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Positron scattering from chiral enantiomers

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We report on total cross section measurements for positron scattering from the chiral enantiomers (+)-methyl (*R*)-2-chloropropionate and (–)-methyl (*S*)-2-chloropropionate. The energy range of the present study was 0.1–50 eV, while the energy resolution of our incident positron beam was ~ 0.25 eV (FWHM). As positrons emanating from β decay in radioactive nuclei have a high degree of spin polarization, which persists after moderation, we were particularly interested in probing whether the positron helicity differentiates between the measured total cross sections of the two enantiomers. No major differences were, however, observed. Finally, quantum chemical calculations, using the density functional theory based B3LYP-DGTZVP model within the GAUSSIAN 09 package, were performed as a part of this work in order to assist us in interpreting some aspects of our data.

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I. INTRODUCTION

Polarized positrons (and electrons) have been used in experiments to investigate the hypothesis that biomolecular optical activity might be sensed by the polarization of β particles [1]. Indeed, a large observed effect involving asymmetric formation of triplet positronium in *L*-amino acids versus *D*-amino acids [2] was originally interpreted as possibly being due to positron helicity. However, that interpretation was later shown to be invalid [3] and in fact the original effect could not be reproduced [4]. Nonetheless, there has been much interesting work examining the role that polarized β particles might have played in the origins of biological chirality. These include a dynamical theoretical model from Hegstrom [5] and a series of measurements from Gidley *et al.* [6] where a spin-polarized low-energy positron beam was used to set limits, of 7×10^{-4} for cystine and tryptophan and 31×10^{-4} for leucine, on asymmetric positronium formation in chiral species. An excellent summary of that work from the University of Michigan can also be found in Rich [7]. A somewhat more recent relevant study, on the effect of β radiation on the crystallization of sodium chlorate from water, by Mahurin *et al.* [8] concluded that the polarization of the electrons (in this case) was correlated with the chirality of the crystals being generated. Finally, for completeness, we also note that early work on the origins of biological chirality was also conducted with energetic β particles rather than slow β particles. An example of this work is by Garay [9] and references therein. Much of this earlier work is, however, now quite old and subsequent improvements in positron beam technology can allow us today to make a better test of the hypothesis.

It is well known [10] that when positrons are emitted from radioactive nuclei, as a result of β decay, they possess a high degree of spin polarization (P). It is also well known [11] that after moderation this degree of spin polarization persists, with

a value of $P \approx 0.5$ being reported for a W moderator [11] of the type we employ here. Connecting this together with the availability of high-purity chiral enantiomers, we decided the time was now ripe to revisit the question of whether or not the scattering of polarized positrons will be affected by the chirality of the enantiomers in question. In particular, here we investigate if there are any differences in the total cross sections (TCSs) for low-energy (polarized) positron scattering off the respective chiral enantiomers (+)-methyl (*R*)-2-chloropropionate and (–)-methyl (*S*)-2-chloropropionate ($C_4H_7ClO_2$), see Fig. 1.

There appears to have been no previous experiments performed for either positrons or electrons scattering from (+)-methyl (*R*)-2-chloropropionate (*R*-MCP) or (–)-methyl (*S*)-2-chloropropionate (*S*-MCP). Hence the present positron *R*-MCP and *S*-MCP TCS scattering measurements are original. Note that there are no corresponding theoretical results either for these species. In fact neither could we find any photoelectron spectroscopy (PES) spectra for either molecule, nor were there any Green's function method [12] results available. Indeed the usual abundance of physico-chemical data that is often available in the literature for many species [13], such as the molecular hard sphere diameter or the first ionization potential, seemed to be completely lacking in this case. The only exceptions to this appear to be for the dipole moment (μ) of MCP, where a single experimental value of ~ 2.67 D from Ghosh *et al.* [14] is available, and the dipole polarizability (α) where a calculated value of 72.61 a.u. can be found [15]. Nonetheless, after our experience [13,16–19] for positron scattering from molecules with relatively high permanent dipole moments and large magnitude dipole polarizabilities, this information is valuable as it leads us to expect that the very-low-energy behavior of the TCSs for both species will be strongly peaked in magnitude as you go to progressively lower energies. However, as a consequence of this scarcity in physico-chemical data, we have also performed quantum chemical calculations using *ab initio* restricted Hartree Fock (RHF)-DGTZVP and density functional theory (DFT) based

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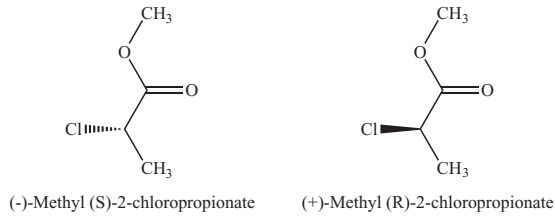


FIG. 1. Schematic diagrams representing the chiral enantiomers investigated in this study.

B3LYP-DGTZVP models within the GAUSSIAN 09 package [20].

In Sec. II, we provide some details of our measurement techniques and analysis procedures, while in Sec. III a brief description of the present quantum chemical computations is given. Thereafter, in Sec. IV, we present and discuss our results. Finally, some conclusions from this investigation will be drawn.

II. EXPERIMENTAL DETAILS

The positron spectrometer at the University of Trento was developed by Zecca and colleagues and has been discussed previously many times (see, for example, [21,22]). We thus do not need to repeat these details again, except to note that a tungsten (W) moderator of thickness $1 \mu\text{m}$ [23] was employed in conjunction with a radioactive ^{22}Na isotope (activity at the time of measurement $\sim 1.1 \text{ mCi}$) and some electrostatic optics in order to produce the positron beam. These optics were originally designed to produce a stable and well-focused (into the scattering cell) positron beam with energies between ~ 0.1 and 50 eV [22]. The operational performance of the Trento spectrometer, over many years now, suggests that these design criteria have been met. In addition we note that it is standard practice in our laboratory, as a check of the validity of our techniques and procedures, to make preliminary validation measurements using targets for which the positron scattering TCSs are considered well known. Such “benchmarked” systems might be drawn from the noble gases [24–26] and molecular nitrogen [22].

The basis of linear transmission experiments is the Beer-Lambert law, as defined by

$$I_1 = I_0 \exp \left[\frac{-(P_1 - P_0) L \sigma}{kT} \right], \quad (1)$$

where I_1 is the positron beam count rate at pressure P_1 , the target gas pressure being measured with it routed to the scattering cell, k is Boltzmann’s constant, and T is the temperature of the target vapor (K), as measured by a calibrated platinum (PT100) resistance thermometer that is in thermal contact with the scattering chamber. In Eq. (1) we also note that σ is the TCS of interest at a given incident positron energy, I_0 is the positron count rate at P_0 , the pressure with the target gas diverted into the vacuum chamber, i.e., away from the scattering cell, and L is the length of the scattering region.

For a physical application of Eq. (1) several crucial precautions should be taken and care must be exercised during the measurements. These considerations include minimizing the double-scattering events and ensuring the TCSs are independent of pressure. In addition, only high-purity sources

of the enantiomers ($>99.0\%$) were used (Sigma Aldrich). The geometrical length of the scattering region is $22.1 \pm 0.1 \text{ mm}$, with apertures of 1.5 mm diameter at both the entrance and exit of the scattering cell. In our application of Eq. (1), the value of L used is always corrected to account for the path increase caused by the gyration of the positrons in the focusing axial magnetic field present in the scattering region. For incident positron energies from 0.1 to 35 eV , $B \approx 11 \text{ G}$ and the value of L increased by $\sim 5.6\%$, while for positron energies between 40 and 50 eV and for S -MCP, $B \approx 12 \text{ G}$, leading to an increase in L of $\sim 6.2\%$. Note that for R -MCP and for positron energies between 40 and 50 eV , $B \approx 4 \text{ G}$, leading to an increase in L of $\sim 2\%$. It is crucial for the energy scale to be calibrated accurately. The zero of the energy scale, in the absence of the target gas, was determined using a retarding potential analysis of the positron beam [27]. Note that an electronic copy of [27] is available on request from the corresponding author of this paper. We believe that the error in our energy scale is $\pm 0.05 \text{ eV}$. The same measurements allow us to evaluate an energy width of the positron beam of $\sim 0.25 \text{ eV}$ (FWHM), with an uncertainty on this determination of at most $\pm 0.05 \text{ eV}$. It is also very important to accurately measure the scattering cell pressure, which we achieve with an MKS 627B capacitance manometer operating at 45°C . As the manometer temperature was different from that for the target gas in the scattering cell ($T = 22 \pm 1^\circ\text{C}$), thermal transpiration corrections to the pressure readings are made using the model of Takaishi and Sensui [28]. Typically, this led to a maximum correction on the TCS of $+3.7\%$.

All linear transmission scattering-cell based experiments invariably have some angular discrimination limitations. They arise from the inability to distinguish between positrons that are elastically scattered at small angles from those in the primary (unscattered) beam and result in the directly measured TCSs being somewhat smaller than the “true” value. The extent of this problem depends on the angular discrimination of the apparatus in question and the nature of the elastic differential scattering cross section (DCS) in this forward angle region ([22] and references therein). From a consideration of the size of the entrance and exit apertures of the present scattering cell, and their separation, the angular acceptance ($\Delta\theta$) of the Trento spectrometer is $\sim 4^\circ$ [22], which compares favorably with that from the Detroit apparatus [29] ($\Delta\theta \approx 16^\circ$) and the Yamaguchi spectrometer ($\Delta\theta \approx 7^\circ$). The gyration of the positrons can also potentially increase the angular discrimination correction compared to the no-field case [30]. Using some of the analytic formulas detailed in Kauppila *et al.* [29], but for the typical conditions of our measurements, estimates of the present energy-dependent angular discrimination varied from $\sim 17^\circ$ at 1 eV to 5.4° at 10 eV positron energy [22]. These can then be used in conjunction with the approach of Hamada and Sueoka [30] to determine the corrections to the TCSs to account for this effect, provided the elastic DCS, at each energy, are known. Unfortunately, no such experimental nor theoretical cross sections are currently available for this task, so that the TCSs we report represent a lower bound on the “true” values for each enantiomer.

All the present data collection and analysis codes were driven by software developed at the University of Trento, for application on a personal computer. The positron energy

range of the present TCS measurements was 0.1–50 eV, with the overall errors on our TCSs estimated as being within the 5%–15% range. Note that the overall uncertainties are formed from the quadrature sum of quantities such as the statistical uncertainties on our data (3.7%–9.8%), the uncertainty in our thermal transpiration corrections, the uncertainty in the value of L , the uncertainty in the value of T , and the uncertainty in the absolute pressure readings ($\sim 0.3\%$), as per the manufacturer’s specification.

Finally we note that the Trento apparatus does not have any contrivance suited for the measurement of positron beam polarization. Therefore, our objective was not to measure the absolute value of the polarization dependency of the cross sections, but rather to make a difference measurement on the two species. We have been aware since the design and construction time of this machine of the similarities with the one of Van House and Zitzewitz [11]. We can assume with a good degree of confidence that the polarization of our beam is possibly close to the one measured in that laboratory. We do not need to know such polarization with a better precision, given the quoted aim of the current investigation.

III. QUANTUM CHEMISTRY CALCULATIONS

Geometry optimizations have been performed for both *S*-MCP and *R*-MCP using quantum mechanical methods, such as RHF-DGTZVP and the hybrid DFT model of B3LYP-DGTZVP [31,32]. The former is for validation purposes and the latter is for a more accurate MCP geometry determination. The DGTZVP basis set due to Godbout *et al.* [33] has proven to be a good basis set for orbital momentum distribution calculations [34,35], which can also be applied to larger molecules [36]. We thus also chose to use it here. The first ionization potentials (IPs) of the enantiomers are calculated

using the outer-valence Green’s function (OVGF) method [12,37–40], combined with the DGTZVP basis set. The geometry (bond angles, bond lengths) for the IPs is based on the optimized geometry using the B3LYP-DGTZVP model, i.e., OVGF-DGTZVP–B3LYP-DGTZVP. Note that all the above electronic and ionization calculations were performed using the GAUSSIAN 09 package [20].

As expected, the models give almost identical total electron energies for each of the enantiomers and identical first ionization potentials for both *S*-MCP and *R*-MCP at 10.66 eV. The calculated spectroscopic pole strengths for the highest occupied molecular orbital of each enantiomer are determined to be 0.91. As this value is greater than 0.85 [12,37–40], it indicates that the independent particle approximation employed is a valid approximation. The RHF-DGTZVP model gives the first IP of MCP as being equal to 11.92 eV, using Koopman’s theorem, which is a little high. That result was not, however, unexpected as RHF-level calculations often overestimate orbital ionization potentials [41]. We note that the present preferred model chemistry gives a total dipole moment for MCP of 2.58 D, which is in good agreement with the available experimental value [14]. The present model also gives a total dipole polarizability of 58.40 a.u., in fair agreement with that from an earlier computation [15], for both enantiomers. At the very least, this latter result confirms that MCP has a dipole polarizability of significant magnitude which is expected to play an important role in the scattering dynamics of these species.

Finally, we note that we employed the MM2 (Minimize Energy Force Field) tool as embedded in the CHEMBIO3D ULTRA 12.0 package [42], to calculate the molecular diameter of both MCP enantiomers to be 6.68 Å. This value was used in our thermal transpiration corrections, as discussed in the preceding section.

TABLE I. Present TCSs ($\times 10^{-20}$ m²) for positron scattering from (+)-methyl (*R*)-2-chloropropionate. The errors given represent the statistical uncertainty component of the overall uncertainty only.

Energy (eV)	TCS (10^{-20} m ²)	TCS error (10^{-20} m ²) ($\pm 1\sigma$)	Energy (eV)	TCS (10^{-20} m ²)	TCS error (10^{-20} m ²) ($\pm 1\sigma$)
0.15	184.74	26.34	2.50	60.30	3.83
0.20	175.29	13.35	3.00	45.40	1.73
0.22	173.31	11.64	4.00	49.25	3.55
0.25	152.38	9.97	5.00	41.26	1.80
0.30	133.60	14.52	7.00	37.13	1.85
0.35	131.38	13.47	9.00	38.19	2.30
0.40	139.44	13.80	10.00	36.58	2.47
0.50	136.13	8.43	12.00	38.02	2.04
0.70	117.58	13.05	15.00	36.03	2.37
1.00	100.93	3.84	17.50	34.79	2.38
1.25	94.16	5.46	20.00	34.46	2.55
1.35	84.85	7.92	25.00	32.23	1.94
1.50	79.56	5.01	30.00	30.04	0.95
1.65	85.10	3.20	35.00	29.46	0.60
1.75	78.93	4.13	40.00	31.02	1.49
1.85	75.22	3.65	45.00	31.20	0.66
2.00	71.54	4.80	50.00	30.49	1.29
2.15	69.10	6.14			

TABLE II. Present TCSs ($\times 10^{-20}$ m²) for positron scattering from (–)-methyl (*S*)-2-chloropropionate. The errors given represent the statistical uncertainty component of the overall uncertainty only.

Energy (eV)	TCS (10^{-20} m ²)	TCS error (10^{-20} m ²) ($\pm 1\sigma$)	Energy (eV)	TCS (10^{-20} m ²)	TCS error (10^{-20} m ²) ($\pm 1\sigma$)
0.10	216.39	23.10	3.00	58.37	5.96
0.15	210.45	12.11	3.50	58.67	6.50
0.20	196.08	20.20	4.00	52.00	7.05
0.22	149.43	4.65	5.00	45.04	5.94
0.25	132.72	6.64	7.00	42.82	3.30
0.30	166.77	12.29	8.00	38.79	3.50
0.40	143.89	14.82	9.00	41.03	4.44
0.50	135.41	11.98	10.00	40.89	3.11
0.70	123.96	9.95	12.00	39.35	1.15
1.00	102.05	5.93	13.50	40.37	1.44
1.25	92.01	4.89	15.00	38.63	3.33
1.35	87.25	6.04	17.50	37.48	1.87
1.50	85.04	3.86	20.00	36.54	2.07
1.65	79.75	5.92	25.00	34.05	1.86
1.75	80.30	4.56	30.00	32.90	1.47
1.85	78.70	4.22	35.00	32.89	1.13
2.00	67.64	4.71	40.00	32.64	1.10
2.25	66.32	0.35	45.00	30.63	0.81
2.50	60.81	3.47	50.00	30.17	1.02

IV. RESULTS AND DISCUSSION

In Tables I and II and Fig. 2, we present our TCS results for positron scattering from the chiral enantiomers (+)-methyl (*R*)-2-chloropropionate and (–)-methyl (*S*)-2-chloropropionate. All the present TCSs are uncorrected for the forward angle scattering effect. It should be immediately apparent from Fig. 2 that there are no other theoretical or experimental TCSs against which we can compare the present positron scattering results. We also note that there are no other electron data against which we might compare to either. Hence the current TCSs are original. Considering now the energy

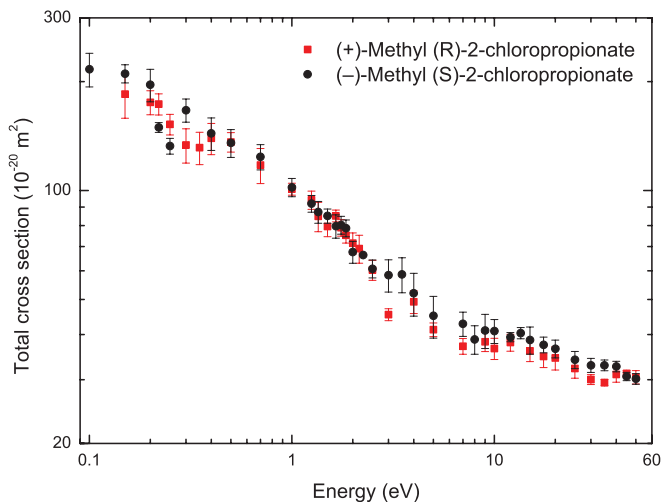


FIG. 2. (Color online) Present measured TCSs ($\times 10^{-20}$ m²) for positron scattering from (+)-methyl (*R*)-2-chloropropionate (filled squares) and (–)-methyl (*S*)-2-chloropropionate (filled circles). Uncertainties plotted are the statistical errors on the data.

dependence of the TCSs for both enantiomers, we see that they are almost identical. Both TCSs rise significantly in magnitude as you go to lower energies which, based on our earlier work with polar polyatomic species [16–19,21,43,44], we believe is indicative for the relatively large dipole moments and the strong magnitude of their dipole polarizabilities that *R*-MCP and *S*-MCP possess. The present TCSs for the *R*-MCP and *S*-MCP enantiomers, at each energy studied, in fact largely appear from Fig. 2 to be identical, to within their errors, in absolute value. We return to this point shortly in more detail.

The magnitude of the present TCSs tends to decrease monotonically in value, as you go to higher incident positron energies, until there is an abrupt change in their slope. This is best illustrated in Figs. 3(a) and 3(b) for *R*-MCP and *S*-MCP, respectively. We had seen in some of our previous studies [16–19,21,43–46] that such a dramatic change in slope can be associated with the opening of the positronium formation channel. As a consequence, we have tried to extract the threshold energy for positronium formation (E_{Ps}) for the two enantiomers with the results of our analysis also being shown in Figs. 3(a) and 3(b). The criteria used in the present analysis was to maximize the slope of the linear fit to a group of points to the left of E_{Ps} (solid line) to that slope for a group of points to the right of E_{Ps} (dashed line). The energy range of these left and right groups of points, to maximize the slope ratio, was found to be the same for both enantiomers (see Fig. 3). Note that TCSs below 0.5 eV were excluded from this analysis, as they suffer relatively more from the effect of our measured TCSs being a convolution over the finite energy resolution of our positron beam (~ 0.25 eV). Further note, this convolution effect tends to lower the magnitude of the TCS from its “true” value. We find that $E_{Ps} = 4.4 \pm 1.2$ eV for *R*-MCP and $E_{Ps} = 4.0 \pm 1.3$ eV for *S*-MCP. In other words,

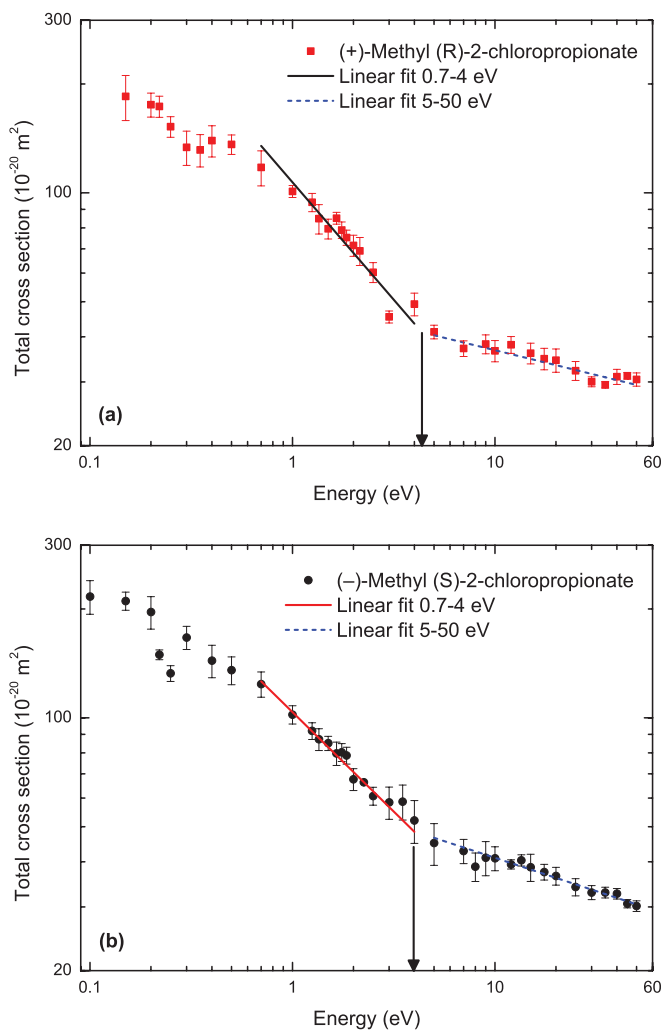


FIG. 3. (Color online) (a). Result from our analysis to determine the positronium formation threshold energy (E_{Ps}) for (+)-methyl (*R*)-2-chloropropionate. A value of $E_{Ps} = 4.4 \pm 1.2$ eV was found. See text for further details. (b) Result from our analysis to determine the positronium formation threshold energy (E_{Ps}) for (-)-methyl (*S*)-2-chloropropionate. A value of $E_{Ps} = 4.0 \pm 1.3$ eV was found. See text for further details.

the values of E_{Ps} that we determine for the two enantiomers are consistent with one another to within the energy uncertainty on our analysis. Taking an average of the above values, we determine $\overline{E_{Ps}} = 4.2 \pm 1.3$ eV. This leads to a value for the first ionization potential of MCP to be $IP \approx 11.0 \pm 1.3$ eV (as $IP = E_{Ps} + 6.8$ eV). That experimental value is in excellent agreement with our OVGf calculation result of 10.66 eV, suggesting in turn that our determination for E_{Ps} is also sound.

We have previously noted, on the basis of Fig. 2, that the TCSs for positron scattering from *R*-MCP and *S*-MCP appear to be identical. To quantify this, in Fig. 4, we plot the percentage difference between the *S*-MCP total cross section and the *R*-MCP total cross section. It is clear from Fig. 4 that at most of the energies considered, this percentage difference is effectively zero to within the uncertainty on the data. Namely, the TCSs for positron scattering from *S*-MCP and *R*-MCP are identical so that the helicity of the

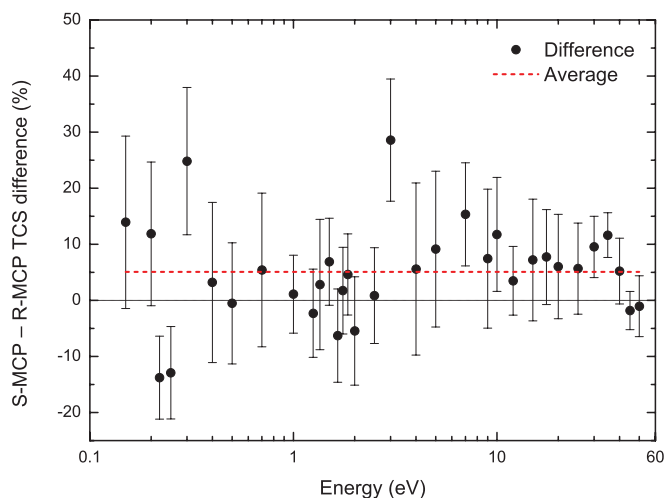


FIG. 4. (Color online) Energy dependence for the percentage (%) difference (filled circles) between the TCSs for positron scattering from *S*-MCP and *R*-MCP. The average percentage difference between them is also plotted (dashed line).

positrons appears to be having no discernible effect on the scattering from the different enantiomers. However, when we also plot the average of those differences, as a dashed red line on Fig. 4, we find that on average the TCS of *S*-MCP is about 5.1% larger than that for *R*-MCP. Of course the error on this average is greater than 5.1%, but nonetheless it would be interesting if a next generation positron spectrometer at, for example, the Australian National University (ANU), was to repeat this experiment. The rationale for this is simple, the spectrometer at ANU has a higher precision (thus smaller uncertainties) capability than the present so that a more accurate determination should in principle be achieved.

V. CONCLUSIONS

We have reported on TCS measurements for positron scattering from the chiral enantiomers *R*-MCP and *S*-MCP. While we could not unequivocally rule out that there was some effect on their TCSs, due to the chirality of the enantiomers when scattering with a polarized positron beam, such an effect would have to be very small. The energy dependence of the present total cross sections was consistent with that expected for polar molecules, with an appreciable dipole moment and dipole polarizability. As a part of this study, we also determined that the positronium formation channel opened at ~ 4.2 eV, leading to a first ionization potential for MCP consistent with that from our OVGf computations (10.66 eV). Calculated values for MCP's dipole moment and dipole polarizability, using quantum mechanical calculations within the GAUSSIAN 09 package, were also fairly consistent with the few corresponding values available in the literature.

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