MASTERFINAL REPORT: STUDY OF PHOTOEXCITED
STATES BY POSITRON METHOD

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Positrons can be used as markers in microscopic studies of molecular systems. This is so because positrons, as antiparticles of electrons, will annihilate with an electron in the medium under conditions that signify the electron density and momenta at the site of the positron. In most insulators, positrons can capture an electron into a stable atomic state before annihilation called positronium (Ps). Positronium, when formed, is a particularly powerful probe of materials since Ps not only annihilates in distinct ways from free positrons. It also has two different spin states which can be perturbed by paramagnetic centers in the medium and, thereby, measure their concentration and properties.

We have taken advantage of this aspect of low-energy positron physics for the study of light-excited electronic states in organic molecules. We were particularly interested in long lived triplet states, which normally yield phosphorescent luminescence on deexcitation. The triplet state has long been the subject of speculation as to its role in biology, the transmission of information, distribution of photo and radiation effects, etc. But interest waned as evidence for the role of triplet states eluded firm experimental confirmation. It was the object of the project under review to assess the potential of the positron method for the detection of trace concentrations of photo-induced triplet states of organic molecules.-

Photomagnetic Positron Annihilation Effects.

Light enters a sample with low concentrations of phosphorescent "markers", i.e., molecules that can be excited by light into triplet state, from which they reach the ground state by intersystem crossing or by slow emission of

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light. The steady-state concentration of randomly distributed molecules diminishes into the sample according to the extinction of the light intensity in the medium. Positrons when injected from an radioactive source, also are implanted with an exponential implantation profile. As fraction of positrons form Ps , positronium diffuses and encounters photo excited triplet states. The interaction can lead to a conversion of o Ps ($S=1$) into p Ps ($S=0$) and a conversion of p Ps into o Ps . Since the former process is proportional to $1/3$, and the latter to $3/1$, the ratio of the probability of p Ps - to - o Ps conversions to o Ps - to - p Ps conversion is 9, provided the process is that of "spin flip" in which the spin state of the photomagnetic species changes from $S=1$ (triplet) to $S=0$ (singlet). The importance of this phenomenon lies in the fact that it is possible only in the case of photo excited spin states, where a change in spin state can occur exothermally. For free radicals in the ground state, or triplet states in the ground state such as O_2 , this is not possible. In consequence only spin "catalysis" can occur here, which leads to a ratio 3.

The experiments are important for two main reasons: they can decide between 9 and 3, and they can give estimates of the interaction cross sections.

2. Results

The changes in positron annihilation induced by photomagnetic molecules clearly support the spin conversion factor 9. Even in photosynthetic systems where triplets are formed and oxygen is produced, the ratio is 9.

The second result is the discovery of giant cross sections for Ps spin flip by photoexcited triplet states in solids, liquids and gases. In fact, cross sections range over a factor 10^6 in going from electron exchange to

spin flip of Ps:

<u>Molecule</u>	<u>S</u>	<u>Process</u>	<u>Cross section</u> <u>$\times 10^{-16} \text{ cm}^2$</u>
O_2	1	electron exchange	1.1×10^{-3}
NO	$\frac{1}{2}$	electron exchange	2.8×10^1
SO_2	1	spin flip	6.8×10^2
ϕCHO	1	spin flip	1.1×10^3

The third result is related to the second. The large cross sections make it possible to detect trace amounts of photo excited triplet states in gases and liquids, even in the presence of O_2 . The sensitivity of gases over a wide range of experimental conditions opens the possibility of applications in pollution research related to photo-chemical reaction in air. The giant interaction and the ratio of 9 of para - to - ortho Ps spin conversion probabilities in such encounters pose intriguing new quantum-theoretic questions about the scattering of leptonic atoms on excited electronic states of matter.

Outlook

The research on photomagnetic Ps spin conversion has lead to the formulation of a problem that pertains to all statistical systems of particles in confined spaces. The confinement can be absorbing walls in small grains, in foams, or in extended media with point traps. In such situations, the fastest diffusing particles disappear first from the volume. In consequence, the mean kinetic energy, $\bar{E}$, of the particle ensemble will differ from the thermal value $(3/2)kT$, where T is the temperature of the medium. This phenomenon of $\bar{E} - (3/2)kT \neq 0$ is now referred to as diffusion fever, which appears to be a pronounced effect in positron annihilation studies. The importance in other contexts are under review.

- Papers related to this work.

W. Brandt, Photomagnetic positron annihilation effects, Adv. Chem. Ser. 175, 89-107 (1979).

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