Similarities and differences between electron and positron scattering from molecules

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Abstract. In this paper a comparative study is carried out between total cross sections (TCS) for electron impact with those for positron impact using both experimental and theoretical procedures. The method used for the measurements is a retarding potential time-of-flight (RP-TOF) while the theoretical procedure is the Continuum Multiple Scattering (CMS) model. The experimental energy range is 0.2 – 1000 eV while that for the CMS is 1.5 – 100 eV. For polar molecules, the increase in TCS observed below 2 eV is expected due to the dipole induced long range interaction that has been observed only for some molecules for electron impact. In the energy range 3 – 60 eV electron TCS are characteristically larger than positron TCS due to resonances in the former. Some peculiar cases have been studied whereby positron TCS become unexpectedly greater than electron TCS at energies below 10 eV. The first Born approximation has been observed to hold for the impact energy region above a few hundred of eV for all molecules studied in this laboratory, albeit with different threshold energies.

1. Introduction
Over the past few years we have investigated and published a lot of research work on the total cross sections for atomic and molecular collisions with electrons and positrons for several gases. The total cross section, for electron or positron collisions, itself includes excitation (electronic, vibrational and rotatoional), ionization, positronium formation and annihilation (for the case of positron collisions), dissociation, and elastic cross sections. It is worth noting that these individual partial cross sections, i.e. excitation, ionization, etc., although existing in both electron and positron scattering, are different in magnitude between these two projectiles, besides being also energy dependent. Most of the differences are observed at energies from zero to about a few hundred eV, wherein various scattering forces are actively at play. Above a few hundred eV, cross sections for electron and positron impact tend to merge suggesting that the Born approximation begins to be valid. It is these differences involved in the scattering between these different projectiles that make the comparative study between them of invaluable importance. With this motivation we have carried out investigations of the scattering of polyatomic molecules with these projectiles over the energy ranges 0.4 – 1000 eV for electron and 0.2 – 1000 eV for positron impact.

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With the development in technology in the second half of the last century, electron partial cross section measurements have been made with large degrees of accuracy. This has led to clearer understanding of electron collision processes, and thus opening up a lot of application possibilities in various industrial fields. Compared to this, the positron impact field has lagged behind due to difficulties associated with the production and control of slow positron beams, despite recent progress made at a few laboratories [1].

Interaction between the electron, or positron, with a molecule consists of three components: electrostatic, exchange and polarization for non-polar molecules. The dipole interaction comes in for polar molecules. It must be noted here that for simplicity of treatment of the potentials involved, the Coulomb interaction is split into two, i.e. static and correlation-polarization (or dipole for polar molecules). The static interaction is the electrostatic interaction between the incident particle and the non-deformed target molecular charge distribution at long range. On the other hand, the correlation–polarization (or dipole) interaction is the result of deformation of the target molecular charge distribution by the approach of an incident electron or positron at a large separation. In fact, when the particle comes sufficiently close to the target charge cloud, the incident particle and the target electrons then correlate strongly with the result that the correlation becomes more complicated, making accurate treatment difficult.

Induced polarization plays a special role in the collision between an electron or positron with a molecule [2]. In the asymptotic (long-range) region, the polarization interaction for the positron-molecule collision system is exactly the same as that for the electron-molecule collision system. As the projectile comes closer to the molecule, the distortion of the molecular charge cloud becomes different for different projectiles. The polarization potential at short to intermediate ranges, particularly its anisotropic part, should be different for the two projectiles. The long-range interaction due to the molecular multipoles is important in the positron molecule collision. The polarization interaction is another example of long-range interaction, but the cumulative effects of the two types of interactions are totally different for the two projectiles, i.e., additive for electron impact and subtractive for positron impact. The effect of polarization and exchange interactions is expected to be large at the low energy range. A comparison of the TCS for positrons with those for electrons gives the difference in the interactions for each molecule. However, it’s not possible to directly derive the magnitude of the interaction, from experimental data, without estimating the magnitude of the cross section due to the resonance phenomena in the low to intermediate energy ranges i.e. the shape and Feshbach resonances. As a matter of fact, in electron scattering, the effect of resonance is very large for most atoms and molecules [3]. However, the effect of the resonance decreases as impact energy increases higher than 30 eV. We can safely assume the resonance effect to be ignorable at energies higher than 50 eV. Although the polarization and exchange interactions decrease with increasing impact energy at higher energies, these interactions however still remain in the neighborhood of 60 eV for most TCS data measured in our laboratory. We assume them to be negligible at energies higher than 100 eV [3,4]. Needless to point out that the extents to which these resonances show up in the TCS are different for electron and positron impact.

In this paper a detailed comparison between the TCS for positron- and electron-molecule collision processes is carried out. The comparison is made on the basis of data for the positron- and electron-molecule collision cross sections studied in this laboratory, i.e. a synthesis from the results of more than 50 molecular targets we have studied over the past two decades. Though some comprehensive reviews have been published on electron-molecule collisions (see for example [5,6]), and a few on positron-molecule collisions [1,7,8], we are not aware of any publications on the comparative study between electron- and positron-polyatomic molecule cross sections, except for our preliminary paper [4] and an earlier publication on diatomic and triatomic molecules [9]. It is worth pointing out here that for some molecules a few detailed studies relevant to this study have been done by other groups covering the investigation of partial cross sections: ionization; vibrational, rotational and electronic excitation; resonance phenomena; dissociative processes; positronium formation and annihilation (in positron scattering); and many other processes. However, although a lot has been achieved in this area

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of partial cross section investigations, because of the difficulties involved in producing low energy positron beams of intensity and resolution high enough for use in some of these measurements, more studies have been carried out mainly for the electron impact experimentally than the positron counterpart.

2. Procedures

2.1. Total cross sections

The total cross sections (TCS) were measured using a linear transmission retarding potential time-of-flight (RP-TOF) method in an apparatus setup similar to our previous measurements [10]. Briefly described, a $^{22}$Na radioisotope with an activity of $\sim 80 \, \mu$Ci was used for the positron source. In order to obtain slow positron beams, a set of tungsten ribbons, later changed to the better seven-overlapping tungsten mesh, baked at $2100^\circ$C was used as the moderator. The energy width of this beam was $\sim 2$ eV at full-width-half-maximum (FWHM). The slow electron beam, with an energy width of $\sim 1$ eV FWHM, is composed of secondary electrons produced via multiple scattering from the same tungsten moderator. The energy resolution, solely determined by the RP-TOF experimental apparatus, is an average $0.3$ eV below $4$ eV, and thus enables discussions of structures observed even below $1$ eV [11]. Magnetic field strengths of $4.5$ G and $9$ G were used for guiding the electron and positron beams, respectively. The TCS values, $Q_m$, were derived from the Beer-Lambert attenuation equation,

$$Q_m = -\frac{1}{nl} \ln \left( \frac{I_g}{I_v} \right)$$

(1)

where $I_g$ and $I_v$ refer to the projectile beam intensities transmitted through the collision cell with and without the target gas of number density $n$, respectively. $l$ refers to the effective length of the collision cell and was established by normalizing our measured positron-$N_2$ TCS to the positron-$N_2$ data of Hoffman et al. [12]. In this procedure, the value of $l$ from the measurement just before the current positron-$N_2$ measurements is assumed correct and used for the determination of the first values of the $N_2$ TCS from the measured spectra over the randomly chosen $14 - 200$ eV range. Ratios of the Hoffman et al. TCS values to our so-measured TCS are then calculated over all the energy points of overlap, with each ratio value typically falling within the range $1 \pm 10\%$, and their average $F$ found. This value of $F$ is then multiplied to the assumed $l$ value to get the new effective cell length. This new value of $l$ also makes sure that any instability of the pressure gauge that might have affected correct reading of the pressure values is accounted for. All the TCS data presented here were confirmed to be pressure-independent in the present energy range by independent test experiments, which is an important aspect of measurements using a collision cell in the transmission RP-TOF setup [13]. The energy calibration was done using positron-$N_2$ TOF spectra measured at $20$ energies in the randomly chosen region of $8$ to $150$ eV [14].

Our experimental apparatus setup has specifically been designed to have a collision cell with as wide as $3$ mm radii for the entrance- and exit-apertures for the weak positron beam intensities, i.e. for positron scattering experiments. As a result the detector detects some projectiles scattered through small angles. We carry out some simulation analysis procedure to account for this effect. The procedure for this takes into account the collision cell geometry, the external magnetic field and the differential cross section (DCS) data from experimental and/or theoretical results on the molecule being studied. The procedure for this has been described in detail previously [10,15]. However, because there is usually no DCS data available for positron scattering, in some cases we attempt the correction for positron TCS using electron the same electron DCS data. Indeed the errors involved in
this process are large, as the positron DCS may turn out to be completely different from the electron DCS in the angular dependence. Nevertheless, from our experience the correction rates for positron TCS, using electron DCS, could just be a few percent less than rates obtained using the actual positron DCS, and thus resulting in no change in the type of structures observed in the TCS. It can not be over-emphasized that positron DCS are needed for a better correction for this forward scattering effect.

The errors shown in the data in the figures are the total uncertainties made up of contributions from errors due to beam intensities, estimation of the effective cell length and fluctuations in the gas density during measurements. This sum of all the uncertainties was estimated to be of the order 4.0 – 8.0% for electron and 5.4 – 12.7% for positron impact.

2.2. Elastic integral cross sections

Elastic cross sections (ECS) as well as vibrational excitation cross sections are calculated theoretically based on the continuum multiple-scattering (CMS) method, which is somewhat a crude, but very efficient and useful model for treating electron scattering from polyatomic molecules since all interactions included are crystal-clear and hence the dynamics are easily extracted [16]. In order to overcome difficulties arising from the intrinsic molecular nature, such as the non-spherical molecular field, the CMS uses the technique of dividing the configuration space into three separate regions: that is, the individual atomic, the interstitial, and the outer surrounding of the molecular regions, respectively. The scattering part of the method is based on the static-exchange-(correlation + polarization for non-polar molecules or dipole for polar molecule)) potential model within the fixed-nuclei approximation. The Schrödinger equation in each region is solved numerically under separate boundary conditions, and by matching the wave functions and their derivatives from each region, we can determine the total wave functions of the scattered electron and hence, the scattering s-matrix element. And corresponding elastic amplitudes f(k_f, k_i; q) at the fixed nuclear configuration q [17]. The scattering cross section can then be easily determined by a standard procedure.

3. Results and discussions

The electron and positron TCS results are discussed in three sections as follows: (i) polar molecules, (ii) peculiar molecules, and the (iii) higher energy range above 100 eV.

3.1. Polar molecules

Figs. 1 and 2 show the TCS results for the fluoromethane family of molecules CH_4, CH_3F, CH_2F_2, CHF_3 and CF_4. This family of molecules has been chosen at random from the more than 50 molecules whose electron and positron TCS have been studied in this laboratory. See also Ref. [18] for some discussions of these results. Though we did not carry out studies of CH_3F, for the sake of completeness we have included the data shown for electron TCS for these molecules by Krzysztofowicz et al. [19].

Table 1 shows the molecular properties of these molecules obtained from Ref. [20]. As shown in Table 1, of these five molecules, three are polar and the increase in fluorination is associated with an increase in the ionization potential (IP) and a corresponding decrease in the dipole moment. The results of Figs. 1 and 2 are analyzed as follows.

Electron TCS The parent molecule CH_4 has TCS that are rather flat below 1 eV, rise thereafter to produce the main peak centered at about 7.5 eV, before the gradual and monotonous decrease beyond this peak towards 1 000 eV. The addition of F atoms, or substitution of H atoms in CH_4 by F atoms, results in the emergence of a shallow dip at 2 – 4 eV, a hump at about 20 eV and a shoulder centered at about 50 eV. Beyond 80 eV, however, all four TCS (CH_3F, CH_2F_2, CHF_3, CF_4) show a gradual
decrease toward 1 000 eV, i.e., thereby resembling CH₄ TCS. We make a closer investigation of the TCS at the low energy range below 3 eV, where some of the interesting differences are observed. It is clear that the TCS for the polar molecules (CH₃F, CH₂F₂, CHF₃) all show a rising trend with decreasing energy below 2 eV.

Table 1 Molecular properties. Abbreviations IP and Eₚₛ refer to the ionization potential and the positronium formation threshold energies respectively. See Ref. [20] for these data.

| Molecule | Dipole moment (D) | IP (eV) | Eₚₛ (eV) | Bond length (Å) |
|----------|-------------------|--------|----------|----------------|
| CH₄      | ─                | 12.51  | 5.71     | C – H 1.087     |
| CH₃F     | 1.858             | 12.47  | 5.67     | C – F 1.382     |
| CH₂F₂    | 1.978             | 12.71  | 5.91     |                |
| CHF₃     | 1.651             | 13.86  | 7.06     |                |
| CF₄      | ─                | 16.25  | 9.45     |                |

This rising trend in the TCS is associated with enhanced scattering due to the long-range interaction as a result of the permanent dipole moment [21-23]. The slope of the rising TCS is in the order CH₂F₂ > CH₃F > CHF₃ which is also the order of the permanent dipole magnitudes, i.e., CH₂F₂ (1.978 D) > CH₃F (1.858 D) > CHF₃ (1.651 D). It is worth highlighting that a similar systematic study of the elastic differential cross sections (DCS) for these five molecules showed increasing DCS below 70⁰ for polar CH₃F, CH₂F₂ and CHF₃, i.e. due to the long-range dipole interaction. Furthermore, above 100⁰, stronger back scattering for polar molecules CH₂F₂ and CHF₃ DCS than those for the non-polar CH₄ and CF₄ [24]. These DCS results thus support the foregoing observations and deductions from the TCS study. Beyond 70 eV the magnitudes of the TCS are in the order CH₄ > CH₃F > CH₂F₂ > CHF₃ > CF₄, i.e. the order of the molecular size (see Table 1). This is rather expected at these higher impact energies since the interaction time between the electron and the molecule is now short so that the static interaction (see Introduction) almost solely determines the collision dynamics. The finer details of the origin and nature of these peaks have already been discussed in the individual publications for these data and thus will not be repeated here, where we are only concerned with the group properties. See Refs 18 and 19.

Positron TCS Except for CF₄, these TCS are characterized by two broad peaks of near equal magnitudes in the regions 0.5 – 2.5 eV and 20 – 120 eV. The CF₄ TCS curve does not show the lower energy peak observed in the TCS for the other three molecules shown in the lower panel of Fig. 1. The reason for this could simply be that our lowest energy range of measurement was not enough for its observation in this molecule. Otherwise the addition of fluorine atoms results in a shift of the (i) lower energy peak center from about 2.5 eV in CH₄ to 2.1 eV in CH₂F₂ and 1.5 eV in CHF₃, and (ii) the higher energy peak center from about 30 eV in CH₄ to 40 eV in CH₂F₂ to 50 eV in CHF₃ and 70 eV in
CF₄. A closer examination of these peaks shows that because the higher energy sides of the lower energy peaks are similar in both the slope and energy positions, the shift to lower energies in fact means a broadening of these peaks towards 0 eV. The peaks in the region 20–120 eV are also similar in both energy positions and slopes so that the shift to higher energies, with increase in fluorination, practically means a broadening of these peaks towards 1000 eV.

Fig. 1 Electron and positron TCS for the fluoroethane molecular family.

These peak shifts and broadening features are only clearly observed in positron TCS and not so much in the electron TCS where the several resonances and long range dipole interactions (see Refs 18 and 19) seem to dominate the scattering dynamics in the low to intermediate regions. Moreover, in a way
contrary to the positron case, the main peak in CH$_4$ electron TCS at 7.5 eV does not seem to shift in position at all for the four fluorinated methanes (CH$_3$F, CH$_2$F$_2$, CHF$_3$ and CF$_4$). Similar to electron TCS discussed above, however, positron TCS also show the molecular size effect above 70 eV, i.e. even much clearer than the electron TCS in the top panel of Fig. 1. In a way similar to the discussion above for the electron TCS case, we now carry a closer analysis of the TCS in the energy region below 3 eV. Firstly, contrary to the electron TCS case where the polar molecules show the rising trend towards 0 eV due long range permanent dipole induced interaction, TCS for both CH$_2$F$_2$ and CHF$_3$ polar molecules show no indication of rising within this energy region. Secondly, the threshold for positronium formation, $E_{Ps}$, for CH$_4$ is 5.71 eV, 5.91 eV for CH$_2$F$_2$ and 7.06 eV for CHF$_3$.

![Graph showing electron and positron TCS for individual fluoroethane molecules.](image)

Fig. 2 Electron and positron TCS for the individual fluoroethane molecules. Error bars show total errors derived as explained in the text.
This thus implies that the lower energy peak positions, i.e. in the region 1.5 – 2.5 eV, discussed above all are at energies lower than these E_p. This is an intriguing observation for these molecules as such structures below E_p are not easily explainable in the limit of known scattering physics. The origins of these peaks for CH_4, CH_2F_2 and CHF_3 will not be clear until partial cross section studies are carried out for these molecules and since it is still to be proved whether shape resonance and bound states of the positron to molecules exist or not. It can not be ruled out though that maybe more physics is to be learnt from the minima at about 4.5 eV than these peaks below E_p. For each molecule, however, the opening up of the positronium formation channel is associated with a corresponding increase of the TCS, albeit with different cross sections [25].

Electron and positron TCS Except for the peculiar case of CH_4, where positron TCS are greater than electron TCS below 2 eV, the TCS for the other molecules shown in Fig. 2 are characterized by electron TCS being about one and a half times greater than positron TCS below 100 eV. This has been the pattern observed for most of the molecules studied in this laboratory, and a few other laboratories where similar studies were carried out. The interested reader is referred to any publication by this group including those appearing in the reference list for this paper. See also the Wayne State University (Detroit) results in Ref. [12] for some simple molecules. The peculiar behavior of electron and positron TCS (like CH_4 below 2 eV) will be discussed in the following section.

The larger TCS for electron than positron below 100 eV are expected due to the presence of shape resonances in the former but not observed in the latter. Even the opening up of the positronium formation, electronic excitation and ionization channels in positron impact do not result in TCS enhancements large enough to equal the electron TCS. Nevertheless, until individual partial cross sections, e.g. vibrational excitation, electronic excitation and ionization, become available for both electron and positron impact with each molecule, it is difficult to make a relative comparison.

A point worth mentioning here too is that although only the electron TCS for the polar molecules studied here show the dipole effect, as discussed above, electron and positron TCS for the other polar molecules H_2O and HCl rise below 2.5 eV with almost the same slopes [26-28]. This thus implies that the treatment of the long range dipole interaction in the scattering potential is non-trivial [22].

3.2. Peculiar Molecules

Fig. 3 shows electron and positron TCS for CO_2 and C_6H_6, randomly chosen from a small class of molecules that we studied in this laboratory as peculiar in that they present a case where positron TCS unexpectedly become larger than electron TCS below a few eV. A similar phenomenon was also observed in the CH_4 TCS shown in Fig. 2. A point to note in each of these cases is that these positron TCS become greater than electron TCS and peak at impact energies below E_p, i.e. the positron peak is at about 1.2 eV while E_p is at 5.71 eV for CH_4, at 2 eV while the E_p is 6.97 eV for CO_2 and at 1.5 eV while E_p is 2.45 eV for C_6H_6. Thus, intuitively, these observations are expected to be either due to vibrational or rotational excitation, or a combination of the two, being greater for positron than electron impact. A possible contribution could be from a positron-molecule attachment resonance. This group carried out a joint theoretical and experimental electron and positron impact vibrational excitation study of the symmetric stretching (100), bending (010) and asymmetric (001) modes of CO_2 molecules at energies 2, 5 and 6 eV [29,30]. The experimental approach was the energy-loss technique while the theoretical approach was the Continuum Multiple Scattering (CMS) model. It was found that vibrational excitation is about three times greater for electron than positron impact for the (100) mode, and nearly equal for the two projectiles for both the (010) and (001) modes. Similar results were also observed from experiments carried out by the Surko group [31]. Gianturco et al. studied the (100) excitation and made a similar conclusion [32]. Thus vibrational excitation can not be the sole source of this observation of TCS magnitude reversal in CO_2.
Fig. 3 Electron and positron TCS for CO$_2$ and C$_6$H$_6$ molecules. The solid and broken curves show the CMS calculation results for C$_6$H$_6$ electron and positron TCS, respectively. The arrows labelled E$_{Ps}$ and E$_{ion}$ indicate the positions of the thresholds for positronium formation and ionisation, respectively.

While not much work exits in literature for sound conclusions on the contribution of the comparative study between electron and positron impact rotational excitation to the TCS at these energies some two literature studies are worth mentioning. The Born approximation was used to study electron and positron impact rotational excitation in the diatomics H$_2$ and N$_2$ and found that cross sections for positron are larger than those for electron impact [33]. The close-coupling theoretical approach was used to study rotational excitation in CH$_4$. The result was that while for the $J = 0 \rightarrow 3$ transition cross sections for positron impact were consistently greater than those for electron impact from threshold up to about 7 eV, the $J = 0 \rightarrow 4$ transition gave an opposite result. Surely more exhaustive theoretical and experimental studies are awaited, for all these molecules highlighted in this section, for any meaningful conclusions on the comparative electron and positron rotational
We now refer to the C₆H₆ results in the bottom panel of Fig. 3. While focusing on the contrasting behaviour of the electron and positron TCS below 1 eV, the CMS analysis reproduced the peaking of C₆H₆ positron TCS at 1.5 eV, i.e. with magnitudes greater than electron TCS, and the decrease with decreasing impact energy below this peak versus a rising trend for electron TCS below 0.5 eV [11]. A careful examination of the phase shifts and interaction potentials was carried out. For electron impact there is no region where the eigenphase sum crosses $\pi$ below 1 eV down to 0.1 eV, a clear indication of no Ramsauer-Townsend-like effect. The specific eigenphase sum for some symmetries (e₂u, b₂g, etc.) shows sudden changes from zero to a large value within a very narrow energy region above 1 eV, which is attributable to a shape resonance at 1.5 eV and a few locations in the energy region from 4 eV to 10 eV. For positron impact however, based on the CMS calculation, we observed no clear and strong evidence for the presence of shape resonance, such as an abrupt change in the eigenphase sum in the energy region up to 10 eV.

The reason we started by carrying out the shape resonance search in C₆H₆ and not the other simpler molecules where similar peculiar phenomena were observed is as follows. Because larger molecules have many valence electrons they intuitively have a larger probability for holding an incoming positron within the molecule by absorbing the extra kinetic energy. Needless to mention that the trapped positron will eventually either (i) escape through the tunneling effect, leaving behind a neutral molecule, or (ii) annihilate by emitting a gamma ray, leaving behind a positive molecular ion. Should mechanism (ii) be possible then a new application for positron impact become possible. This comes from the fact that fragile molecular ions become easily producible, with long lifetimes and can exist in both electronic and nuclear states. Nevertheless, studies for shape resonances in positron impact with some of these smaller peculiar molecules using the CMS are also planned.

These few studies, though not exhaustive, indicate that the cause for the peculiar phenomena in these molecules is unique to some molecules. Though the phenomenon for each molecule has its origins in vibrational excitation, rotation excitation and positron-molecule resonance, the degree of contribution of each process to the TCS is a case-by-case issue. Furthermore, the electron and positron impact comparative study shows that the results of the vibrational excitation cross sections are model-dependent and the rotational excitation transition-dependent.

3.3. Higher energy region above 100 eV

In Fig. 4 we show electron and positron TCS for CH₄ and CH₃I, and the positron to electron TCS ratio, $Q^+_{t}/Q^-_{t}$. A common method of expressing the TCS at these intermediate and higher energies is to use the optical theorem, which expresses the conservation of particle flux in the scattering process as a relationship between the TCS and the imaginary part of the elastic scattering amplitude in the forward direction ($\text{Im} f_{el}(\theta = 0)$), as follows.

$$\text{TCS} = (4\pi/k) \text{Im} f_{el} (\theta = 0),$$

where $k$ is the incident electron/positron wave number. Furthermore, at these energies the forward direction amplitude, $f_{el}(\theta = 0)$, can be expanded in a Born series as:

$$f_{el}(\theta = 0) = \sum_{n=1}^{\infty} \beta_{el} \left( \theta = 0 \right),$$

so that a reasonably good approximation to the forward scattering amplitude should then be given by the sum of the first few terms in the expansion. In an analysis of the terms of this Born expansion the first term on the right-hand of Eq. (3) is real and therefore, according to the optical theorem, does not
make a contribution to the TCS so that the lowest order contribution to the TCS is from the second term, $f_{el}^{B_2}(\theta = 0)$.

Fig. 4 Electron and positron TCS for CH$_4$ and CH$_3$I above 100 eV. $Q^+/Q^-$ is the ratio of the positron TCS to electron TCS. Error bars show total errors derived as explained in the text.

It has been observed by a number of research groups that at high energies of a few hundred eV, this first Born approximation yields reasonably accurate cross sections for elastic scattering and for the various inelastic processes (see Ref. [7], and references therein) Furthermore, these cross sections have the same values for both electrons and positrons, except for the positronium (Ps) formation, which is absent in electron collisions. However, at these high energies the Ps formation cross section is negligible, and therefore the first Born approximation to the TCS is essentially the same for both electron and positron scattering. To further quantify this argument for merging electron and positron
TCS at these energies, with reference to the optical theorem and the Born expansion of Eq. (3), it is also worth looking at the exchange interaction in electron scattering. If exchange is ignored in electron scattering, then the first non-zero contribution to the Born expansion is the second order term \( f_{el}^{B_{e}} (\theta = 0) \), which is the same for both electrons and positrons because it is a quadratic in the projectile-target interaction potential or charge \( Z \), i.e. imaginary part of the scattering amplitude is \( f_{el}^{B_{e}} (\theta = 0) = 2Z^2 / k_i Z \), where \( k_i \) denotes the initial electron vector. Similar identities exist for all the even-order terms in the Born series with \( n \geq 3 \). But Dewangan [34] has managed to prove that even though the Born expansion odd-order terms are not actually zero, their magnitudes are so small compared with the adjacent even terms, and so can be neglected in this analysis. Therefore, even though the above argument is not rigorous, particularly in its neglect of electron exchange, it nevertheless gives a plausible explanation of the merging of the electron and positrons TCS at these energies.

The ratio of the positron TCS to the electron TCS, \( Q_{+}/Q_{-} \), data for CH₄ shows the two TCS merging at energies up to 400 eV. However, above this energy electron TCS are seen to be increasingly greater than positron TCS although the difference between the two is minimal and in fact starting to show tendency towards merging again, as shown by the kind of leveling off of the ratio data towards 1000 eV. The CH₃I data shown in the bottom panel of Fig. 4 presents a case where the merging of the two TCS starts ‘earlier’, i.e. at about 80 eV. For the more than 50 different types of atoms and molecules we have studied over the years, in general three types of merging patterns have been observed. Some (1) merge ‘early’ like CH₃I, (2) slowly tend toward merging with increasing energy toward our highest measurement energy of 1 000 eV and (3) like CH₄, merge and then stay slightly above or below unit. Class (1) has mainly been associated with hydrocarbons and rare gases while many fluoroalkanes have shown merging patterns characteristic of Class (2). Other families of molecules did not show special characteristics as they randomly classified into any of these three classes. Indeed no simple explanation can be given that suffices to explain these differences for different molecules. However, recently similar differences have been observed in cross sections for two electron processes like double ionization by positive and negative charged particles at velocities above 500 eV and explained as arising from electron correlation effects [35,36]. Similar analyses are awaited for the investigation of the possibility of such phenomena in these molecules.

4. Conclusions

In this paper we present a joint experimental and theoretical study of the similarities and differences between electron and positron scattering from molecules over the energy range 0.2 – 1 000 eV. This analysis draws from the results of our studies of more than 50 polyatomic molecules. The low energy range below 3 eV has been dominated by the long-range dipole interaction in the polar molecules CH₃F, CH₂F₂, CHF₃, presented in this study, and others like CH₃Cl, CH₃Br and CH₃I (Kimura et al. 2001 J. Chem. Phys. 115 7442). However, this has been observed only in electron impact and not in positron impact in the present lowest energy range. The intermediate energy range of about 3 – 60 eV has been generally characterized by electron TCS being about 1.5 times greater than positron TCS, an observation attributed to resonances in the former and not in the latter. Some interesting cases have been studied whereby, for a few molecules, TCS for positron have peaked and become greater than electron TCS at energies lower than the positronium formation threshold. Although this phenomenon for each molecule should have its origins in vibrational excitation, rotation excitation and positron-molecule resonance, the degree of contribution of each process to the TCS is a case-by-case issue. Electron and positron TCS for each molecule have shown a pattern towards merging above a few hundred eV, as expected from the first Born approximation.
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References

[1] Surko C M, Gribakin G F and Buckman S J 2005 J. Phys. B 38 R57
[2] Morrison M A 1986 Positron (Electron)-Gas Scattering ed Kauppila W E, Stein T S and Wadehra J M (World Scientific, Singapore)
[3] Kimura M, Sueoka O, Makochekanwa C, Kawate H and Kawada M 2001 J. Chem. Phys. 115 7442
[4] Kimura M, Sueoka O, Hamada A and Itikawa Y 2000 Adv. Chem. Phys. 111 537
[5] Burke P G and Williams J F 1977 Phys. Rep. 34 325
[6] Trajmar S, Register D F and Chutjian A 1983 Phys. Rep. 97 219
[7] Charlton M and Humberston J W 2001 Positron Physics ed Dalgarno A, Knight A P L, Read F H and Zare R N (Cambridge University Press) p 45
[8] Armour E A G 1988 Phys. Rep. 169 1
[9] Kauppila W E and T S Stein 1989 Adv. At. Mol. Opt. Phys. 26 1
[10] Sueoka O, Mori S and Hamada A 1994 J. Phys. B27 1452
[11] Kimura M, Makochekanwa C and Sueoka O 2004 J. Phys. B 37 1461
[12] Hoffman K R, Dababneh M S, Hsieh Y F, Kauppila W E, Pol V, Smart J H and Stein T S 1982 Phys. Rev. A 25 1393
[13] Kennerly R E and Bonham R A 1978 Phys. Rev. A 17 1844
[14] Sueoka O and Mori S 1986 J. Phys. B 19 4035
[15] Sueoka O, Makochekanwa C and Kawate H 2002 Nucl. Inctr. and Meth. B 192 206
[16] Kimura M and Sato H 1991 Comments At. Mol. Phys. 26 333.
[17] Fujima K, Sato H and Kimura M 1988 Chem. Phys. Lett. 145 21
[18] Sueoka O, Takaki H, Hamada A, Sato H and Kimura M 1998 Chem. Phys. Lett. 288 124, and ibid. (2000) Chem. Phys. Lett. 330 34
[19] Krzysztofowicz A M and Szmytkowski C 1995 J. Phys. B 28 1593
[20] CRC Handbook of Chemistry and Physics, 81st Ed. (2000-2001), CRC Press, NY, David R. Lide (Editor-in-Chief).
[21] Kimura M, Sueoka O, Makochekanwa C, Kawate H and Kawada M 2001 J. Chem. Phys. 115 7442
[22] Altshuler S 1957 Phys. Rev. 107 114
[23] Morrison M A 1987 Adv. At. Mol. Phys. 24 51
[24] Tanaka H, Masai T, Kimura M, Nishimura T and Itikawa Y 1997 Phys. Rev. A 56 R3338
[25] C. Makochekanwa, O. Sueoka and . Kimura 2006 Nucl. Instr. and Meth. B 247 79
[26] Hamada A and Sueoka O 1994 J. Phys. B 27 5055
[27] Sueoka O, Mori S and Katayama Y 1986 J. Phys. B 19 L373
[28] Sueoka O, Mori S and Katayama Y 1987 J. Phys. B 20 3237
[29] Kawada M I, Sueoka O and Kimura M 2000 J. Chem. Phys. 112 7057
[30] Kimura M, Takekawa M, Itikawa Y, Takaki H and Sueoka O 1998 Phys. Rev. Lett. 80 3936
[31] Sullivan J, Gilbert S J and Surko C M 2001 Phys. Rev. Lett. 86 1494
[32] Gianturco F A, Mukherjee T and Paioletti P 1997 Phys. Rev A 56 3638
[33] Takayanagi K and Inokuti M 1967 J. Phys. Soc. Jpn 23 1412
[34] Dewangan D P 1980 J. Phys. B 13 L595
[35] B. Bapat and E. Krishnakumar 1997 Phys. Rev. A 55 3937
[36] A. S. Kheifets 2004 Phys. Rev. A 69 032712