ANALYTICAL APPLICATIONS OF POSITRONS

CONF-850657--1

J. M Dale, L. D. Hulet, S. Pendyala,** W. S. Lyon
Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

DE85 013627

Abstract

In using positrons as analytical tools the experimenter has two quite different options. The first and more obvious is to duplicate electron methods with positrons and see what differences (if any) result. The second is to exploit a unique characteristic of positrons, such as the formation and decay of the positronium atom, to study chemical composition and surface characteristics.

Because positrons do not exist freely in our world, they must be obtained from radioactive sources or nuclear interactions. Source intensity has consequently been a limiting factor in experiments that attempt to duplicate electron applications. Some methods of producing and moderating positrons that have been developed here (and elsewhere) are described as well as results from studies using the sources. Surface measurements require less intense sources and yield useful data on materials such as zeolites, silica gels, graphite and alumina. Experimental apparatus, data and interpretation will be discussed.

*Research sponsored by the Office of Energy Research, U. S. Department of Energy, under Contract DE-AC05-84OR21400, with Martin Marietta Energy Systems, Inc.

**State University of New York at Fredonia

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Introduction

Several years ago our group in the Analytical Chemistry Division (ACD) at ORNL decided to study a new technique: the use of positrons as an analytical tool. Electron spectroscopy has been successful, so why, we wondered shouldn't positron spectroscopy be an equally useful tool. Our program was roughly divided into three parts: (1) development of a modest source of monoenergetic positrons, (2) demonstration of some useful applications of such positrons, (3) production of large quantities of positrons for laboratory analyses. During the time that we have been involved in this annual 2 man year effort, we have seen groups at other laboratories pursue various applications of positrons. This paper will report primarily on the work done in the ACD.

Generation of Monoenergetic Positrons

Positrons have the same rest mass, but charge equal and opposite to that of electrons. Emitted from radioisotopes, their spectra show continuous energy distributions, ranging over several hundred thousand electron volts. Each positron emitter has a characteristic maximum energy; for the commonly used radionuclide ^{22}Na , E_{max} is 550 keV. Many annihilation experiments have been done using fast positrons directly from the source, but the experiments we report on use low energy positrons produced in monoenergetic positron guns which are counterparts of ordinary electron guns. Such guns allow not only the improvement of older spectrometries, but also the development of new methods heretofore not possible. These new fields are in a very rapid state of development.

Fast positrons can be captured and moderated to low energies, and then released at a well-defined energy by certain solids having suitable bulk and surface properties. The moderating material is placed about the positron source so as to intercept a large solid angle. A cavity configuration, such as that shown in Figure 1a is presently being used by the authors. Positrons enter the moderator and are thermalized by electronic collisions. Their kinetic energies become equal to that of the valence electrons of the moderator, approximately 0.025 eV, but the magnitudes of their potential energies are usually much greater than this and may be either larger or smaller than potentials outside the moderator (vacuum level). If the potential is greater inside the moderator than outside, the moderator is said to have a negative work function for positrons, and those positrons that are sufficiently close (50-100 nm) to the moderator surface at the time they become thermal are ejected into the vacuum level with a kinetic energy equal to the work function. Those that become thermalized at greater depths are annihilated before they can escape. Some of the better moderators yield as much as 0.01-0.1% of the thermalized positrons, which means that for a 50 mCi ^{22}Na source the fluxes of monoenergetic positrons can be as high as 10^5 - 10^6 /sec. Thus we are able to generate usable intensities. The monoenergetic positrons can be accelerated to any desired energy by biasing the moderator cavity and coupling it to an electrostatic lens. The radioactive source, moderator, and accelerator and focusing lens assembly is shown in Figure 1b, all surrounded by a radioactive shield. This is the gun design presently being used. It is portable, rugged, and free of radiation

hazard, provided that elementary precautions are taken. The ^{22}Na source presently has an activity of ~ 16 mCi. Fluxes of monoenergetic positrons $>10^5/\text{sec}$ have been obtained. Effective moderators are W, Mo, and Ir. Tungsten moderators are easily prepared and quite stable; they are annealed in vacuum to temperatures above the volatilization point of WO_3 ($>1473^\circ\text{C}$). In addition to removing surface oxides, annealing greatly reduces the concentration of defects (vacancies, grain boundaries) which tend to trap and promote annihilation of thermalized positrons. After cooling, the tungsten surfaces can be exposed to air when being mounted in the moderator cavity. During the first few hours of use positron fluxes decrease rapidly, by factors of 50% or more, but after about 24 hours they become constant. Vacuum pressures in the moderator cavity can be as high as 1×10^{-5} , and the moderator can be intermittently exposed to air without greatly changing its efficiency. The stability and ruggedness of the tungsten moderator is probably due to its innate resistance to oxidation.

The tungsten moderator has a disadvantage, however, of producing a relatively broad positron energy distribution, sometimes as large as 2 eV. Single crystal copper moderators described by Mills (1) and also by Lynn (2), produce positron beams with energy distributions less than 0.5 eV but their techniques require ultra high vacuum conditions.

Figure 2 shows a slow positron spectrometry system presently being tested. Monoenergetic positrons are guided by spherical electrostatic lenses to the entrance of the stainless steel bell jar, and are transferred by cylindrical lenses to the center of the jar where the specimen to be studied is placed. It is necessary to place the radioactive source in a

remote position so that gamma rays are not projected directly into the detector region; otherwise the background due to secondary electrons will be excessive.

Slow positrons can be detected by NaI scintillation counters, but channel electron multipliers are preferable because detection efficiency is high, and the positron must make a direct hit on the cone of the multiplier in order to be counted. Stray positrons that are annihilated by collisions with lenses or slits are not registered because electron multipliers are insensitive to gamma rays. Thus the background of channel electron multipliers is very low. Channel electron multipliers can be miniaturized and fabricated into arrays called "microchannel plates". Distances between individual microchannels can be made as small as 25 μm . Microchannel plates are more commonly used as position sensitive detectors for electrons (3), but our group has recently demonstrated that they can also be used for positrons. we are able to use microchannel plates in focal planes of spectrometers to increase effective counting rates, and to record positron diffraction patterns.

The spectrometer indicated in the bell jar in Figure 2 was constructed according to the design by Lindau (4). It was chosen because of its wide solid angle and high transmission. Since moderated positrons are generated from rather large surfaces, they cannot be condensed into small areas of high flux without having wide convergence angles; this is dictated by the Liouville theorem. Thus the side solid angle of the Lindau spectrometer should better accommodate some of the optical restraints of positron experiments.

Applications of Positrons

For several years the main thrust of our work was toward comparing the scattering of β^+ and β^- from surfaces. We originally hoped to see effects due to core electrons. Source intensity was never as great as we wished, but an early experiment seemed to show a marked difference in structure between scattering peaks for β^+ and β^- and from different materials. These results were non-reproducible and unexplainable after numerous efforts to obtain reliable β^+ scattering data. We have abandoned this effort at least until higher fluxes of positrons become available.

More successful have been our efforts to study surfaces and internal structure in solids. The idea of using positrons for such studies is neither new nor original with us. The method does not require mono-energetic positrons and source strengths as low as 10 Ci have been used.

When a positron enters a solid, it may annihilate directly or it may pick up an electron and form a bound state, the positronium (Ps) atom. The Ps atom has two possible ground states; the o-Ps (triplet spin state) has an intrinsic lifetime of 1.4×10^{-7} sec while the p-Ps (singlet spin state) has a lifetime of 1.2×10^{-10} sec. This long o-Ps lifetime can be observed only in the vacuum or in media with high surface area. Experimentally o-Ps shows lifetimes in the bulk of solids of a few 10^{-9} sec due to a process, called pick-off.

Very long-lived o-Ps ($>10 \times 10^{-9}$ sec) states in porous media have been observed in various systems, where the nature of the pore, and of the gas filling the pore has a significant effect on the rate and mechanism of Ps formation. Thus one can study properties of porous surfaces and processes occurring internally.

To make surface and measurements one embeds a small β^+ source within the material to be studied. As the β^+ 's pass into the material the presence of positronium can be measured in several different ways. We have used coincidence counting to measure half-lives. Using a ^{22}Na source one gates on the 1.23 MeV γ ray and records coincidence between it and the 511 γ rays. Figure 3 shows a simplified version of what happens when β^+ 's interact with matter. The main paths of concern to us are underlined.

It is apparent from Figure 3 that decay measurements should show the presence of at least 3 components: the short lived o-Ps, and two longer-lived o-Ps components representing pores, voids and dislocations and defects. Figure 4 reproduces data obtained from an experiment in which ^{22}Na was imbedded in a fumed SiO_2 sample. Three components were found with relative intensities as shown. The longest lived component is believed to be a measure of porosity, whereas the middle lived component represents electron pick-off. When a non porous material such as Al is used as the annihilator one sees only the fast component: no voids.

A number of investigators have reported similar results (5,6). Some efforts have been made to construct a "universal curve" that relates o-Ps intensity to surface area; here one measures o-Ps lifetimes of "known" surface area materials. This work is continuing.

Production of High Fluxes of Positrons

One of the goals of our project since its inception has been to obtain brighter sources. With higher fluxes of β^+ we might be able to repeat our scattering experiments and understand them. We attempted to prepare a hotter radioisotopic source using 270 d ^{68}Ge , which has a short lived positron emitting daughter, ^{68}Ga . This source was configured in such a way that the brightness was markedly improved, but the yield of electroplated ^{68}Ge was an order of magnitude lower than we expected.

A logical source of positrons is an accelerator. Several members of the group visited Livermore National Laboratory (LNL) where a facility to produce positrons is under development. Encouraged by LNL's progress we have combined with physicists and solid state researchers at ORNL in outlining a program to use the Oak Ridge Electron Linear accelerator (ORELA) as a β^+ source. We would hope to back up the present tantalum converter (which intersects the electron beam to produce γ rays, which in turn interact to produce positrons and electrons by pair production) with a tungsten moderator. The latter would produce a low energy β^+ beam of perhaps 10^8 β^+ /s. With such a flux many interesting possibilities exist excluding a positron microscope. Some of these ideas have been explored in other papers from the group (7,8) and in the future if our plans materialize, perhaps some positive applications can come from our positron work.

REFERENCES

1. A. P. Mills, Jr., Appl. Phys. Lett. 35 (1979) 427.
2. K. G. Lynn, Rev. of Sci. Instrum. 51 (1980) 977.
3. C. D. Moak, S. Datz, F. G. Santibanez, T. A. Carlson, J. Electron Spec. and Related Phenomena 6, (1975) 151.
4. I. Lindau, J. C. Helmer, J. Uebbing, The Review of Scientific Instruments 44 (1973) 265.
5. H. Nakanishi, Y. Ujihira, J. Phys. Chem. 86 (1982) 4446.
6. K. Venkateswaran, K. L. Cheng. Y. C. Jean, J. Phys. Chem. 88 (1984) 2465.
7. L. D. Hulet, J. M. Dale, S. Pendyala, Materials Science Forum 2 (1984) 133.
8. L. D. Hulet, et al., Proc. Intern. Sym. Appl. Tech. Ion. Rad. 3 (1982) 1443, King Saud Univ. Press, Riyadh, Saudi Arabia.

Figure Captions

Figure 1. Positron Source and Positron Gun

Figure 2. Slow Positron Spectrometry System

Figure 3. High Energy Positron Interacts with A Solid

Figure 4. Data From Surface Analysis Experiment Using Positrons

Figure 1. Positron Source and Positron Gun

(a) POSITRON SOURCE AND MODERATOR CAVITY
(b) SHIELDED MONOENERGETIC POSITRON GUN

Figure 2. Slow Positron Spectrometry System

MONOENERGETIC POSITRON SPECTROMETRY

Figure 3. High Energy Positron Interacts With a Solid

High Energy Positron Interactions with a Solid

Figure 4. Data From Surface Analysis Experiment Using Positrons

CONVERGENCE OBTAINED AFTER 15 + 0 ITERATIONS

PARAMETERS FOR SPECTRUM NO 49418

FUMED SiO2 (AMORPH) HS-5

TIME SCALE = 0.8800 NSEC/CHANNEL

PROMPT CURVE

FWHM (NSEC) 4.000

INTENSITIES (%) 100.000

SHIFT (NSEC) 0.000

SPECTRUM ANALYSIS STARTS IN CH. 47 AND ENDS IN CH. 500

NUMBER OF TERMS = 3 NUMBER OF LIFETIME CONSTRAINTS = 0
NUMBER OF CONSTRAINTS FOR RELATIVE INTENSITIES = 0

FREE BACKGROUND

FREE TIME-ZERO

NO SOURCE CORRECTION

VARIANCE OF THE FIT = 2.195

ITS DISTRIBUTION SHOULD BE APPROXIMATELY NORMAL (1, .067)

EXCESS PROBABILITY = 0.00 PCT

<u>LIFETIMES IN NSEC</u>	<u>1.382</u>	<u>10.616</u>	<u>90.608</u>
STANDARD DEVIATIONS	0.004	0.382	0.622

<u>RELATIVE INTENSITIES IN PCT</u>	<u>82.50</u>	<u>2.54</u>	<u>14.96</u>
STANDARD DEVIATIONS	0.06	0.05	0.04

BACKGROUND	94.44
STANDARD DEVIATION	2.31

TIME-ZERO	CHANNEL NUMBER	51.519
STANDARD DEVIATION		0.003

AREA CHECK	AREA FROM FIT	= 0.24655E+07
	AREA FROM TABLE	= 0.24627E+07

MATRIX OF TOTAL CORRELATIONS AMONG FREE PARAMETERS.

THE ORDER IS: RELATIVE INTENSITIES, BACKGROUND, LIFETIMES, TO.

1.000	-0.736	-0.618	0.374	0.546	0.495	-0.220	-0.318
-0.736	1.000	-0.077	-0.219	-0.542	-0.252	0.285	0.330
-0.618	-0.077	1.000	-0.296	-0.174	-0.436	-0.007	0.086
0.374	-0.219	-0.296	1.000	-0.144	-0.414	-0.863	0.084
0.546	-0.542	-0.174	-0.144	1.000	0.558	0.214	-0.801
0.495	-0.252	-0.436	-0.414	0.558	1.000	0.602	-0.314
-0.220	0.285	-0.007	-0.863	0.214	0.602	1.000	-0.120
-0.318	0.330	0.086	0.084	-0.801	-0.314	-0.120	1.000

JOB NO 1

RAW SPECTRUM

IDENTIFICATION NO49418

512	49418	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	366	285	108	104	86	87	94
88	103	104	86	92	92	99	88	89	112
114	120	171	433	1574	5884	19137	51376	113935	202875
295271	342913	328702	259552	180328	110624	64711	37531	22497	14976
10634	8195	6662	5769	5290	4850	4396	4345	4224	3928
3830	3805	3622	3535	3504	3449	3359	3326	3230	3107
3096	3153	3071	3087	3036	3001	2999	2877	2777	2815
2761	2593	2656	2602	2609	2562	2514	2474	2366	2217
2413	2370	2323	2265	2254	2181	2191	2289	2133	2099
2048	2173	2066	1994	1971	1959	1994	1959	1977	1821
1838	1907	1779	1839	1854	1819	1799	1726	1809	1767
1801	1691	1731	1687	1685	1623	1618	1530	1617	1575
1614	1571	1534	1498	1492	1455	1412	1366	1435	1444
1401	1359	1435	1355	1320	1331	1295	1431	1267	1283
1287	1261	1272	1252	1268	1253	1235	1155	1223	1162
1199	1097	1101	1119	1230	1119	1151	1088	1099	1068
1130	1053	1112	1067	1020	1092	1092	1081	1008	977
1005	937	945	978	938	946	945	975	918	963
895	849	971	845	889	899	872	790	887	872
845	790	816	792	813	762	798	816	754	780
708	797	763	772	753	696	755	702	709	710
694	719	644	642	668	691	690	656	621	659
614	649	698	640	605	576	621	606	626	545
621	573	617	564	603	599	569	559	565	592
544	519	550	524	559	519	516	566	549	482
505	489	524	474	491	467	506	478	455	457
469	473	484	498	492	467	473	434	456	426
465	420	428	457	424	408	428	443	425	412
431	398	394	434	404	374	377	415	371	378
365	380	427	387	362	357	351	376	343	370
350	350	336	345	383	314	328	329	357	342
355	322	341	326	348	326	316	317	295	303
326	331	311	312	283	309	319	298	295	302
276	273	285	281	268	301	295	266	287	277
303	246	250	255	285	245	227	260	261	269
270	261	252	256	208	222	248	206	265	277
237	247	204	233	234	221	210	264	232	236
243	238	212	250	194	196	212	253	212	214
181	213	223	199	199	219	196	199	199	236
198	206	224	217	185	188	210	180	189	185
219	176	165	179	189	176	187	214	196	167
173	165	209	180	171	168	167	164	155	200
199	200	202	171	192	170	182	170	169	170
176	165	153	152	188	159	155	143	172	177
144	158	147	149	148	173	147	158	150	175
135	178	139	145	153	162	135	169	143	147
137	135	133	133	147	149	169	132	144	141
140	138	147	137	147	145	113	129	130	128
146	139	134	130	151	129	103	122	141	136
134	134								

GUESSED LIFETIMES

0.3000 2.0000 74.0000

INITIAL T0 = 52.5000

SIGN EXCURSION

SIGN EXCURSION