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Low-energy positron scattering from methanol and ethanol: Total cross sections

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We report total cross sections for positron scattering from two primary alcohols, methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$). The energy range of the present study is 0.1–40 eV. The ethanol measurement appears to be original while for methanol we compare our data to the only previous result from Kimura and colleagues [Adv. Chem. Phys. **111**, 537 (2000)], with a significant discrepancy between them being found at the lower energies. Positronium formation threshold energies for both species, deduced from the present respective total cross section data sets, are found to be consistent with those expected on the basis of their known ionization energies. There are currently no theoretical results against which we can compare our total cross sections.

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I. INTRODUCTION

An excellent description for why positron scattering from biological molecules is of interest to the community was recently provided by Surdutovich *et al.* [1]. In summary, they proffered two main reasons in support of their claim; namely, that there are many unanswered questions about the interactions of positrons with biomolecules, e.g., the effect of positronium formation in positron emission tomography (PET) and that positrons, like electrons and heavy-ion projectiles currently do, may serve as a useful tool to study the fragmentation of DNA, proteins, and their various components when they are irradiated [1]. In addition, a knowledge of total cross sections is fundamental in any attempt to simulate the effect for the interaction of radiation, such as positrons or electrons, with matter [2]. For example, the stopping power of such radiation can only be determined if the relevant total cross sections are known [2].

In this short paper we present total cross section results for low-energy positron scattering from the primary alcohols methanol (CH_3OH) and ethanol ($\text{C}_2\text{H}_5\text{OH}$). While significant work has been undertaken with both these species using electrons as a probe (see Ref. [3] and references therein), very little experimental work has been performed using positrons. Indeed there appears to be only the positron-methanol total cross section measurements of Kimura *et al.* [4], from 0.7 to 600 eV incident energy, presently available in the literature. In addition, to the best of our knowledge, no theory currently exists for when positrons interact with either methanol or ethanol.

In the next section of this paper we briefly describe our apparatus and measurement techniques. Thereafter, in Sec. III, our results and a discussion of those results are given. Finally, some conclusions from the present study are provided.

II. EXPERIMENTAL APPARATUS AND MEASUREMENT TECHNIQUES

The positron spectrometer used to make the present measurements was developed by Zecca and co-workers and has already been described earlier in some detail [5]. We therefore do not repeat those details again here, except to note that a tungsten moderator is employed in conjunction with a radioactive ^{22}Na isotope and some electrostatic optics to produce our positron beam. We also highlight that it is standard practice in our laboratory, as a check of the validity of our experimental techniques and procedures, to perform preliminary measurements with molecular nitrogen (N_2). Molecular nitrogen was chosen because of the availability of a nice set of data from Hoffman *et al.* [6], against which we could benchmark our results.

The basis of all our 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 P_1 , the pressure measured with either CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ routed to the scattering cell, k is Boltzmann's constant, T is the temperature of the gas (K), σ is the total cross section of interest, I_0 is the positron beam count rate at P_0 , the pressure with either CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ diverted to the vacuum chamber, and L is the length of the scattering region. Note that in our measurement scheme all the data were initially gathered for methanol, before the source was changed and corresponding data for ethanol were recorded.

For a physical application of Eq. (1) several crucial precautions should be taken and care must be exercised during the measurements. Those considerations include minimizing double-scattering events and ensuring the total cross sections (TCSs) are pressure independent. These were achieved by

keeping the ratio I_1/I_0 to values larger than 0.7 and by establishing the linearity of the plots of $\ln(I_1/I_0)$ versus pressure at selected energies. In addition the high-purity (>99.9% in each case) methanol and ethanol samples used throughout our studies were subjected to several freeze-pump-thaw cycles to ensure they were appropriately degassed. Another possible issue, that polar gases like methanol and ethanol may stick on the surfaces of the gas handling system, scattering cell, or vacuum chamber [3], was not found to be a problem in our studies of these species.

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 chamber [5]. End effects [7] were also considered in the current investigation. It has been demonstrated [8], however, that the effects due to the entrance and exit apertures cancel if the two apertures have equal diameters, so that in our geometry their contribution to the uncertainty in the value of L is likely to be less than 0.2%. In our application of Eq. (1), the value of L used has been corrected to account for the path increase caused by the gyration of the positrons in the focussing axial magnetic field (~ 8 – 10 G) present in the scattering region (typically this was $\sim 5\%$ or less here). The gyration of the projectile particles can also potentially increase the angular resolution error with respect to the no field case [9]. However absolute differential cross sections are not currently known for either e^+ -CH₃OH or e^+ -C₂H₅OH scattering, so that a correction for this effect cannot be made. We note that if such differential cross sections were available, then the true TCSs for methanol and ethanol would be somewhat larger than the values published in Tables I and II, respectively, with no correction.

It is very important in these types of studies for the energy scale to be calibrated accurately. The zero for the energy scale, in the absence of the target gas, was determined here with a retarding potential analysis of the beam [10]. This measurement suggests a probable error of ± 0.2 eV in our energy scale, and an energy width of the positron beam of ~ 0.3 eV (full width at half maximum). It is also crucial to accurately measure the scattering cell pressure, which was achieved with an MKS Baratron capacitance manometer (Model 627 BX, 1 mBar full scale) operated at 45 °C. Since the scattering chamber was at room temperature (25 ± 2 °C), a thermal transpiration correction has been applied to the pressure readings. This correction has been calculated according to the model of Takaishi and Sensui [11], and is less than 2% over the entire energy range. The molecular diameters of methanol and ethanol, used in this procedure, were taken from Van der Bruggen *et al.* [12] and were 4.1 Å for methanol and 5.2 Å for ethanol.

The data collection and analysis codes were driven by software developed at the University of Trento, for application on a personal computer. Measurement time at each discrete energy, for both species, was about 1 h, with each point being the average of 100 single determinations. Note that the standard deviation of that average was also calculated from these respective (methanol or ethanol) data, with these errors being given in Tables I and II along with the present methanol and ethanol TCSs. The positron beam obtained with our apparatus [5] is typically very stable over times ~ 1 month, and all the TCS results reported were taken under stable

TABLE I. The present experimental total cross sections (10^{-16} cm²) for positron scattering from methanol. The errors given represent one standard deviation on the measured cross section at a given energy.

Positron energy (eV)	Cross section (10^{-16} cm ²)		Positron energy (eV)	Cross section (10^{-16} cm ²)	
	Value	Error		Value	Error
0.1	184	12	7	17.1	0.2
0.15	152	21	8	15.8	0.2
0.2	129	15	9	15.6	0.3
0.25	120	4	9.5	15.4	0.2
0.3	112	6	10.5	15.1	0.4
0.4	87	5	12	14.8	0.7
0.5	76	3	13	14.5	0.3
0.6	74	5	14	14.3	0.4
0.7	70	3	15	14.0	0.4
0.8	62	5	16	14.3	0.1
0.9	60	3	17	14.2	0.7
1	57	1	18.5	14.3	0.1
1.3	45.4	0.2	20	13.7	0.8
1.6	39	2	22.5	14.0	0.6
2	32	1	25	14.2	0.4
2.5	28.5	0.3	27.5	13.2	0.3
3	24.2	0.3	30	13.4	0.2
4	20.5	0.7	35	13.3	0.5
5	18.8	1.5	40	12.8	0.1
6	17.3	0.1			

positron beam conditions. The absolute errors on our measurements (not given in either Table I or Table II) were evaluated as the root of the quadratic sum of the contributing errors. We estimate that the absolute TCS errors on both our methanol and ethanol data were typically in the range 5–9 %, with the larger errors occurring only at the lowest energies.

III. RESULTS AND DISCUSSION

In Fig. 1 and Tables I and II we present our positron total cross sections for scattering off methanol and ethanol. We have previously seen in our studies on tetrahydrofuran [7], water [13], 3-hydroxy-tetrahydrofuran [14], and formic acid [15] that at low energies ($E \lesssim 2$ eV) the scattering is dominated by the permanent dipole moment of the polar molecule in question, as well as a significant contribution from the species dipole polarizability. The results for methanol and ethanol, with total cross sections that both increase significantly as one goes to lower incident positron energies, are also consistent with those observations in our earlier work [7,13–15]. That is, at low positron energies, the scattering process is dominated by the permanent dipole moment and important dipole polarizability of the target species. Interestingly, in this case the dipole moments of methanol (1.70 D [16]) and ethanol (1.69 D [17]) are almost equal, although

TABLE II. The present experimental total cross sections (10^{-16} cm^2) for positron scattering from ethanol. The errors given represent one standard deviation on the measured cross section at a given energy.

Positron energy (eV)	Cross section (10^{-16} cm^2)		Positron energy (eV)	Cross section (10^{-16} cm^2)	
	Value	Error		Value	Error
0.1	219	14	7	23.8	0.4
0.15	189	20	8	23.1	0.5
0.2	146	12	9	23.0	0.4
0.25	143	3	10.5	21.7	0.7
0.3	134	16	11	20.4	0.1
0.4	108	6	12	20.2	0.4
0.5	95	3	13	20.4	0.4
0.6	81.0	0.5	14	19.4	0.3
0.7	82	6	15	20.0	0.8
0.8	74	3	16	19.6	0.6
0.9	69	4	17	18.9	1.6
1	70.6	0.9	18.5	19.9	0.6
1.3	58	2	20	19.9	0.2
1.6	45.1	1.2	22.5	19.6	0.3
2	39.8	1.4	25	18.9	0.1
2.5	35	3	27.5	19.3	0.1
3	31.1	0.1	30	18.9	0.1
4	27.7	1.4	35	18.7	1.0
5	25.7	0.4	40	17.6	0.1
6	23.9	0.1			

their dipole polarizabilities (α) are quite different (methanol $\alpha \approx 3.28 \times 10^{-24} \text{ cm}^3$, ethanol $\alpha \approx 5.26 \times 10^{-24} \text{ cm}^3$) [18]. Therefore, as seen in Fig. 1, the fact that the low-energy ethanol TCS data are uniformly larger than the corresponding methanol TCS is possibly due to the dipole polarizability for ethanol being larger than that of methanol. Another possible explanation for this observation is semiclassical in nature, with the ethanol TCS being larger than the methanol TCS simply because ethanol is larger in size compared to methanol (see Sec. II), so that the probability of scattering is greater. Indeed, it is interesting to note that the low-energy ratio of the ethanol to methanol TCS (which is essentially constant) tracks the square of the ratio of those species' respective hard-sphere diameters. However, we believe that the major reason for the ethanol TCS being larger than the methanol TCS at the lower energies is most likely due to ethanol's larger polarizability compared to methanol. At higher energies the interpretation is complicated by the fact that more channels become open.

In Fig. 2 we now present a comparison between the current $e^+ \text{-CH}_3\text{OH}$ total cross section and the earlier data from Kimura *et al.* [4]. Here we see fairly good agreement between the two data sets for common energies greater than about 15 eV. At lower energies, however, the agreement is rather poor, the TCS of Kimura *et al.* [4] both significantly underestimating the magnitude of the scattering and also fail-

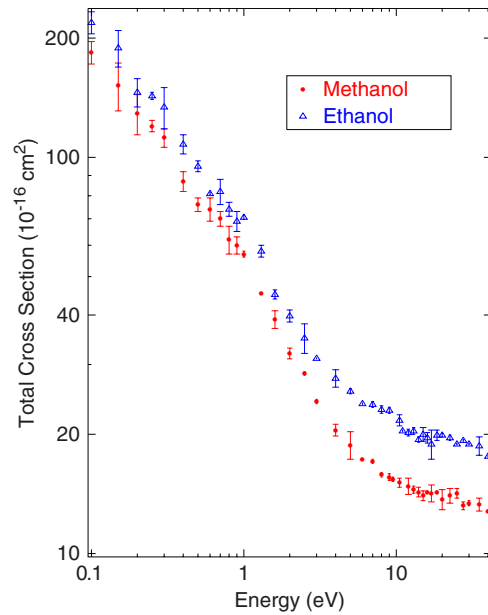


FIG. 1. (Color online) Present experimental total cross sections (10^{-16} cm^2) for positron scattering from methanol (●) and ethanol (△). The errors on the present data represent the standard deviation in the measured cross section at a given energy. See the text for a discussion of the absolute error.

ing to qualitatively reproduce the shape of our TCS. This observation has been previously noted by us in our earlier studies on both H_2O [13] and CO_2 [19], and we believe is indicative of poorer angular resolution in the apparatus of Kimura and colleagues [4] and also possibly due to other deleterious instrumental effects with their apparatus. We note that shapes of our TCSs in both water [13] and CO_2 [19] recently received strong independent support from sophisti-

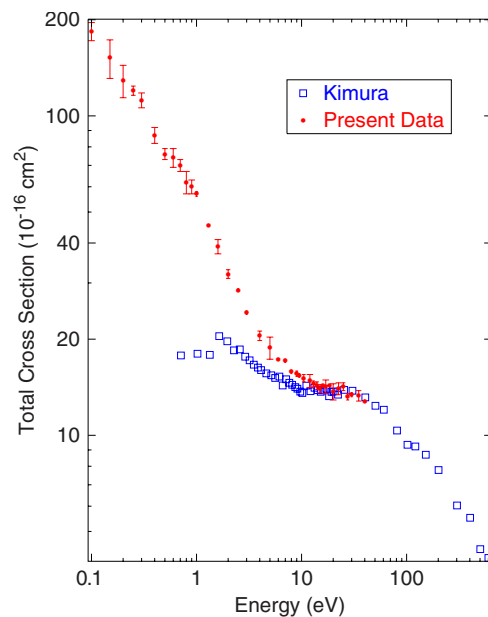


FIG. 2. (Color online) Comparison between the present total cross section (●) and the earlier data of Kimura *et al.* [4] (□) for positron scattering from methanol.

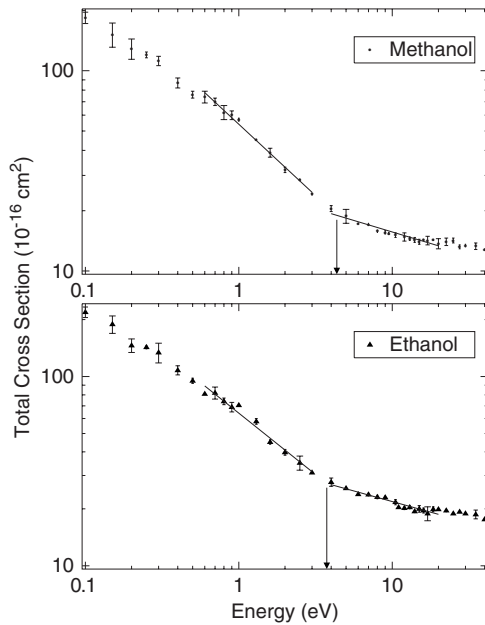


FIG. 3. Present total cross sections for methanol (●) and ethanol (▲) as a function of positron impact energy. Lines of best fit are shown in each case for data points in energy ranges (0.6–3.0 eV) and (4.0–20.0 eV), with the vertical arrow indicating the energy at the intersection of the two lines. The division between the two energy ranges was chosen to maximize the correlation between the fitted lines and the experimental data for ethanol.

cated calculations from Tennyson and co-workers (H_2O) [20] and Lima and co-workers (CO_2) [21]. We are therefore also confident in the validity of our current TCS data, at the lower energies, for positron scattering from methanol. Furthermore, we believe that any low-energy data ($E \lesssim 15$ eV) from the group of Kimura and colleagues should be treated with caution.

Finally, in Fig. 3 we attempt to see if we can determine the corresponding positronium formation thresholds for methanol and ethanol from our TCS results. To this end, in each case, lines of best fit, which seek to highlight at about what energy the monotonic decrease in the TCS with energy changes slope, are plotted. Note that the very low-energy results are ignored in this analysis, due to the possibly important effect that the energy resolution convolution has on the measured TCS. With this caveat in mind, for methanol the slope is seen to change at 4.4 ± 0.3 eV and for ethanol at 3.7 ± 0.3 eV. As the first ionization potential (V_{ion}) for

methanol is 10.84 ± 0.1 eV [17] and for ethanol is 10.48 ± 0.1 eV [17], and as the general rule [22] is that the positronium threshold energy (E_{Ps}) can be obtained from

$$E_{\text{Ps}} = V_{\text{ion}} - 6.8 \text{ eV}, \quad (2)$$

we find that $E_{\text{Ps}} = 4.04 \pm 0.1$ eV for methanol and 3.68 ± 0.1 eV for ethanol. These values for the respective positronium thresholds are consistent with those determined from Fig. 3, so that the energy in each case where the TCS changes slope is indicative of the positronium channel becoming open. Note that we have previously seen similar behavior, for the effect of the opening of the positronium channel on the TCS, in 3-hydroxy-tetrahydrofuran [14] and formic acid [15].

IV. CONCLUSIONS

We have reported on total cross section measurements for positron scattering from the primary alcohols methanol and ethanol. In both cases the effects of these species' permanent dipole moments, important dipole polarizabilities, and the opening of the positronium channel on the total cross sections, were apparent. A comparison with previous data from Kimura *et al.* [4], for e^+ - CH_3OH scattering, suggested serious errors in the earlier data for energies less than about 15 eV. Finally, we note that it would be desirable for the sophisticated electron (e^-) scattering theory that currently exists for e^- - CH_3OH and e^- - $\text{C}_2\text{H}_5\text{OH}$ scattering [3] to be extended to the positron scattering process in each case.

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[1] E. Surdutovich, G. Setzler, W. E. Kauppila, S. J. Rehse, and T. S. Stein, *Phys. Rev. A* **77**, 054701 (2008).
 [2] A. Muñoz, F. Blanco, G. Garcia, P. A. Thorn, M. J. Brunger, J. P. Sullivan, and S. J. Buckman, *Int. J. Mass. Spectrom.* (to be published).
 [3] M. A. Khakoo *et al.*, *Phys. Rev. A* **77**, 042705 (2008).
 [4] M. Kimura, O. Sueoka, A. Hamada, and Y. Itikawa, *Adv. Chem. Phys.* **111**, 537 (2000).

[5] G. P. Karwasz, M. Barozzi, R. S. Brusa, and A. Zecca, *Nucl. Instrum. Methods Phys. Res. B* **192**, 157 (2002).
 [6] K. R. Hoffman, M. S. Dababneh, Y.-F. Hsieh, W. E. Kauppila, V. Pol, J. H. Smart, and T. S. Stein, *Phys. Rev. A* **25**, 1393 (1982).
 [7] A. Zecca, C. Perazolli, and M. J. Brunger, *J. Phys. B* **38**, 2079 (2005).
 [8] H. J. Blaauw, F. J. de Heer, R. W. Wagenaar, and D. H.

- Barends, J. Phys. B **10**, L299 (1977).
- [9] A. Hamada and O. Sueoka, J. Phys. B **27**, 5055 (1994).
- [10] A. Zecca and M. J. Brunger, in *Nanoscale Interactions and their Applications: Essays in Honour of Ian McCarthy*, edited by F. Wang and M. J. Brunger (Research Signpost, Trivandrum, India, 2007), p. 21.
- [11] T. Takaiishi and Y. Sensui, Trans. Faraday Soc. **59**, 2503 (1963).
- [12] B. Van der Bruggen, J. Schaep, D. Wilms, and C. Vandecasteele, J. Membr. Sci. **156**, 29 (1999).
- [13] A. Zecca, D. Sanyal, M. Chakrabarti, and M. J. Brunger, J. Phys. B **39**, 1597 (2006).
- [14] A. Zecca, L. Chiari, A. Sarkar, and M. J. Brunger, J. Phys. B **41**, 085201 (2008).
- [15] A. Zecca, L. Chiari, A. Sarkar, M. A. P. Lima, M. H. F. Bettega, K. L. Nixon, and M. J. Brunger (unpublished).
- [16] National Institute of Standards and Technology, standard reference data, <http://srdata.nist.gov/crcbdb/default.html>.
- [17] *CRC Handbook of Chemistry*, 58th ed. edited by R. C. Weast (CRC Press, Boca Raton, FL, 1977).
- [18] M. A. P. Lima and M. H. F. Bettega (private communication).
- [19] A. Zecca, C. Perazzolli, N. Moser, D. Sanyal, M. Chakrabarti, and M. J. Brunger, Phys. Rev. A **74**, 012707 (2006).
- [20] K. L. Baluja, R. Zhang, J. Franz, and J. Tennyson, J. Phys. B **40**, 3515 (2007).
- [21] S. d'A. Sanchez, F. Arretche, and M. A. P. Lima, Phys. Rev. A **77**, 054703 (2008).
- [22] C. M. Surko, G. F. Gribakin, and S. J. Buckman, J. Phys. B **38**, R57 (2005).