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Positronium chemical reactions in solutions: magnetic quenching of *ortho*-positronium in solutions of nitrobenzene in *n*- and *iso*-octane

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Abstract

The magnetic quenching of *ortho*-positronium (*o*-Ps) has been studied for the solutions of nitrobenzene in *n*- and *iso*-octane (2, 2, 4-trimethylpentane). Static magnetic fields up to 20 kG were applied to the solutions and the lifetime of the $m = 0$ state of *o*-Ps was determined as a function of the field strength at 24, 50, and 77 °C. The observed lifetime of *o*-Ps substantially deviates from the quadratic Zeeman effect in *iso*-octane solutions (0.1 and 0.2 M) in the range of several kG at 24 and 50 °C. A small deviation appears at 24 °C and 50 °C but disappears at 77 °C in *n*-octane solution (0.3 M). It is suggested that particular bound states formed during the attachment-detachment of *o*-Ps on nitrobenzene in a solution with a certain range of surface tension may be responsible for the deviation from the quadratic Zeeman effect.

1. Introduction

Positronium (Ps) is the bound state between a positron and an electron. Ps presents either as a singlet (*para*- or *p*-Ps, the magnetic quantum number, $m = 0$) or a triplet (*ortho*- or *o*-Ps, $m = -1, 0, +1$) state with respective intrinsic lifetimes of 125 ps or 140 ns in vacuum. The *o*-Ps lifetime dramatically decreases to a few *nano*-seconds in media due to *pick-off* annihilation of the positron by surrounding electrons. The application of a magnetic field causes the mixing of *para*- and *ortho*- states of the Ps atom with quantum number $m = 0$, resulting in the decrease of the longest-lived *o*-Ps component in the positron lifetime spectrum. Ročanek and Schrader studied the effect of an external magnetic field on the lifetime of positronium (Ps) in several liquids and solutions [1]. They found most systems including solutions of nitrobenzene in cyclohexane and benzene showed a normal quadratic Zeeman effect, i.e. the *o*-Ps lifetimes were decreased in a manner predicted by the elementary atomic theory. However, the lifetime data for the solutions in *n*-hexane could not be fitted to the theoretical equation. The reduction of the *o*-Ps lifetime, especially at low fields, was too large to be accounted for by a small perturbation to the Ps atom in solutions. The anomalous effect by nitrobenzene in *n*-hexane was later confirmed by Billard et al [2] and Shen et al [3]. The largest anomalous effect was observed when the nitrobenzene in *n*-hexane solution was 0.07 - 0.1 M.

Although several different explanations have been proposed for this anomalous effect: (1) spur reactions in *n*-hexane [4], (2) complicated chemical reactions in the kinetic scheme between Ps and *n*-hexane [5], (3) formation of particular Ps states upon the reaction of Ps with nitrobenzene [6], the question why only the solution of nitrobenzene in *n*-hexane gives anomalous effect remains unanswered. Therefore

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it is very important to search for any other systems showing a similar anomalous effect. In the present study, we have chosen *iso*-octane as a solvent because it has a similar physical property of surface tension as *n*-hexane, and *n*-octane as a comparison. Part of results in *iso*-octane has been reported elsewhere.

II. Theoretical Calculation

Under a magnetic field, the lifetime of positron and *p*-Ps with $m = \pm 1$ remains constant, and that of *o*-Ps with $m = 0$ is reduced by the well-known magnetic quenching mechanism—the Zeeman effect. The theoretical equation can be written as:

$$\tau_3 = \frac{1 + a^2}{a^2(\tau_1^0)^{-1} + (\tau_3^0)^{-1}} \quad (1)$$

with

$$a = \frac{\sqrt{1 + X^2} - 1}{X} \quad (2)$$

and

$$X = 4 \frac{\mu_B B}{\Delta E} = \frac{B}{36.4} \quad (3)$$

where τ_1^0 and τ_3^0 are the lifetimes of *p*-Ps and *o*-Ps at the zero field, respectively, μ_B is the Bohr magneton, B is the field strength in kG, ΔE is the hyperfine splitting of the ground state of Ps, which may be different in vacuum and in condensed matter. The effect of the medium on the lifetime of *p*-Ps (τ_1^0) and *o*-Ps (τ_3^0) and ΔE can be described through a phenomenological parameter η :

$$\tau_1^0 = \frac{1}{\lambda_p + \eta \lambda_s} \quad (4)$$

$$\tau_3^0 = \frac{1}{\lambda_p + \eta \lambda_t} \quad (5)$$

$$\Delta E = \eta \Delta E_{\text{vacuum}} \quad (6)$$

where λ_s , λ_t and λ_p are the intrinsic singlet, triplet and *pick-off* decay rate, respectively, and ΔE_{vacuum} is 8.45×10^{-4} eV, the hyperfine splitting energy in vacuum. Since a chemical reaction also may decrease the Ps lifetime, the *o*-Ps with $m = 0$ lifetime is affected by both magnetic and chemical quenchings. Equation 4 and 5 can be rewritten as:

$$\tau_1^0 = \frac{1}{\lambda_k + \lambda_p + \eta \lambda_s} \quad (7)$$

and

$$\tau_3^0 = \frac{1}{\lambda_k + \lambda_p + \eta \lambda_t} \quad (8)$$

where λ_k is the rate of chemical reaction between Ps and other molecules.

III. Experimental

Procedures of positron lifetime measurement and sample preparation were essentially the same as those previously described [7, 8]. The magnetic quenching experiment was conducted for the 0.1 and 0.2 M solution of nitrobenzene in *iso*-octane (2, 2, 4-trimethylpentane), 0.03 M in *n*-octane and pure solvents at three temperatures, 24, 50 and 77 °C. Steady magnetic fields up to 20 kG were applied to the sample and the lifetime of *o*-Ps with quantum number $m = 0$ was determined as a function of the field strength.

The lifetime spectra at the zero field were analyzed assuming three exponential components. The

Fig. 1 The lifetime of *o*-Ps with $m = 0$ in 0, 0.1, 0.2 M nitrobenzene(NB)/*iso*-octane as a function of magnetic field at (a) 24°C and (b) 50°C. Solid and dashed curves represent the theoretical Eq.1 with the best fitted η to the data for pure solvent and NB solutions, respectively. Dotted curves are calculated using η fitted to the data for the pure solvent in the presence of NB.

short lifetime, τ_1^0 , 0.1–0.15 ns, and the intermediate, τ_2^0 , 0.4–0.5 ns, are due to the annihilation of *p*-Ps and free positron, respectively. The longest component with lifetime τ_3^0 and the corresponding intensity I_3^0 was easily attributed to the annihilation of *o*-Ps atoms with $m = 0$ and ± 1 . To determine the lifetime of *o*-Ps with $m = 0$ as a function of magnetic field, the rest of the spectra were then decomposed into four components by constraining the lifetime (τ_4) and the intensity (I_4) of the longest component due to the annihilation of *o*-Ps with $m = \pm 1$ to τ_3^0 and $\frac{2}{3}I_3^0$, respectively. The intensity (I_3) of the third component due to *o*-Ps atom with $m = 0$ was fixed to $\frac{1}{3}I_3^0$. A correction for the positrons annihilating in the source material was applied. All the spectra were analyzed by using the RESOLUTION and POSITRONFIT programs in the PATFIT package [9].

IV. Results and Discussion

The lifetimes of *o*-Ps with quantum number $m = 0$ (τ_3) at 24 , and 50 and 77 °C for 0, 0.1 and 0.2 M nitrobenzene (NB) in *iso*-octane solutions are shown as a function of magnetic field strength in Figs. 1 and 2, respectively. The lines show the behaviors expected from the elementary atomic theory for the quadratic Zeeman effect, and the values of η are obtained from mathematical fitting. In pure solvent,

Fig. 2 The lifetime of *o*-Ps with $m = 0$ in 0, 0.1, 0.2 M NB/*iso*-octane as a function of magnetic field at 77°C. About the various fitted/calculated curves, see Fig.1.

Fig. 3 The lifetime of *o*-Ps with $m = 0$ in *n*-octane and 0.03 M NB/*n*-octane at 24°C, 50°C and 77°C. About the various fitted/calculated curves, see Fig.1.

the lifetimes of *o*-Ps with $m = 0$ agree with the Zeeman effect prediction with reasonable η values (0.5–0.7, see Table 1). However, the reduction of the lifetime with magnetic field in nitrobenzene/*iso*-octane solutions at 24 and 50°C is too large to be explained by applying Eq.1. An example is given in Fig. 4. Whatever η is (0–1), the calculated curves are apparently different from the measurements. Furthermore, the "best-fit" η 's may be too small to be considered as an influence of a non-polar organic solvent. This is the so-called anomalous effect, like the one in nitrobenzene/*n*-hexane [1–3] under the

experimental conditions. In Figs. 1, 2 and 3, all solid and dashed curves represent the theoretical Eq.1 with the η value obtained from the corresponding pure solvent. Since τ_4 is already included the chemical quenching, these solid lines should represent the normal magnetic quenching under the reaction of Ps with nitrobenzene.

The results obtained from 0.03 M nitrobenzene in *n*-octane at 24, 50 and 77°C are illustrated in Fig. 3. Similarly, the *o*-Ps lifetime with $m = 0$ can be fitted with Eq.1 in the pure solvent but a small deviation is shown at 24 and 50°C. A interesting result obtained at 77°C is that τ_3 as a function of

magnetic field strength can be described very well by Eq.1, and the η value (0.58) is close to that obtained from the pure solvent (0.52). That is the magnetic quenching become normal when the temperature increases. In 0.1 M nitrobenzene in *iso*-octane solution, the observed τ_3 also can be fitted properly by Eq.1 with a lower η (0.43) compared with that obtained from the pure solvent (0.74). The anomalous effect become small when the temperature

Table 1 Coefficient η fitted from the Zeeman effect.

Solvent	conc. (M)	η		
		24°C	50°C	77°C
<i>iso</i> -octane	0	0.56*	0.64*	0.74*
	0.1	0.16	0.16	0.43*
	0.2	0.20	0.16	0.14
<i>n</i> -octane	0	0.46*	0.55*	0.52*
	0.03	0.23	0.16	0.58*

*: The lifetimes of *o*-Ps ($m = 0$) agree with the calculation with these η values.

increases. From these results, we conclude that the anomalous magnetic effect is strongly temperature-dependent. This implies that the normal effect is directly related not only to the surface tension of the solvent but also to the Ps-molecular chemical reactivities.

As is well known, nitrobenzene is a effective Ps quencher. The reaction of Ps with this compound causes the reduction of the *o*-Ps lifetime. It is believed that the chemical quenching is due to the reversible formation of a Ps complex [PsNB] [10–14]:

One of the present authors studied the solvent effect on this reaction systematically and showed that the relative stability of the Ps complex depends strongly on the surface tension of solvent [14]. In a solvent with a higher surface tension, the Ps atom is forced to reside in a bubble state with a smaller radius and having a larger total energy. As a result of this larger energy difference between the free Ps and the Ps complex, overall quenching rate constant assumes a higher value. An empirical correlation was found between the rate constants of nitrobenzene and the surface tensions for various solvents.

Table 2 summarizes the values of the surface tensions and the quenching rate constants of nitrobenzene for the five solvents, cyclohexane, benzene, *n*-hexane, *iso*-octane and *n*-octane. It is interesting to note that *n*-hexane and *iso*-octane have very similar surface tensions at about the same

Fig. 4 The lifetime of *o*-Ps ($m = 0$) in 0.2 M solution of *iso*-octane as a function of magnetic field at 24°C. Curves are calculated by Eq.1.

temperature. The Ps quenching rate constants are also similar to each other in these two liquids. Cyclohexane and benzene, giving the normal magnetic effect, have much higher surface tensions and quenching rate constants at the same temperature. It has been suggested that in solvents with a surface tension larger than 26 dyn/cm the quenching reaction proceeds in an irreversible manner by a diffusion-controlled mechanism [13,14]. However, for the solvent with very low surface tension, its nitrobenzene solution shows a normal magnetic effect, and the solution with lower concentration of nitrobenzene gives smaller anomalous magnetic quenching

Thus the anomalous magnetic field effect appears to be remarkable in solutions with a range of relatively low surface tension where the rate constants show an anti-Arrhenius behavior. In a solvent with a low surface tension, the interaction between Ps and nitrobenzene is weakened. We therefore suggest that particular bound states [Ps ... NB], which pertain certain spins of o-Ps, may be formed during the

Table 2 Surface tension (σ) of some solvents and quenching rate constants (k_{ps}) of nitrobenzene solutions.

Solvent	$\sigma^{(a)}$ (dyn/cm)	k_{ps} (M ⁻¹ ns ⁻¹)	magnetic quenching
cyclohexane (20°C)	25.24	15	normal ^(b)
n-hexane (20°C)	18.40	1.6	anomalous ^(b)
benzene (20°C)	28.88	26	normal ^(b)
iso-octane (24°C)	18.77	2.0	anomalous
iso-octane (50°C)	16.11	0.5	anomalous
iso-octane (77°C)	13.5	0.2	normal
n-octane (20°C)	21.4	5.1	anomalous
n-octane (50°C)	18.77	1.9	anomalous
n-octane (77°C)	15.91	0.3	normal

(a) From ref. [15].

(b) From ref. [1].

attachment-detachment of o-Ps on nitrobenzene in such solutions. In these particular states, the interaction between Ps and the electrons in nitrobenzene is weakened. In the case of very low surface tension, these particular states may not form since the bubble size would become larger, and the distance between Ps and nitrobenzene molecule is too long to have this the weak interaction. Detailed structure of the states is unknown and more theoretical study will be required. In a solvent with a higher surface tension, such as benzene and cyclohexane, the Ps complex [PsNB] is tightly bound and the spin properties of Ps in the complex may be completely lost. Therefore, no anomalous effect can be observed in these solvents. This particular state

exists only at a certain range of medium surface tension (around 16-22 dyn/cm) which is counter-balanced by a loosely bounded Ps-molecular state. More experimental results are needed to verify this hypothesis. Experiments in other solutions are in progress at our laboratories.

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