

eter-dependent cross section for Coulomb K -shell ionization by slow particles is confirmed in detail with protons by coincidence measurements between the emerging scattered particles and the characteristic target K -shell x rays emitted in the process of filling the K -shell hole created by the penetrating particle. This provides a well-documented basis for the quantitative search of impact-parameter-dependent deviations that must occur when $Z_1 \rightarrow Z_2$ and Pauli excitation of the K shell becomes dominant.

One of us (W.B.) had the benefit of discussions with G. Basbas, L. C. Feldman, and R. Laubert.

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Photomagnetic Positronium-Spin Conversion in Solids*

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We have observed spin conversion of orthopositronium and parapositronium in interaction with photoexcited, metastable, paramagnetic triplet states of phosphorescent molecules in rigid solutions, through changes in the positron lifetime spectra induced by light. The results bear on the statistics of the spin conversion processes, and on the diffusion of positronium in solids.

Phosphorescence of organic molecules in solid solutions is attributed to the slow (relative to fluorescence) emission of light in symmetry-forbidden transitions from the lowest paramagnetic triplet state T (spin quantum number $S = 1$) to the diamagnetic singlet ground state ($S = 0$).^{1,2} Photomagnetism was first demonstrated in the pioneering work of Lewis, Calvin, and Kasha³ through measurements of the magnetic susceptibility of phosphorescent solids under illumination. Since then, the properties of molecular triplet states have been investigated extensively by electron-spin resonance and in the framework of exciton physics.⁴

We report first observations of the photomagnetic spin conversion of orthopositronium o -Ps (electron and positron spins parallel, $S = 1$) and of parapositronium p -Ps (electron and positron spins antiparallel, $S = 0$) in interaction with molecules in photoexcited triplet states, imbedded in rigid diamagnetic matrices. Our results open the possibility for measurements of the spin-statistic probabilities of ortho-to-para and of para-to-ortho positronium conversion. Moreover because of its monotonic dependence on the light intensity, spin conversion provides a flexible new method for the study of Ps propagation in solids through the interaction with conversion

sites of continuously variable steady-state concentration.

Conceptually the experiment is straightforward. Light of wave number $\bar{\nu}$ and intensity $I_0(\bar{\nu})$ enters, at $x=0$, a solid slab of thickness D of a transparent solvent of molecular density n , containing phosphorescent molecules at the concentration c . At the depth x , the light produces a steady-state concentration $c_T(x, \bar{\nu})$ of randomly distributed triplet-excited molecules T . In the validity range of Lambert-Beer's law,

$$c_T(x, \bar{\nu}) = c \frac{\varphi_T \tau_T \epsilon(\bar{\nu}) I_0(\bar{\nu}) \exp[-\epsilon(\bar{\nu}) cnx]}{1 + \varphi_T \tau_T \epsilon(\bar{\nu}) I_0(\bar{\nu}) \exp[-\epsilon(\bar{\nu}) cnx]}, \quad (1)$$

where φ_T is the triplet-formation efficiency and τ_T the phosphorescent lifetime; $\epsilon(\bar{\nu})$ denotes the photoabsorption cross section which is proportional to the usual extinctions coefficient.

Positrons enter from an Na^{22} source through the opposite surface of the slab, at $x=D$.⁵ They are stopped and form Ps at x , with probability

$$\delta p_{\text{Ps}}(x) \approx \beta \mu \exp[-\mu(D-x)] \delta x, \quad (2)$$

where β is the Ps yield, and $\mu = 49.9\rho \text{ cm}^{-1}$ is the electronic-mass absorption coefficient⁶ in terms of ρ , the density of the solvent in grams per cubic centimeter. In our experiments ($c_T \leq 10^{-2}$) the solids remain diamagnetic under illumination with regard to Ps formation in the sense that o -Ps is formed relative to p -Ps in the ratio 3:1. Practically all positrons bound to an electron propagate as Ps through the solid and annihilate with an electron into two γ 's: p -Ps predominantly by self-annihilation at the rate $\gamma_p \approx (0.2 \text{ nsec})^{-1}$, and o -Ps by electron pickoff from the solid at the rate $\gamma_o \approx (1 \text{ nsec})^{-1}$. In competition with annihilation, Ps encounters photomagnetic sites T at the rate $\chi c_T(x)n$ (χ being the volume rate), where p -Ps converts into o -Ps with probability α_p , and o -Ps into p -Ps with probability α_o either through Ps- T compound formation or scattering.⁷ As a result, p -Ps contributes to the o -Ps concentration in the sample at the conversion rate $\kappa_p(x)$, and o -Ps concentration at the conversion rate $\kappa_o(x)$, where

$$\kappa_p(x) = \alpha_p \chi c_T(x)n, \quad \kappa_o(x) = \alpha_o \chi c_T(x)n. \quad (3)$$

Two coupled rate equations govern this behavior, of the same structure as treated earlier.⁸ The solution has two lifetime components of the probability, $\delta p_{\text{Ps}}(x, t)$, that Ps formed at the time

$t=0$ at x has not yet annihilated at t ,

$$\delta p_{\text{Ps}}(x, t) = \delta p_{\text{Ps}}(x) \left[\frac{\gamma - \Gamma_2}{\Gamma_1 - \Gamma_2} \exp(-\Gamma_1 t) + \frac{\Gamma_1 - \gamma}{\Gamma_1 - \Gamma_2} \exp(-\Gamma_2 t) \right]_x. \quad (4)$$

In the present context $\gamma = (\gamma_p/4) + (3\gamma_o/4)$ and, since $c_T \ll 1$,

$$\Gamma_1(x) = \gamma_p + \kappa_p(x), \quad \Gamma_2(x) = \gamma_o + \kappa_o(x). \quad (5)$$

The experiment registers the mean two-component positron lifetime spectrum of the cell assembly. We fold into an average short component the shortlived term of Eq. (4) and the positron fraction $(1 - \beta)$ that annihilates as "free" without forming Ps with a $c_T(x)$ -independent rate $\sim 2\gamma_p$, and integrate from $x=0$ to $x=D$. To leading terms in the lifetime ranges resolved in our experiment, the resulting spectrum is of the form Eq. (4) where the κ 's in Eq. (5) are replaced by mean conversion rates

$$\bar{\kappa}_{p,o} = \kappa_{p,o}^0 f(\epsilon, \mu, D), \quad (6)$$

with the abbreviation $\kappa_{p,o}^0 = \kappa_{p,o}(x=0)$. The function

$$f \approx [\mu/(\epsilon cn - \mu)] [\exp(-\mu D) - \exp(-\epsilon cn D)]$$

accounts for the overlap between the positron-range distribution and the light-intensity distribution in the sample. Since ϵ , μ , and D are known, the measured changes of Γ_1 and Γ_2 between light on and light off (and the concomitant changes in the intensities of the two components) via Eq. (6) yield, respectively, the conversion rates κ_p^0 and κ_o^0 for the calibrated light intensity I_0 entering the cell at $x=0$. The ratio of the spin-conversion factors is given by

$$\bar{\kappa}_p/\bar{\kappa}_o = \alpha_p/\alpha_o. \quad (7)$$

The Ps propagation rate follows through Eqs. (1), (3), and (6) from the measured dependence of $\kappa_{p,o}^0$ on I_0 .

Dilute solutions ($cn \sim 10^{-2}$ mole/liter) of phosphorescent molecules were prepared in the solvents cyclohexane, glycerol, and boric acid. Benzene was studied pure. A solution was pipetted into a cell consisting of thin quartz walls clamped against variable Teflon spacers ($D \sim 1 - 2$ mm), a Na^{22} positron source backed by a metal strip affixed to one cell wall, and the assembly submerged in liquid nitrogen inside a quartz Dewar. A high-pressure mercury lamp, with a water filter (to reduce sample heating) and ex-

TABLE I. Measured mean conversion rates κ_p and κ_o in several solid solutions. The widely ranging properties and experimental conditions are summarized in the first columns and in Table II. Our experimental data ($\pm 25\%$ uncertain) and the inferred Ps volume-propagation rates are listed in the last four columns. Exponents of 10 are given in parentheses.

Solution	Solute	Solvent ^b (77°K)	c_n (10^{19} cm^{-3})	$c_T(0)$ (ppm)	$\bar{\kappa}_o$ (μsec^{-1})	$\frac{\bar{\kappa}_p}{\bar{\kappa}_o}$	$\alpha_o \chi$ ($\text{cm}^3 \text{sec}^{-1}$)
C.0	benzene	--	6.6 (2)	5.4 (3)	158	1.7	1.4 (-7)
C.1	1,2 benzantracene	c-hexane	1.8	1.9 (3)	55	2.3	2.2 (-6)
C.2	bopq ^a	c-hexane	1.2	7.3 (1)	144	1.9	7.0 (-6)
C.3	chlorophyll	c-hexane	2.4	1.7 (2)	138	2.0	9.1 (-6)
G.1	fluorescein	glycerol	7.2 (-1)	2.5 (3)	103	1.6	5.2 (-9)
G.2	fluorescein	boric acid ^c	1.2	1.9 (3)	22	1.8	1.1 (-8)
G.3	rhodamine B	glycerol	8.4 (-1)	3.2 (3)	103	1.6	3.3 (-8)

^aAbbreviation for bisbutyloxyloxy-*p*-quaterphenyl.

^bBenzene and cyclohexane are crystalline solids; glycerol and boric acid are glasses.

^cAt room temperature.

changable color and gray filters, illuminated the sample with accurately calibrated intensities for fixed time periods (\sim minutes) and was shuttered off for equal time periods. The counts of coincidences between the 1.3-MeV γ issuing from the Na²² source at the creation of a positron and one of the two 0.5-MeV γ 's emitted in the annihilation with an electron were stored separately during light on and off in the halves of a 400-channel analyzer. The two light-on and -off spectra thus accumulated concurrently during a day or so. The light-off spectra have lifetime components that are in good agreement with published data of

the solvents, and are independent of c . The lifetime apparatus and the data analysis are the same as used earlier.⁹ Details of this experiment will be reported elsewhere.

Some of our results, and the conditions under which they were obtained, are summarized in Tables I and II. We have confirmed the dependences of the conversion rates on $I_0(\bar{\nu})$ and D discussed above. Figure 1 shows, as an example, the linear increase of $\bar{\kappa}_o$ with I_0 and its variation with D , as expected from Eqs. (1), (3), and (6).

We conclude: (1) Photomagnetic Ps conversion has been observed through a dependence of posi-

TABLE II. Triplet parameters and illumination conditions of the solutions listed in Table I. Most of the T parameters are quoted from C. Parker, *Photoluminescence of Solutions* (Elsevier, New York, 1968). Exponents of 10 are given in parentheses.

Solution	$\bar{\nu}$ (10^4 cm^{-1})	$\epsilon(\bar{\nu})$ (10^{-16} cm^2)	$I_0(\nu)$ (10^{15} photons $\text{cm}^{-2} \text{ sec}^{-1}$)	Φ_T	τ_T (μsec)
C.0	3.92	3.1 (-3)	7.8	0.8	3.0
C.1	3.45	1.2	15	0.8	1.0
C.2	3.25	1.9	62	0.6 ?	5 (-3) ?
C.3	2.33	2.1	140	0.24	4 (-3)
G.1	2.13	6.9 (-1)	60	0.85	2.5
G.2	2.28	9.2 (-1)	520	0.85	2.5 ?
G.3	1.82	4.2	240	0.3	2 ?

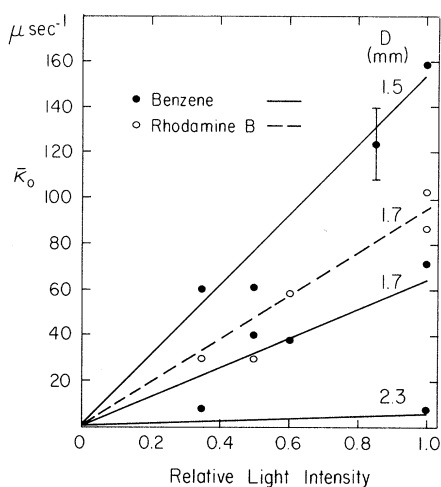


FIG. 1. The conversion rate $\bar{\kappa}_0$ versus light intensity. The slope varies with cell thickness as predicted by Eq. (6) (straight lines) yielding the rate κ_0^0 independent of cell geometry. The absolute error in $\bar{\kappa}_0$ is $\pm 25\%$ (error flag); the relative errors are comparable to the scatter about the theoretical lines.

tron lifetime spectra on sample illumination. The effects can be enhanced and the accuracy of the measurements improved by altering the cell geometry and increasing the light intensity without inducing intolerable temperature fluctuations in the sample, e.g., through the use of lasers. (2) Within experimental error, $\alpha_p/\alpha_o = 2.0 \pm 0.4$ is the same for all triplet states investigated here. Although a detailed discussion of this result is outside the scope of this communication, we note that the ratio is decidedly lower than the value 3 expected for the conversion by a spin- $\frac{1}{2}$ impurity (free radical).⁷ It indicates that Ps-*T* conversion proceeds through catalysis (*T* remains unchanged in the process) as well as through spin flip (*T* converts to a singlet). (3) Since α_o is of order 1, the volume rates χ vary from $\sim 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ in solid cyclohexane and $\sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ in solid benzene to $\sim 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ in the glycerol and boric-acid glasses. If Ps propagation is treated as a diffusion process,^{10,11}

these values indicate relatively large Ps diffusion constants for these open molecular solids, ranging from 10^{-1} and $1 \text{ cm}^2 \text{ sec}^{-1}$ in polar glasses to 10^{-1} and $1 \text{ cm}^2 \text{ sec}^{-1}$ in the Van der Waals solids benzene and cyclohexane.

We have observed similar effects of illumination on positron lifetime spectra in biological systems such as algae, but we are not sure, as yet, whether the changes indicate photomagnetic conversion proper, or whether they signify increases in the oxygen concentration attendant to photosynthesis.

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