Positron scattering from methane

A. Zecca,[1] L. Chiari,[1,2] E. Trainotti,[1] A. Sarkar,[3] S. d'A. Sanchez,[4] M. H. F. Bettega,[4] M. T. do N. Varella,[5] M. A. P. Lima,[6] and M. J. Brunger[2,7]

[1]*Department of Physics, University of Trento, Via Sommarive 14, I-38123, Povo (Trento), Italy*

[2]*ARC Centre for Antimatter-Matter Studies, School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia*

[3]*Department of Physics, Bangabasi Morning College, 19 R.C. Sarani, Kolkata 700 009, India*

[4]*Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531–990 Curitiba, Paraná, Brazil*

[5]*Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315–970, São Paulo, SP, Brazil*

[6]*Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, Caixa Postal 6165, 13083–970, Campinas, São Paulo, Brazil*

[7]*Institute of Mathematical Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia*

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We report on measurements of total cross sections for positron scattering from the fundamental organic molecule methane (CH_4). The energy range of these measurements was 0.1–50 eV, whereas the energy resolution was ∼100 meV when our Ni moderator was used and ∼260 meV when the W moderator was employed. To assist us in interpreting these data, Schwinger multichannel calculations were performed at both static and static plus polarization levels of approximation for elastic positron scattering from 0.001 to 10 eV. These calculations are found to be in quite good qualitative agreement with our measured data, and they clearly educe the crucial role played by the target polarization in the low energy positron–CH_4 scattering dynamics.

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I. INTRODUCTION

The significance of methane in many atmospheric (e.g., on Jupiter and on Earth where it is a greenhouse gas with a global warming power some 20 times larger than CO_2) and technological (e.g. as an active constituent in radiation detectors and flame processes) applications has long been appreciated [1]. In the context of this quite fundamental study, however, its qualities as a stable and nonreactive gas, which can be easily sourced with high purity, make it attractive to experimentalists, while the fact that it is a relatively small molecule (Z=10) with high symmetry, that it possesses no permanent dipole moment [2] and that it has a dipole polarizability (α) of moderate magnitude ($\alpha = 17.61$ a.u. [3]), makes it attractive to scattering theoreticians. This latter assertion follows as with the available high-speed supercomputers, an accurate description of the methane (CH_4) molecule that can be incorporated into the scattering computations is feasible. As a consequence, methane might be considered as a sort of prototypical molecule for studying the scattering of positrons from small nonpolar polyatomic species.

Given the above, it is thus not surprising that positron scattering from CH_4 has been already relatively well studied. In this regard we note the experimental total cross sections (TCSs) from Charlton *et al.* [4,5], Sueoka and Mori [6], Floeder *et al.* [7], and Dababneh *et al.* [8], and the discrete vibrational excitation integral cross sections from Sullivan *et al.* [9]. From a theoretical perspective, various model calculations from Jain and Thompson [10], Jain [11], Gianturco *et al.* [12], Jain and Gianturco [13], and Baluja and Jain [14] are noted and are of relevance to the present study. As we shall see in detail later, it is fair to characterize the level of agreement between the various experimental TCSs (at least for energies below the positronium formation threshold energy E_{Ps}) as being marginal, the agreement between the various theoretical results is generally rather poor and thus the overall level of accord between experiment and theory is also at present quite marginal. Indeed one rationale for the present investigation is to try and shed more light on this state of affairs. Another rationale is that none of the available measurements [4–8] extend below an incident positron energy of about 1 eV, whereas it is expected that the effect of the target polarization on the scattering dynamics will become very important at those lower energies [15,16].

In the next section we give a summary of our experimental apparatus and techniques. Thereafter, in Sec. III we provide details of our Schwinger multichannel (SMC) level calculations. In Sec. IV we report the present results and provide a discussion of those results, before we draw some conclusions from our investigation.

II. EXPERIMENTAL DETAILS

The positron spectrometer at the University of Trento was developed by Zecca and collaborators, and has been described in some detail recently (e.g., [17,18]). We therefore do not need to repeat all those details here, except for noting that either a tungsten (W) moderator of thickness 1 μm [19] or a nickel (Ni) moderator of thickness 2 μm [19] was employed in conjunction with a radioactive ^{22}Na isotope (activity at the time of measurement ∼1.6 mCi) and some electrostatic optics in order to produce the positron beam. Note that in our laboratory, as a check for the validity of our techniques and procedures, we carry out initial validation measurements using targets for which the positron scattering TCSs might now be considered to be well understood. Such systems might be drawn from molecular nitrogen [18] or from the rare gases ([20,21] and references therein).

The basis of all linear transmission measurements 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 pressure being measured with the CH_4 routed to the scattering cell, k is Boltzmann's constant, and T is the temperature (in K) of the CH_4 gas, as accurately measured using a calibrated platinum (PT100) resistance thermometer that is in excellent thermal contact with the scattering chamber. 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 CH_4 diverted into the vacuum chamber, that is, 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 double-scattering events and ensuring the TCSs are independent of pressure. In addition only a high-purity methane sample (∼99.95%) was used (Air Liquide). The geometrical length of the scattering region is 22.1 ± 0.1 mm, with apertures of 1.5 mm diameter at both the entrance and exit of the scattering cell. As in our previous experiments, a further aperture of diameter 2 mm is placed 8 mm downstream of the scattering cell. This aperture has a twofold function: as a skimmer-like diaphragm, it reduces the gas pressure at the channeltron detector. In addition, it reduces the angular acceptance of the detector thus reducing somewhat the angular discrimination effect (see below) on the TCS measurements. End effects were minimized in this configuration by having equal and relatively small diameter entrance and exit apertures in our scattering cell. As a consequence, we evaluate that their contribution to the uncertainty in the value of L is less than 0.2%. 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 9 eV, $B \sim 12$ G and the value of L increased by ∼6%, for incident positron energies from 10 to 30 eV, $B \sim 11$ G and the value of L increased by ∼5.6%, while for energy values between 32.5 and 50 eV, $B \sim 4$ G leading to an increase in L of ∼2.1%. It is crucial for the energy scale to be calibrated accurately. The zero for the energy scale, in the absence of the target gas, was determined using a retarding potential analysis of the positron beam [22]. We believe that the error in our energy scale is ±0.05 eV. The same measurements allow us to evaluate an energy width ΔE (FWHM) of the positron beam of $\Delta E \sim 0.1$ eV when the Ni moderator was used and $\Delta E \sim 0.26$ eV when the W moderator was employed, with an uncertainty on these determinations of at most ±0.05 eV. It is also very important to accurately measure the scattering cell pressure, which we achieve with a MKS 627B capacitance manometer operated at 45 °C. As the manometer temperature was different to that for the target gas in the scattering cell, thermal transpiration corrections to the pressure readings are made using the model of Takaishi and Sensui [23]. Typically this led to a maximum correction in the TCSs of +3%.

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 TCS being somewhat smaller than the "true" value. The extent of this problem depends on the angular discrimination of the apparatus and the nature of the elastic differential scattering cross section (DCS) in this forward angle region [24]. Hence it will be an energy-dependent effect. From a consideration of the size of the entrance and exit apertures of our scattering cell, and their separation, the angular resolution ($\Delta\theta$) of the Trento spectrometer is ∼4°, which compares favorably with that from the Yamaguichi spectrometer ($\Delta\theta \sim 7°$) and the Detroit apparatus [25] ($\Delta\theta \sim 16°$). The gyration of the positrons can also potentially increase the angular discrimination correction compared to the no-field case [26]. Using some of the analytic formulas detailed in Kauppila *et al.* [25], but for the typical experimental conditions of our measurements, estimates of the present energy-dependent angular discrimination varied from ∼17° at 1 eV to 5.4° at 10 eV positron energy. These estimates compare very well to those determined by the ANU group (see Table I in Makochekanwa *et al.* [27]) for their spectrometer even though the Trento and ANU apparatus are very different. An alternative approach to using the formulas of Kauppila *et al.* [25] and the method of Hamada and Sueoka [26] is to employ a Monte Carlo simulation to investigate this forward angle scattering effect. To this end we have adapted an $E \times B$ Monte Carlo code [28] for investigating transport phenomena, to the present case. Using the argon [21] and krypton [20] convergent close coupling cross sections, the results obtained for both gases, Monte Carlo versus Kauppila *et al.* plus Hamada and Sueoka, for the forward angle scattering effect corrections to the TCSs, were consistent to better than 5% at all energies studied. We thus believe that if positron–methane elastic DCSs were available, we would be able to correct our measured TCSs for this effect. In principle, such DCSs are available from our SMC-level calculations (see next section). However, as we shall see later in our results and discussion section, at this time employing those DCSs in the manner outlined above might be a little premature and so we have not done so. As a consequence, the TCSs we report here (see Table I) represent a lower bound on the exact values.

Finally, we note that the 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%–12% range. Note that the overall errors are formed from the quadrature sum of quantities such as the statistical uncertainties (typically around 3%, at worst ∼7.4%) on our data (see Table I), the uncertainty in our thermal transpiration correction, the uncertainty in the value of L, the uncertainty in the temperature reading, and the uncertainty in the absolute pressure readings (∼0.3%), as per the manufacturer's specifications.

III. THEORETICAL DETAILS

The Schwinger multichannel method (SMC) is a fully *ab initio* method to calculate scattering cross sections for electron and positron scattering by molecules. It has been well described elsewhere [29–33] and so only the main aspects will be highlighted here. The final working expression to

TABLE I. The present experimental TCSs (10^{-20}m^2) for positron scattering from methane (CH_4). The uncertainties cited are purely statistical and are at the one standard deviation level.

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)($\pm 1\sigma$)
0.1	36.1	1.3	8.0	8.5	0.3
0.2	29.2	1.0	8.3	8.9	0.4
0.3	24.5	0.6	9.0	9.4	0.2
0.4	21.3	0.7	10.0	9.6	0.1
0.5	18.8	0.6	11.0	10.1	0.1
0.6	18.0	1.1	12.0	10.5	0.2
0.7	16.6	0.9	13.0	10.5	0.1
0.8	15.2	0.2	14.0	10.5	0.1
0.9	14.6	0.3	15.0	10.8	0.1
1.0	13.4	0.4	16.0	10.8	0.1
1.2	12.5	0.5	17.5	10.9	0.1
1.5	12.1	0.6	20.0	11.1	0.2
1.9	10.8	0.8	22.0	11.1	0.1
2.0	10.4	0.4	25.0	11.2	0.3
2.5	9.3	0.1	27.0	11.0	0.2
3.0	8.4	0.4	30.0	11.1	0.2
4.0	7.7	0.4	32.5	10.9	0.2
4.5	7.6	0.3	35.0	10.9	0.3
5.0	7.5	0.3	37.5	10.8	0.2
6.0	7.2	0.2	40.0	10.8	0.2
6.3	7.3	0.2	42.5	10.7	0.3
6.7	7.5	0.3	45.0	10.6	0.2
7.0	7.8	0.3	50.0	10.4	0.2
7.3	8.1	0.2			

the scattering amplitude in the molecular reference frame (body-frame BF) is

$$f(\vec{k}_f,\vec{k}_i) = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V\big|S_{\vec{k}_i}\big\rangle, \quad (2)$$

in which

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle \quad (3)$$

and

$$A^{(+)} = Q\hat{H}Q + PVP - VG_P^{(+)}V. \quad (4)$$

In the above equations, $|S_{\vec{k}_{i,f}}\rangle$ is the solution of the unperturbed Hamiltonian H_0; V is the interaction potential between the incoming positron and the target; $\{|\chi_m\rangle\}$ is a configuration state function (CSF), a product of the target state and scattering orbital of the incident particle; $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$; P is a projection operator onto the energy allowed (or open) channels space defined by the target eigenfunctions: and $Q = (\mathbb{1} - P)$ is the projector onto the closed electronic channels of the target. The boundary conditions are included in $G_P^{(+)}$, the free-particle Green's function projected on the P space.

Calculations were performed in the static (S) and static plus polarization (SP) approximations. In the first, the CSF is constructed as

$$|\chi_i\rangle = |\Phi_1\rangle \otimes |\varphi_i\rangle, \quad (5)$$

where $|\Phi_1\rangle$ is a N-electron Slater determinant of the target ground state obtained at the Hartree-Fock level and $|\varphi_i\rangle$ is an one particle function which represents the incoming positron. The distortion of the electronic cloud due to the incoming positron (polarization effects) is included through virtual single excitations from the occupied molecular (hole) orbitals to a set of unoccupied molecular (particle) orbitals.

Our calculations were performed in the C_{2v} symmetry group with the molecule in the ground state equilibrium geometry as given in Ref. [34]. The basis sets employed in both the bound state and scattering calculations for carbon and hydrogen are shown in Table II. For these basis sets we obtain a dipole polarizability of 15.98 a.u., which compares reasonably well with the experimental value [3].

For the polarization effects we chose modified virtual orbitals (MVOs) [35] obtained from a cationic Fock operator with charge +4 to represent particle and scattering orbitals. In the present calculations we considered all valence occupied orbitals as hole orbitals and considered excitations to MVOs with energies less than 0 hartrees to represent the particle orbitals, which gives a total of 59 MVOs. With this procedure we obtained a total of 30 099 CSFs. To test the convergence of our work, we also performed calculations with an extra f-type function on the carbon atom (with exponent 0.001), just as an extra scattering orbital, which gives a total of 32 509 configurations.

Finally, we note that throughout the rest of this paper we designate our SMC calculation at the static level as SMC–S, our SMC calculation that includes for polarization

TABLE II. Exponents of the uncontracted Cartesian Gaussian functions used for the respective carbon and hydrogen atoms. The corresponding coefficients are unity in each case.

Type	C	H
s	4232.610	33.640 00
s	634.882 0	5.058 000
s	146.097 0	1.147 000
s	42.497 40	0.321 100
s	14.189 20	0.101 300
s	5.147 700	0.036 000
s	1.966 600	–
s	0.496 200	–
s	0.153 300	–
s	0.050 000	–
s	0.020 000	–
s	0.010 000	–
s	0.004 000	–
p	18.155 70	2.000 000
p	3.986 400	0.500 000
p	1.142 900	0.150 000
p	0.359 400	0.020 000
p	0.114 600	–
p	0.050 000	–
p	0.020 000	–
p	0.007 000	–
d	1.097 000	–
d	0.318 000	–
d	0.090 000	–

effets as SMC–SP and our SMC calculation that includes for polarization effects and incorporates the extra f-type function as SMC–SP+f.

IV. RESULTS AND DISCUSSION

In Table I and Figs. 1–3 the results for the present positron–CH_4 TCS measurements are given. Note that the errors listed in Table I and typically plotted in Figs. 1–3 are purely statistical and are at the one standard deviation level. However, representative total errors (in violet at 0.1, 1, and 10 eV) are also plotted in those figures, to enable a better comparison to be made to the current SMC results and the earlier experimental data [4–8] and previous computations [10–14]. The arrows in Figs. 1 and 3 indicate, respectively, the approximate thresholds for positronium formation (Ps) and the direct (first) ionization potential (IP) in methane. It is known [36] that the first IP of CH_4 has a value of ∼12.61 eV, leading to a positronium threshold energy of ∼5.81 eV as in general:

$$E_{\mathrm{Ps}} = \mathrm{IP} - 6.8\ \mathrm{eV}. \tag{6}$$

A close examination of the present TCS in Fig. 1 suggests the existence of a quite marked change in its slope at about 6 eV, which we believe corresponds to the opening of the positronium channel. Note that as the present elastic SMC calculations do not incorporate the positronium formation channel, an intrinsically difficult problem due to the multicenter nature of positronium, one would not expect them to compare well with the present measured TCS at energies above 5.81 eV.

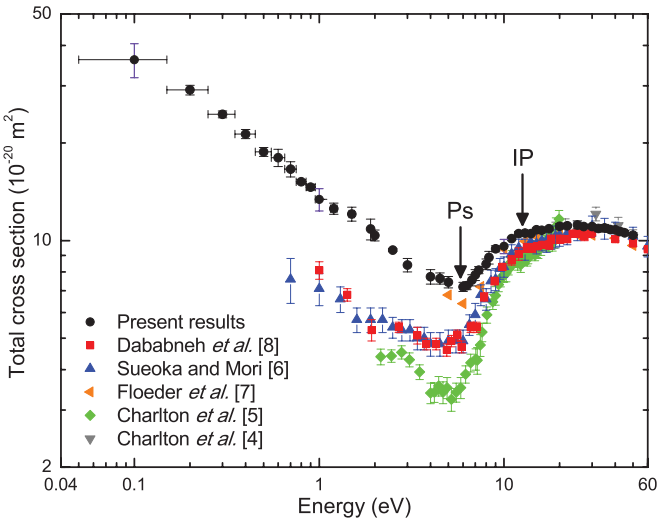

FIG. 1. (Color online) Present experimental TCSs (10^{-20} m^2) for positron scattering from methane. Also shown are the earlier results from measurements by Charlton *et al.* [4,5], Sueoka and Mori [6], Floeder *et al.* [7], and Dababneh *et al.* [8]. See legend on figure for further details. The positronium formation threshold and the first ionization potential are indicated by arrows labeled Ps and IP. Representative total errors are plotted in violet at 0.1, 1, and 10 eV.

Considering Fig. 1, which affords a comparison of the present TCS to those from the earlier measurements [4–8], in more detail, it appears that generally quite marginal agreement between the various data sets is found except above incident positron energies of about 15 eV. Indeed, at those higher energies, to within the total uncertainties on the various TCSs, one might characterize the level of agreement between all the experiments as being very good. Below 15 eV, however, with the possible exception of the present TCS and that of Floeder *et al.* [7] which are in fair accord, our current result is significantly larger in magnitude, over the common energy range, than the TCS data from Charlton *et al.* [5], Sueoka and Mori [6], and Dababneh *et al.* [8]. Sullivan *et al.* [24] recently demonstrated just how important the forward angle discrimination effect on TCS measurements can be, so that the discrepancies observed at the lower energies (see Fig. 1) might well simply be a reflection of the earlier data needing larger angle-discrimination corrections being made to them (they are all uncorrected for this effect at this time), relative to the present data, rather than an error in their measurement and/or analysis procedures. The most striking feature in Fig. 1 is just how dramatically the present TCS increases in magnitude as one goes to lower (below E_{Ps}) incident positron energies (note the log-log x and y axes). This behavior (see also later) reflects the moderately strong value for α [3] that methane possesses, a statement that is consistent with what was previously found in studies on formaldehyde [15] and formic acid [16], although the picture is complicated a little as those species both also have quite significant permanent dipole moments.

In Fig. 2 we present the current elastic SMC integral cross section results at the static plus polarization and static plus polarization plus f-type function levels, and compare them to earlier TCS calculations from Jain [11], Gianturco *et al.* [12], Jain and Gianturco [13], and Baluja and Jain [14],

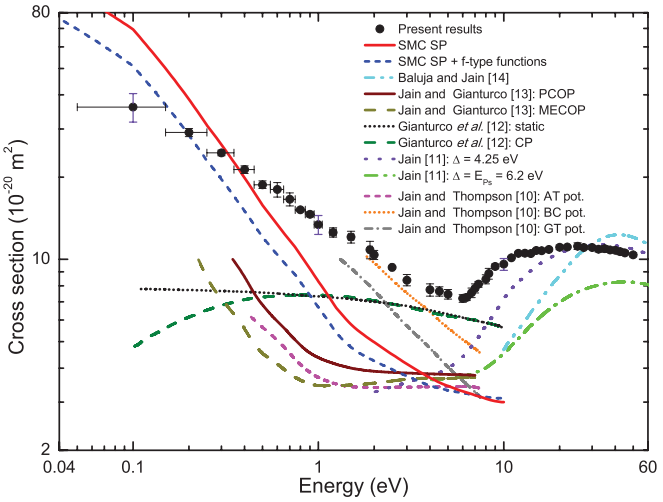

FIG. 2. (Color online) Present experimental TCSs (10^{-20} m^2) and elastic SMC integral cross sections (10^{-20} m^2) for positron scattering from methane. Also shown are TCS results from previous calculations by Jain [11], Gianturco *et al.* [12], Jain and Gianturco [13], and Baluja and Jain [14], as well as an earlier elastic integral cross section computation from Jain and Thompson [10]. See legend on figure for further details. Representative total errors are plotted in violet at 0.1, 1, and 10 eV.

as well as an earlier elastic ICS computation from Jain and Thompson [10]. For completeness the present TCS data is also included. Three of the earlier calculations [11,14], which employed model optical potential approaches, attempted to describe the collision process above $E_{\rm Ps}$, with one of those from Jain [11] being the most successful, for energies greater than 20 eV, in terms of reproducing the current (and thus earlier) experimental TCSs. Unfortunately, to achieve this that author had to use an absorption threshold value ($\equiv E_{\rm Ps}$) of 4.25 eV, which is quite a bit lower than the physical energy. Therefore, the agreement here must be considered to be somewhat fortuitous.

When looking at how all the earlier theories [10–14] compare against the present TCS, below $E_{\rm Ps}$, what is immediately apparent from Fig. 2 is just by how much they underestimate the magnitude of the experimental total cross section. Indeed, one can reasonably characterize the level of agreement between them and the present data as being rather poor. The only exception to this is the elastic ICS model potential calculation result from Jain and Thompson [10], which utilized the potential of Burke and Chandra [37]. However, that calculation is certainly not at an *ab initio* level and so this agreement is probably also somewhat fortuitous. An interesting total cross section versus energy distribution, using a model potential that attempted to account for the target polarization, was reported by Gianturco *et al.* [12]. In this case the TCS magnitude actually decreased as the positron energy decreased below 1 eV, a prediction that is at odds with the results from Jain and Thompson [10], Jain and Gianturco [13], and the present SMC results incorporating polarization. We thus do not believe that calculation from Gianturco *et al.* [12] is physical. The current SMC–SP and SMC–SP+f-type function results are also only in marginal agreement with the results from the earlier computations [10–14], although as shortly discussed in more detail they do provide a qualitatively accurate representation of the experimental TCS and are in better agreement, in terms of the magnitude of the TCS, with the current data below about 2 eV, than any of the previous calculations. As the SMC formalism is *ab initio*, we therefore suggest the current theoretical results represent a genuine advance on what has hitherto been available in the literature. The scattering length (a) is a fundamental concept in quantum physics, with applications in both atomic and molecular and nuclear scattering phenomena [38]. Of particular relevance to this study is its utility in aiding one's understanding of the physics for positron–molecule interactions at low energies. For instance, targets with relatively large dipole polarizabilities lead to a strongly attractive scattering potential, which manifests itself in quite large negative values in their scattering lengths and the existence of a virtual level for the positron projectile. Both the present SMC–SP and SMC–SP+f-type function results predict a positron–methane scattering length of $a \sim -7.4$ a.u. which, although quite small, does support the existence of a virtual state for this scattering system. We note that this value is smaller than that from a semiempirical estimate by Frongillo *et al.* [39].

Finally, in Fig. 3 we compare exclusively the present TCS data and theoretical results at the SMC–S, SMC–SP, and SMC–SP+f levels. Clearly, as noted above, there is a good qualitative correspondence (shape) between the current measured data and computations, with both indicating that the cross section rises significantly in magnitude as one goes to lower incident positron energies. If we compare our SMC–SP and SMC–SP+f results, to that for the SMC–S

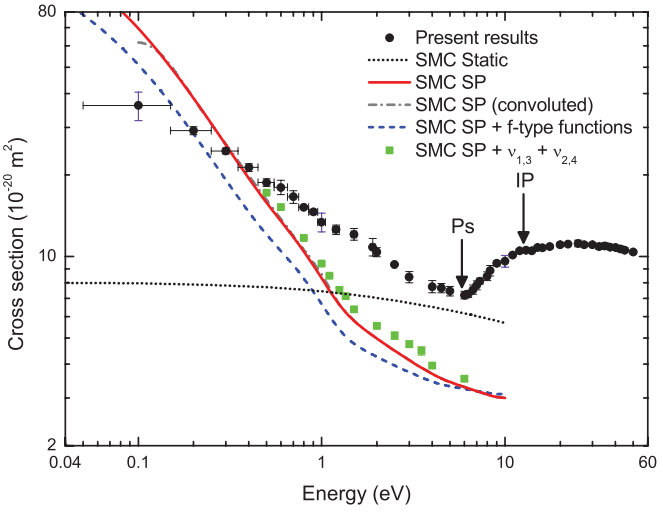

FIG. 3. (Color online) Present experimental (●) TCSs (10^{-20} m^2) and elastic SMC integral cross sections (10^{-20} m^2) for positron scattering from methane. The SMC calculations are at the static (· · ·), static plus polarization (—), and static plus polarization plus f-type function (- - -) levels. A version of our SMC–SP result, but convoluted with the experimental energy resolution (— · — · —), is also shown. Note that it largely lies under the unconvoluted SMC–SP result, except at the lowest energies. Additionally, we plot the SMC–SP result when the vibrational ICSs from Sullivan *et al.* [9] is added to it (■). See also the legend on the figure. Representative total errors are plotted in violet at 0.1, 1, and 10 eV.

level calculation, we immediately confirm the very important role played by the target polarizability in the low-energy positron–methane scattering dynamics. If we now consider the very low energy ($\lesssim$0.4 eV) behavior of the cross sections, then there are two likely reasons for the discrepancy in magnitude between the present measurements and SMC calculations that incorporate for target-polarization. The first, which we have already discussed in some detail, is the angular discrimination effect, which is energy dependent and will have the effect of increasing the magnitude of the experimental TCS more at the lower energies than at the higher energies [20,21,24]. Allowing for this would certainly raise the magnitude of the TCS data toward the SMC results and thus improve the level of agreement between them at the very low energies. The second possible reason is that all the present measured TCSs are actually a convolution over the finite energy resolution of our positron beam, although in practice this is potentially only a major issue at the lower energies. In addition, in this study we tried to reduce this effect by using a Ni moderator [$\Delta E \sim 100$ meV (FWHM)] for positron energies between 0.1 and 9 eV, with the W moderator ($\Delta E \sim 260$ meV) only being employed between 10 and 50 eV. To simulate this situation we have convoluted our SMC–SP result with Gaussian functions of FWHM $\sim$100 meV, with the result of this process also being given in Fig. 3. Clearly this effect (reducing the magnitude of the elastic ICS by $\sim$11% at 0.1 eV) is only important at the lowest energies and also it is really not too significant in this case.

If we now consider the energy regime between 0.4 eV and the positronium formation threshold energy, we see in Fig. 3 that the magnitude discrepancy between the present TCSs and our SMC–SP elastic ICSs becomes progressively worse as the energy increases from 0.4 eV. Of course part of the reason for this is simply that the TCS incorporates all open scattering (elastic, rotational, vibrational, electronic-state) channels in this energy regime, whereas the SMC results are for the elastic channel only. Having said that the lowest singlet electronic state in methane has an excitation energy of $\sim$8.6 eV [40] and so in this case the electronic states do not make a contribution to the observed discrepancy. To investigate this point a little further, we have added the fundamental vibrational mode ICSs from Sullivan *et al.* [9] to the present elastic SMC–SP ICSs, and plotted (as discrete points) the outcome of this process in Fig. 3. While clearly there is some improvement in the level of agreement between our TCS experiment and the theory, there remains a quite significant discord. Note that as the data from Sullivan *et al.* [9] was only for the fundamental mode vibrational excitations, there are many more overtone and combination transitions that still need to be added in. While this will certainly further improve the agreement between us in this energy range, it is hard to credit that these additional modes would explain all the observed differences. There are three possible final factors that we will advance to try and explain, in part, the discrepancies between our measurements and computations. The first is that in the experiment the methane sample exists in a distribution of allowed rotational states, given by the Boltzmann distribution, whereas the computations are for scattering only from the ground rotational level. The second possibility is that as a result of the radioactive decay process, the emitted positrons are highly polarized. Remarkably this degree of polarization persists after moderation [41], perhaps to as high as about 50%, for a range of metallic moderators [41]. Thus while the present experimental beam of positrons is actually quite highly polarized, in our calculations we are effectively scattering with unpolarized positrons. Finally we note that the present calculation finds a Ramsauer-Townsend (RT) minimum in the $\ell = 0$ partial wave around 2.2 eV, which can be responsible for the significant lowering of the cross section for energies above 1 eV. With a further improvement in our description for the target polarization, this RT minimum might move in energy, thereby affecting the comparison between our measured and calculated cross sections. Thus an improved description of the target polarization might well also lead to an improvement in the level of agreement between our measured TCS and SMC–SP calculated elastic ICS. Unfortunately, as the methane molecule has high symmetry, which is not well suited for applications of the SMC method, we have not yet tested this hypothesis. This is due to the great amount of computational effort that would be required to do so. Nonetheless, it is something to be revisited theoretically.

V. CONCLUSIONS

We have reported experimental TCSs for positron scattering from methane, which at the lower common energies are in relatively poor accord with the results from earlier measurements. However, this lack of agreement is likely to be due to the poorer angular discrimination of the earlier spectrometers relative to the current apparatus. In addition, TCSs for positron energies below $\sim$1 eV were presented. SMC-level computations were also carried out as a part of this study, with the important role of the target polarization clearly being educed. The present SMC calculations, that incorporated polarization, were found to be in good qualitative (shape) agreement with the measured TCSs. Discrepancies between them in terms of the magnitude of the cross sections were noted, with possible reasons for those discrepancies being advanced. Finally, our SMC computations determined a scattering length of $a = -7.4$ a.u. for positron–methane scattering and the existence of a virtual state for positron binding.

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