Positron Scattering from Atoms and Molecules

School of Chemical and Physical Sciences

Faculty of Science and Engineering



Luca Chiari

Thesis submitted for the fulfilment of the degree of

Doctor of Philosophy

February 2012

Contents

List of figures	
List of tables	
Summary	
Declaration	
Acknowledgements	
 Introduction Historical foreword to positron physics research Motivations behind this thesis Motivations behind this thesis Overview of positron scattering theory	1 1 5 7 7 11 17 18
 2. Experimental details and measurement techniques 2.1. PAIS apparatus (University of Trento) 2.1.1. Description of the apparatus 2.1.1.1. The source stage 2.1.1.2. The moderator conditioning chamber 2.1.1.3. The vacuum system 2.1.1.4. The scattering region 2.1.1.5. The detection stage 2.1.1.6. Computer control 2.1.2. Experimental techniques and measurement procedures 2.1.2.1. Moderator conditioning and positron emission properties 2.1.2.1.1. W-moderator 	 20 20 22 26 28 30 31 32 34 35 35 39
2.1.2.1.2. Ni-moderator 2.1.2.2. Energy scale calibration and energy resolution of	43 45
 2.1.2.3. Positron transport 2.1.2.4. Preparation of the target sample 2.1.2.5. Experimental precautions and measurement practices 2.1.3 Data analysis and corrections 	51 57 57 60
2.1.3.1. Calculation of the total cross section 2.1.3.2. Thermal transpiration	61 61

	2.1.3.3. Positron path length increase	64
	2.1.3.4. Forward angle scattering effects	66
	2.1.3.5. Overall uncertainties	69
	2.1.4. Validation of our experimental techniques and	70
	apparatus performance	
	2.1.4.1. Positron scattering from argon	70
	2.1.4.2. Positron scattering from krypton	74
	2.2. Atomic and molecular buffer-gas trap and positron beam	78
	apparatus (Australian National University)	
	2.2.1. Description of the apparatus	79
	2.2.1.1. The source and moderation stage	81
	2.2.1.2. The buffer-gas trap	82
	2.2.1.3. The scattering region	85
	2.2.1.4. The retarding potential analyser	86
	2.2.1.5. The detection system	87
	2.2.1.6. Computer control	87
	2.2.2. Measurement procedures	88
	2.2.2.1. Positron moderation technique	88
	2.2.2.2. Trap operation and positron beam formation	89
	2.2.2.3. Preparation of the target sample and scattering in	92
	the cell	
	2.2.2.4. Beam energy calibration and analysis	93
	2.2.3. Data analysis and correction	95
	2.2.3.1. Positron scattering in a strong magnetic field	96
	2.2.3.2. Calculation of the cross sections	97
	2.2.3.2.1. Total cross section	99
	2.2.3.2.2. Differential cross sections	99
	2.2.3.2.3. Inelastic scattering	102
	2.2.3.2.4. Positronium formation cross section	103
	2.2.3.3. Missing angles and forward angle scattering	103
	effects	100
	2.2.3.4. Background scattering	106
	2.2.3.5. Thermal transpiration	107
	2.2.3.6. Overall uncertainties	107
3.	Positron scattering from H ₂	109
	3.1. Introduction	109
	3.2. Experimental details	110
	3.3. Results and discussion	111
	3.4. Summary and conclusions	116
4.	Positron scattering from the isoelectronic molecules N ₂ , CO,	117
	C_2H_2	117
	4.1. Introduction	117
	4.2. Experimental details	119
	4.5. Kesuits and discussion	120
	4.5.1. Molecular nitrogen	121
	4.3.2. Carbon monoxide	125
	4.5.5. Acetylene	128

	4.4. Comparison of the isoelectronic molecules	130
	4.5. Summary and conclusions	132
5.	Positron scattering from the primary alcohols methanol and	133
	5.1 Introduction	133
	5.2. Experimental details	135
	5.3. Results and discussion	136
	5.4. Summary and conclusions	140
6.	Positron scattering from molecules of biological interest	142
	6.1. Introduction	142
	6.2. Formic acid	147
	6.2.1. Experimental details	148
	6.2.2. Results and discussion	150
	6.3. Tetrahydrofuran	155
	6.3.1. Experimental details	158
	6.3.2. Results and discussion	163
	6.3.2.1. Total cross section	163
	6.3.2.2. Positronium formation cross section	167
	6.3.2.3. Inelastic scattering	169
	6.3.2.4. Elastic differential cross sections	172
	6.4. 3-hydroxy-tetrahydrofuran	174
	6.4.1. Experimental details	175
	6.4.2. Results and discussion	176
	6.5. α-tetrahydrofurfuryl alcohol	180
	6.5.1. Experimental details	182
	6.5.2. Results and discussion	183
	6.6. 3,4-Dinydro-2H-pyran	186
	6.6.2 Desults and discussion	18/
	6.7 Dyrimiding	100
	6.7.1 Experimental details	190
	6.7.2 Results and discussion	192
	6.8 Comparison between the molecules of biological interest	196
	6.9. Summary and conclusions	201
7.	Conclusions	202
Ar	opendix A: Curriculum Vitae	205
Ap	Appendix B: Publications	
Re	ferences	208

List of figures

- 1.1. Photograph by Carl Anderson of a track of one of the first positrons ever observed originating from cosmic radiation and passing through a lead plate in a cloud chamber.
- 1.2. Schematic diagram of a typical differential scattering geometry.
- 1.3. Schematic diagram representing a scattering experiment.
- 2.1. Schematic design for the configuration of the positron apparatus at the University of Trento.
- 2.2. Photograph of the positron spectrometer at the University of Trento.
- 2.3. Detail of the first stage of the positron spectrometer at the University of Trento.
- 2.4. Activity of the radioactive ²²Na source of fast positrons, employed in the spectrometer at the University of Trento, as a function of time.
- 2.5. Simulation of the electron beam ray-tracings for the moderator electron gun.
- 2.6. Picture of the cup containing the channeltron used to detect the positrons.
- 2.7. Moderation efficiency of a tungsten, copper and nickel moderator as a function of the foil thickness.
- 2.8. Positron count rate, with a beam energy of 9 eV positrons, as a function of the number of conditioning cycles for a new 1 μm-thick W-moderator.
- 2.9. Typical pattern of the electron power density at the moderator surface as a function of the elapsed time, since the beginning of one conditioning cycle of a 1 μm-thick W-moderator.
- 2.10. Typical apparatus response function measured with a 1 μm-thick Wmoderator in the region of retarding potentials corresponding to the "zero energy peak".
- 2.11. Typical apparatus response function measured with a 2 μm-thick Nimoderator in the region of retarding potentials corresponding to the "zero energy peak".
- 2.12. Schematic representation for a generic positron scattering apparatus for total cross section measurements.
- 2.13. The lowest energy region of an (a) idealised apparatus response function assuming an infinitely small energy width of the positron beam, and (b) the same function but now accounting for the finite energy width of the beam.
- 2.14. Typical apparatus response function of the Trento spectrometer as measured with a 1 μ m thick W-moderator.

- 2.15. An ideal linear (in log-log scale) cross section and the same cross section convoluted with Gaussian functions of FWHM of 260 meV and 100 meV.
- 2.16. Electrical schematic of the PAIS apparatus, depicting the various elements and their power supplies.
- 2.17. Positron count rate against solenoid current, with a 1 μm-thick Wmoderator at 18 eV positron energy.
- 2.18. Positron count rate with respect to the deflector voltage for a 2 μmthick Ni-moderator at 50 eV positron energy and a 1 μm-thick Wmoderator at 9 eV energy.
- 2.19. Schematic diagram showing SIMION ray-tracing outputs for positron energies at the scattering cell of (a) 0.1 eV, (b) 1 eV and (c) 10 eV.
- 2.20. Schematic flow chart of the software-driven events during a standard measurement cycle.
- 2.21. Typical thermal transpiration correction curves.
- 2.22. Schematic diagrams showing SIMION ray tracing simulations of the gyration of the positrons in the focussing axial magnetic field in the scattering region.
- 2.23. The present positron-argon total cross section results compared with (a) previous experiments and (b) calculations.
- 2.24. The present total cross sections for positron scattering from krypton compared with (a) previous experimental results and (b) model calculations.
- 2.25. Schematic diagram of the positron beam apparatus at the Australian National University.
- 2.26. A schematic drawing of the section of the beamline containing the radioactive source and the moderator.
- 2.27. Schematic design of the ANU buffer-gas trap.
- 2.28. Schematic drawing of the scattering cell, together with (a) the first retarding potential analyser and (b) a shielding mesh that prevents any voltage penetration from the scattering cell into the positron beam transport region.
- 2.29. Schematic representation of the potential configurations of the various trap electrodes during the three stages of a typical trapping cycle: (a) loading, (b) cooling and (c) dumping.
- 2.30. Schematic representation of the potentials applied during the various stages of the apparatus: (1) the dump stage and (2) the exit gate of the trap with a potential V_{trap} , and (3) the scattering cell at a potential V_{cell} .
- 2.31. A typical RPA cut-off curve for a nominal scattering energy of 25 eV.
- 2.32. Schematic of the typical profile for a retarding potential analysis of the positron beam with the target present in the scattering cell and for a given collisional energy of 60 eV.
- 2.33. RPA cut-off curves for positrons with incident energy higher than the first inelastic threshold in the absence of the target and after scattering from the target, with (a) M = 1 and (b) M = 35.
- 3.1. The present total cross sections for positron scattering from H_2 are compared with previous experimental measurements.

- 3.2. The present total cross sections for positron scattering from H_2 are compared with results from theoretical models.
- 4.1. Schematic diagram illustrating the Lewis structures for N_2 , CO and C_2H_2 .
- 4.2. (a) The present total cross sections for positron scattering from N₂, compared against theoretical results at the total cross section and elastic integral cross section level. (b) The present total cross sections for positron scattering from N₂, compared against previous experimental results.
- 4.3. The present total cross sections for positron scattering from CO compared against previous experimental results and available computations.
- 4.4. The present total cross sections for positron scattering from C₂H₂ compared against previous experimental results and theoretical elastic integral cross sections.
- 4.5. The present total cross sections for positron scattering from the isoelectronic molecules N_2 , CO and C_2H_2 .
- 5.1. Schematic diagrams of the structures of the primary alcohols methanol and ethanol.
- 5.2. The present total cross sections for positron scattering from the primary alcohols methanol and ethanol.
- 5.3. The current total cross sections for positron scattering from methanol compared to the previous experimental results.
- 5.4. The present total cross sections for positron scattering from methanol (a) and ethanol (b) together with lines of best fit.
- 6.1. Schematic diagram of the structure of the molecules of biological interest under investigation in the present thesis.
- 6.2. The percentage of dimer target composition in formic acid as a function of pressure at room temperature.
- 6.3. The present total cross sections for positron scattering from formic acid.
- 6.4. The present total cross sections for positron scattering from formic acid are compared with the calculations and other experimental results.
- 6.5. Schematic diagrams of the energy minima structures of the three symmetric conformers of tetrahydrofuran.
- 6.6. Schematic diagram of an unrolled segment of DNA, with the tetrahydrofuran and 3-hydroxy-tetrahydrofuran components highlighted.
- 6.7. Schematic plot of the different electrode potentials set during the trap stages of the present measurements.
- 6.8. The present total cross sections for positron scattering from tetrahydrofuran are compared with the only previous experimental results.
- 6.9. The present total and positronium formation cross sections for positron impact on tetrahydrofuran.
- 6.10. Long range cut-off curve with tetrahydrofuran vapour in the scattering cell and with a beach ratio of M = 5.

- 6.11. The present elastic differential cross sections for positron scattering from tetrahydrofuran, at selected scattering energies.
- 6.12. The present total cross section results for positron scattering from 3hydroxy-tetrahydrofuran as a function of the incident energy.
- 6.13. The present total cross section results for positron scattering from 3hydroxy-tetrahydrofuran are compared with the measurements on tetrahydrofuran performed with the same apparatus.
- 6.14. Schematic drawings comparing the structures of the α -tetrahydrofurfuryl alcohol and 2-deoxy-D-ribose molecules.
- 6.15. The present total cross section results for positron scattering from α -tetrahydrofurfuryl alcohol are compared to theoretical and experimental electron impact cross sections.
- 6.16. The present total cross section results for positron scattering from dihydropyran.
- 6.17. Schematic diagram comparing the structure of pyrimidine with that of the pyrimidine-derived nucleobases cytosine, thymine and uracil, which are found in the nucleic acids.
- 6.18. The present total cross section results for positron scattering from pyrimidine.
- 6.19. Comparison of the present total cross sections for positron scattering from the molecules of biological interest pertaining to this thesis.

List of tables

- 1.1. A list of the most important scattering processes for a low-energy positron colliding with an atom or molecule.
- 2.1. Typical values of the potentials at the electrostatic elements in the electron gun used to produce a collimated and well-focussed electron beam onto the moderator film.
- 2.2. Typical parameters employed at the University of Trento during the heating stage of one conditioning cycle of a W-moderator.
- 2.3. Typical parameters employed at the University of Trento during the warming stage of a conditioning cycle for a Ni-moderator.
- 2.4. The set of potentials applied at the electrodes E5-E10, in order to obtain the ray-tracing results shown in Fig. 2.19, for each of the three selected scattering energies.
- 2.5. The angular discrimination (θ_s) of the spectrometer at the University of Trento, at selected positron energies, as calculated using Eq. (2.27) for the typical conditions of the present experiments.
- 2.6. The present total cross sections for positron scattering from argon.
- 2.7. The present positron-krypton total cross sections.
- 2.8. The angular resolution achievable in a differential cross section measurement at selected incident positron energies.
- 2.9. The angular discrimination at selected incident positron energies, for a typical cross section measurement undertaken with the ANU beamline.
- 3.1. The present total cross sections for positron scattering from H_2 .
- 4.1. A selection of the most relevant physico-chemical properties of the isoelectronic molecules N₂, CO and C₂H₂.
- 4.2. The present total cross sections for positron scattering from N_2 .
- 4.3. The present positron-CO total cross sections.
- 4.4. The present total cross sections for positron scattering from C_2H_2 .
- 5.1. A selection of the most important physico-chemical properties of the primary alcohols methanol and ethanol.
- 5.2. The present total cross sections for positron scattering from methanol.
- 5.3. The present total cross sections for positron scattering from ethanol.
- 6.1. The present total cross sections for positron scattering from formic acid.
- 6.2. The present buffer-gas trap settings.
- 6.3. Estimates of the missing angles at selected energies for the present total cross section measurements with M = 1.

- 6.4. Estimates of the missing angles, influencing the present elastic differential cross section measurements, are given at the investigated positron scattering energies together with the corresponding *M* value.
- 6.5. The present total cross sections for positron scattering from tetrahydrofuran.
- 6.6. The present positronium formation cross sections for positron scattering from tetrahydrofuran.
- 6.7. List of electronic transitions in THF and their corresponding experimental energy thresholds.
- 6.8. List of experimental threshold energies for the ionisation potentials in THF.
- 6.9. The present elastic differential cross section data for positron scattering from tetrahydrofuran, at selected scattering energies.
- 6.10. The present total cross sections for positron scattering from 3hydroxy-tetrahydrofuran.
- 6.11. Present model chemistry results for the dipole moment and dipole polarisability of THF and the two energetically most stable conformers of 3H-THF.
- 6.12. The present total cross sections for positron scattering from α -tetrahydrofurfuryl alcohol.
- 6.13. The present total cross sections for positron scattering from dihydropyran.
- 6.14. The present total cross sections for positron scattering from pyrimidine.
- 6.15. A selection of the most important physico-chemical properties of the biologically relevant molecules under investigation in the present thesis.

Summary

This thesis reports on total cross section results of positron scattering measurements for fourteen atomic and molecular targets in the energy range between ~0.1-50 eV. The investigated targets include the noble gases argon and krypton, the diatomic species molecular hydrogen, the isoelectronic molecules carbon monoxide, molecular nitrogen and acetylene, the primary alcohols methanol and ethanol, and some molecules of biological interest: specifically formic acid, tetrahydrofuran, 3-hydroxy-tetrahydrofuran, tetrahydrofurfuryl alcohol, dihydropyran and pyrimidine. In addition, positronium formation and elastic differential cross sections for tetrahydrofuran are also presented. The experiments were undertaken with the positron spectrometer at the University of Trento in Italy, and with the atomic and molecular buffer-gas trap and positron beam apparatus at the Australian National University in Canberra.

The present total cross section measurements on ethanol and all the biomolecules, except for tetrahydrofuran, appear to be original. The current results for the other pre-studied targets, instead, extend the range of the existing measurements to much lower energies and therefore provide the very first results to validate the available theoretical models in this energy range.

Discussion of the present results is provided in terms of the role played by the relevant physico-chemical properties of the target on the low energy scattering dynamics. The more or less significant dipole polarisability and permanent dipole moment of the investigated species, are found to be responsible for the large magnitude and the dramatic energy dependence of the measured cross sections at very low energy. These properties can considerably affect the attractive dipole interaction between the incoming positron and the target, so that it overcomes the repulsive static potential, leading to a nett attractive interaction. This is, in turn, reflected by the increased probability of scattering at those low energies, as compared to the higher energies.

Comparison with earlier experimental data and existing calculations, where available, is also presented. Fairly good agreement with previous measurements is typically found only above the positronium formation threshold energy. Below that threshold, the present cross sections are usually higher in magnitude, possibly owing to the superior angular discrimination of the spectrometer employed in the current measurements. Poor or marginal agreement is often found with the available calculations, except for the atomic targets where the accord turns out to be good when we compare with the most recent results. This indicates that some further quite significant development in positron scattering models is needed.

Declaration

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Luca Chiari

Acknowledgements

There is a whole bunch of people that I must thank, because they somehow helped me in carrying out this project. I have tried to mention everybody here, however, I may have inevitably forgotten about someone. My sincerest thanks to everyone.

First of all I would like to thank my two extraordinary supervisors Michael J. Brunger and Antonio Zecca, without whom this PhD would have not been possible. Thanks in particular to Michael for giving me the chance of doing this PhD and visiting Australia, but also for his profitable advice. Thanks to Antonio for sharing his vast scientific knowledge with me and for his constant support over many years now. I also have to say thank you to both for the several productive discussions that helped augment my own knowledge and for enriching the content of this dissertation as well.

I must thank both Laurence Campbell and Darryl Jones for their help in settling me down at Flinders University, the fruitful discussions we had and for helping making me feel in Adelaide as if I was at home.

I am very grateful to Stephen Buckman and James Sullivan for giving me the chance of visiting and working with the positron beamline at the Australian National University. I have really appreciated the research carried out in Canberra and the results I got undoubtedly represent an asset to this thesis. The work done and the time spent in Canberra would have not have been the same without a team, and therefore I need to thank Casten Makochekanwa, Joshua Machacek, Wade Tattersall and Emma Anderson. Thanks also to Robert McEachran for his irreplaceable theoretical assistance and of course for sharing some good Aussie red wine at theory nights too.

Special thanks also to the administrative and technical staff at both Flinders and ANU, for their invaluable help in dealing with forms and solving problems and for always being so nice to me.

Last, but not least, I would like to warmly thank my family and friends for their continuous support from overseas. Even if a huge distance separated us, I knew I could always rely on you and this helped me bear the distance with a little less difficulty.