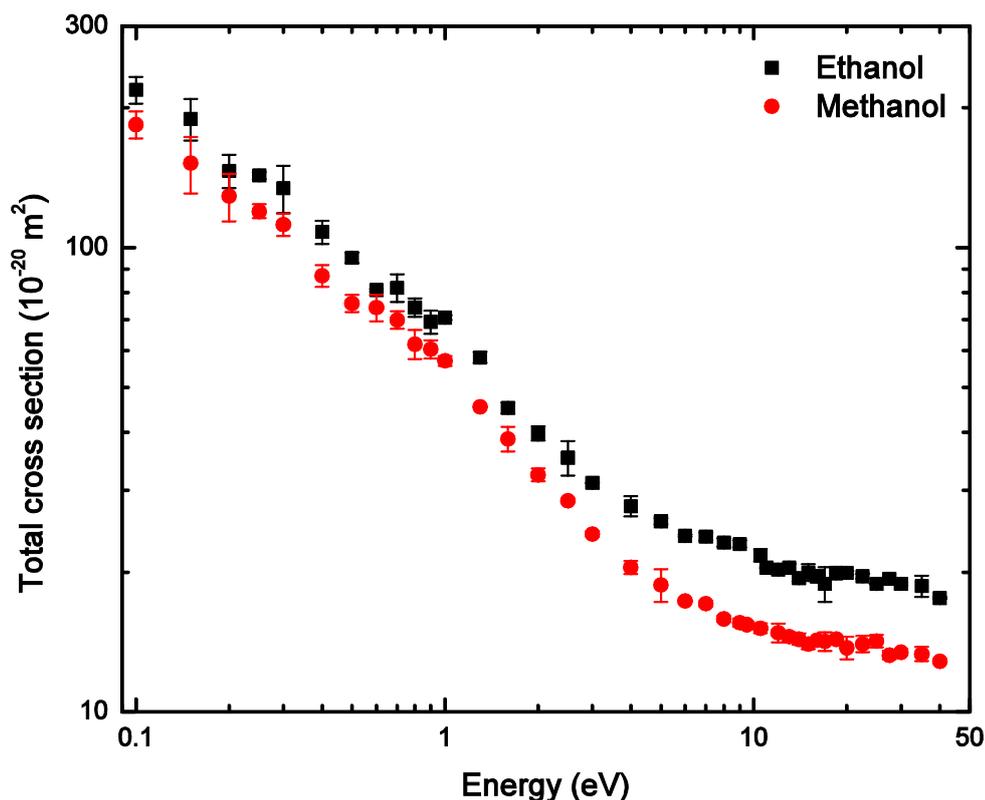


Figure 5.2. The present total cross sections for positron scattering from the primary alcohols methanol and ethanol. The statistical uncertainties ($\pm 1\sigma$) on the TCSs are also shown.

However, some of this low-energy behaviour may also be explained in a semiclassical perspective: the TCS of ethanol is larger than that of methanol, simply because the ethanol molecule is bigger in size compared to the methanol molecule (see Table 5.1), so that the probability of scattering is greater. In fact, the low-energy ratio of the ethanol to methanol TCS (which is almost constant as a function of the energy) interestingly appears to track the square of the ratio of the respective molecular hard-sphere diameters. Nevertheless, we believe that the discrepancy in the low energy magnitude of the TCSs of the two primary alcohols is more likely due to the ethanol possessing a larger dipole polarisability compared to that of methanol. At energies above the positronium formation threshold the interpretation becomes more complicated owing to the fact that more scattering channels start opening.

In Fig. 5.3 we compare the present methanol TCSs and the corresponding results from the only previous experimental investigation by Kimura *et al.* (2000). The data by Kimura *et al.* (2000) range from 0.7 to 600 eV incident energy, however we compare them with the present data set only up to 50 eV energy. We observe a fairly good agreement, to within the combined overall rather than statistical error bars, between the two data sets for common energies greater than about 10 eV. However, this accord gradually disappears towards progressively lower energies, with the TCS of Kimura *et*

al. (2000) being significantly lower in magnitude and showing also a rather different trend in shape compared to the present one. This circumstance is likely to be reflected in the poorer angular resolution of the Yamaguchi University apparatus ($\Delta\theta \sim 7^\circ$; Makochekanwa, 2010, private communication), as compared to the Trento spectrometer ($\Delta\theta \sim 4^\circ$; see Section 2.1.3.4), and may also be due to other deleterious instrumental effects affecting that apparatus. This sort of discrepancy in the low energy TCS has already been observed in the previous studies carried out with the Trento spectrometer on both H_2O (Zecca *et al.*, 2006a) and CO_2 (Zecca *et al.*, 2006b) and also in the present investigations on the isoelectronic molecules N_2 and CO (see Chapter 4), when comparing with the measurements made at Yamaguchi University. Hence, we think that the low energy results (below ~ 10 eV) obtained for any target with the Yamaguchi University apparatus should be treated with caution, unless they have been appropriately corrected for the forward angle scattering effect.

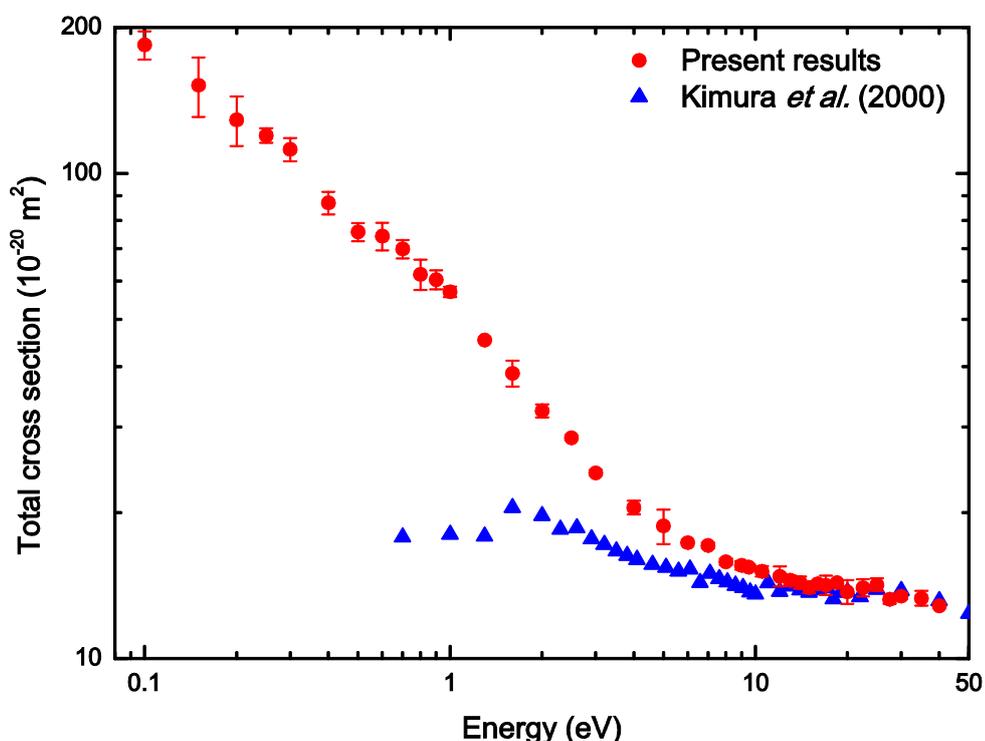


Figure 5.3. The current total cross sections for positron scattering from methanol compared to the previous experimental results by Kimura *et al.* (2000). The error bars represent the statistical components ($\pm 1\sigma$) of the overall uncertainties on the TCSs.

In Fig. 5.2 we have observed how considerably the TCSs of both methanol and ethanol decrease with increasing positron energy at low energy. However, we also note that the monotonic decrease in the TCSs with increasing energy appears to significantly change trend above ~ 4 eV and then again at ~ 10 eV, which correspond approximately to the

positronium formation energy threshold and the first ionisation potential of the two species, respectively (see Table 5.1). In Fig. 5.4(a) and 5.4(b) we attempt an evaluation of the corresponding positronium formation thresholds for methanol and ethanol, respectively, from the present TCS results by tracing, on each log-log plot, lines of best fit in order to highlight at about what energy the monotonic decrease in the TCS with energy changes slope. Owing to the possibly important convolution effect that the finite energy resolution of the present positron beam has on the measured TCS at very low energy, we choose to ignore the first data points in each plot and perform a linear fit of the data in the energy ranges 0.6-3.0 eV and 4.0-20.0 eV. The partitioning between these two energy ranges is selected such as to maximize the correlation factor of the linear analysis on the ethanol data. This analysis yields an estimate of the energy where the TCS changes slope of 4.4 ± 0.3 eV for methanol (Fig. 5.4a) and 3.7 ± 0.3 eV for ethanol (Fig. 5.4b). As the positronium formation energy threshold P_s of a target can be calculated by subtracting the positronium binding energy (6.8 eV) from its first ionisation potential IP (Eq. 3.1), and given the values for the first ionization potentials of the two alcohols reported in f 5.1, we find that $P_s = 4.04 \pm 0.10$ eV for methanol and $P_s = 3.68 \pm 0.10$ eV for ethanol. These values are consistent with those determined from the linear analyses of the TCSs shown in Fig. 5.4, to within the respective error bars, so that we can ascribe the change of the TCSs slope at these energy values to the positronium formation channel becoming open. This is also further evidence for the validity of the positron energy calibration technique for the Trento apparatus that we outlined previously in Section 2.1.

5.4 Summary and conclusions

In this chapter we have reported on low energy TCS measurements for positron scattering from the primary alcohols methanol and ethanol. The effect of the very similar permanent dipole moments and somewhat different dipole polarisabilities of the two species on the magnitude and trend of the TCSs below the positronium formation energy was apparent. The opening of the positronium channel and, subsequently, of the direct ionisation channel were also manifest on the shape of the TCSs: changes in the slope of the TCS were found to occur at energy values that are consistent with the respective energy thresholds of those scattering channels. Comparison with the only other experimental result for the two primary alcohols presently available in the literature, namely the previous investigation on methanol by Kimura *et al.* (2000), shows that the earlier data significantly underestimated the TCS for energies less than about 10 eV. Finally, we note that it would be appropriate if the current theories for electron scattering from methanol and ethanol (Khakoo *et al.*, 2008) were to be extended to the investigation with positrons as the probes, in order to address the existing lack of calculations on these two species.

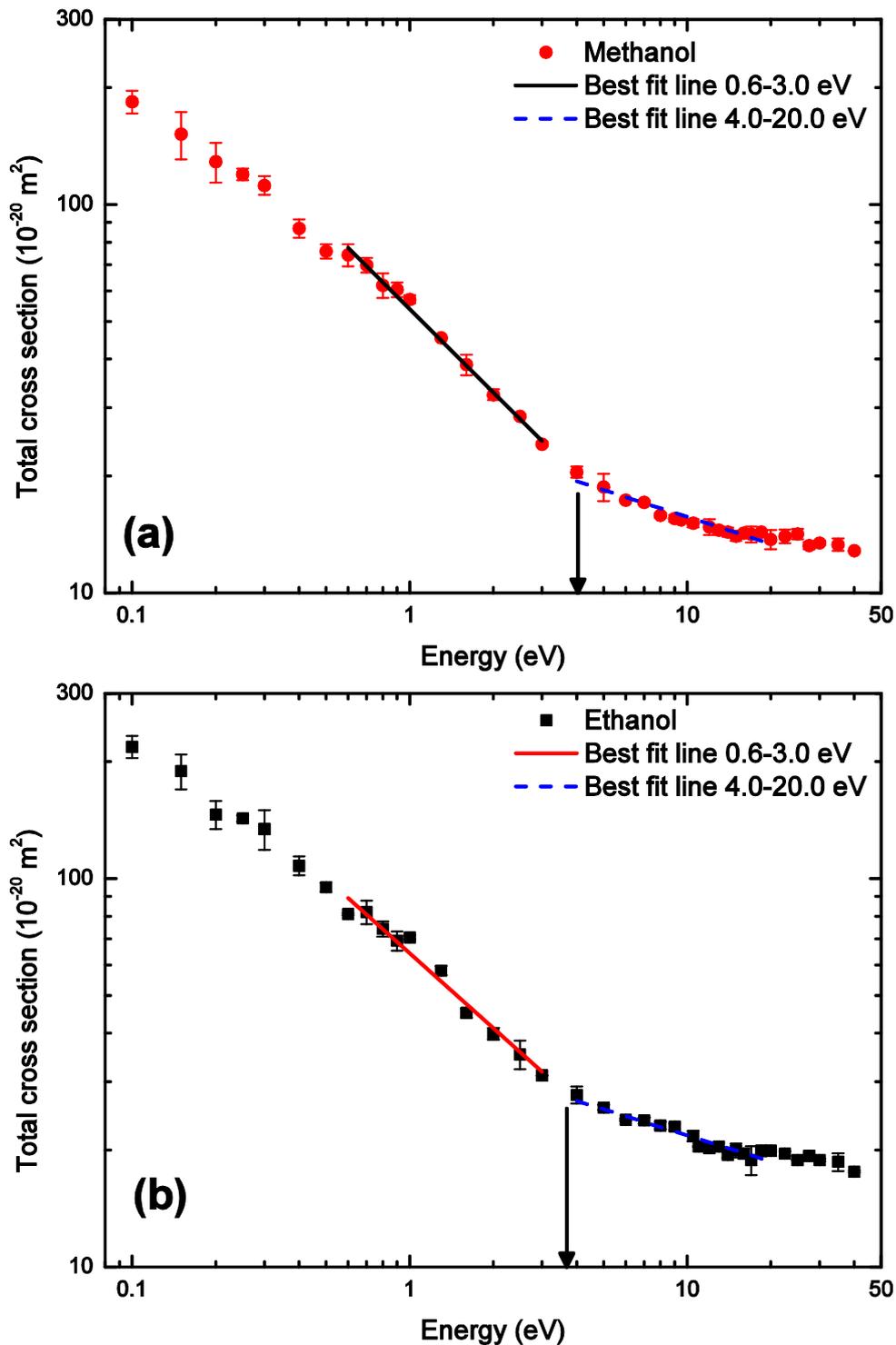


Figure 5.4. The present total cross sections for positron scattering from methanol (a) and ethanol (b) together with lines of best fit for the data points in the energy ranges 0.6-3.0 eV and 4.0-20.0 eV. The vertical arrows indicate the energy value at the intersection between the two lines. Shown also are the statistical uncertainties ($\pm 1\sigma$) on the data.