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Anomalous Magnetic Quenching of *ortho*-Positronium in Solutions of Nitrobenzene and 1,3-Dimethyl-2-nitrobenzene

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The magnetic quenching of *ortho*-positronium (*o*-Ps) has been studied for various solutions of nitrobenzene and 1,3-dimethyl-2-nitrobenzene. Static magnetic fields were applied to the solutions and the average *o*-Ps lifetimes were measured as a function of the field strength up to 1 T. Anomalous magnetic quenching, similar to that observed for nitrobenzene in hexane, was found for solutions of nitrobenzene in isopentane, pentane, diethyl ether and heptane as well as 1,3-dimethyl-2-nitrobenzene in dodecane and toluene. It is suggested that *o*-Ps detached from a weakly bound complex between positronium (Ps) and the nitrocompound may be responsible for the anomalous effect.

In 1988, Rochanakij and Schrader reported on a magnetic-field effect of the lifetime of *ortho*-positronium (*o*-Ps), the spin-parallel bound state between a positron and an electron, in several liquids and solutions.[1] The application of a magnetic field causes a mixing of spin-antiparallel *para* and spin-parallel *ortho* states of positronium (Ps) with magnetic quantum number $m=0$, resulting in quenching of the long-lived *o*-Ps component in the positron lifetime spectrum. Most of the systems studied by Rochanakij and Schrader, including solutions of nitrobenzene in cyclohexane and benzene, showed the normal quadratic Zeeman effect, i.e., the average *o*-Ps lifetimes were decreased in a manner predicted by elemental atomic theory. However, the result for solutions of nitrobenzene in hexane could not be fitted to a theoretical equation. The shortening of the *o*-Ps lifetimes, especially at low fields, was too large to be accounted for by a small perturbation to the Ps atom. The anomalous magnetic quenching of *o*-Ps in solutions of nitrobenzene in hexane was later confirmed by Billard et al.[2] and Shen et al.[3] More recently, a similar anomalous effect was observed for a 0.1 $\mathrm{mol\,dm^{-3}}$ solution of nitrobenzene in isooctane (2,2,4-trimethylpentane) by Kobayashi et al.[4]

Although Rochanakij and Schrader proposed a different explanation,[1] it was suggested in more recent studies that the formation of a weakly bound complex between Ps and nitrobenzene may be responsible for the anomalous effect.[2,5] According to Mogensen, the formation of such a complex causes strongly expanded Ps species, having a hyperfine interaction of only 10% of its vacuum value.[5] If the weakly bound Ps complex is really important, the anomalous magnetic quenching should not be limited to solutions of nitrobenzene in hexane and isooctane, because nitrobenzene and other Ps quenchers are believed to form such complexes in a number of solvents. We tested the hypothesis by performing positron-lifetime measurements for various solutions of nitrobenzene and 1,3-dimethyl-2-nitrobenzene under static magnetic fields of up to 1 T.

Experimental

The following solutions were studied in the present work: nitrobenzene in isopentane (2-methylbutane), pentane, diethyl ether, heptane, dodecane and toluene, and 1,3-dimethyl-2-nitrobenzene in dodecane and toluene. Because the Ps quenching capability of nitrobenzene and 1,3-dimethyl-2-nitrobenzene is different from one solvent to another, different additive concentrations were used for different solutions.

Positron lifetime measurements were carried out with a fast-fast coincidence system employing plastic scintillators. The scintillators and magnetically shielded photomultiplier tubes were separated by light guides having a length of 25 cm. Magnetic fields were generated with a commercially available electromagnet (IDX, ISM-130W) having a gap of 2.5 cm. The overall time resolution of the lifetime spectrometer was about 350 ps FWHM and independent of the magnetic field strength. The positron sources were approximately 1 MBq of ^{22}Na sealed in thin Kapton foils. Reagents of the highest purity available were used without further purification. The solutions were degassed by the vacuum freeze-thaw technique to remove oxygen. All of the measurements were carried out at room temperature.

The lifetime data at zero field were decomposed into three exponentially decaying components. The shortest-lived lifetime, $\tau_1=0.1$ ns, is mainly due to the annihilation of *para*-positronium (*p*-Ps). The intermediate lifetime, $\tau_2=0.4$ ns, is due to the annihilation of positrons, which do not form Ps. The longest-lived component with lifetime $\tau_3(0)$ and intensity $I_3(0)$ is attributed to the annihilation of *o*-Ps with $m=0$ and ±1. To determine the average *o*-Ps lifetime ($\tau_3(B)$) as a function of the magnetic field strength (B), the data obtained under nonzero magnetic fields were analyzed into three components by fixing the intensity of the longest-lived component ($I_3(B)$) to $I_3(0)$. All of the analysis was performed using the POSITRONFIT program.[6]

Results and Discussion

The observed average lifetimes of *o*-Ps in solutions of nitrobenzene in isopentane, pentane, diethyl ether, heptane, dodecane and toluene are plotted versus the magnetic field strength in Fig. 1. The solid lines show theoretical curves for the quadratic Zeeman effect, which were obtained using the following equations:[1)]

$$\tau_3(B) = \{\tau_3^{m=0}(B) + 2\tau_3^{m=\pm 1}(B)\}/3 = \{\tau_3^{m=0}(B) + 2\tau_3(0)\}/3, \quad (1)$$

$$\tau_3^{m=0}(B) = (1+a^2)/\{a^2\lambda_{p\text{-Ps}} + \lambda_3(0)\}, \quad (2)$$

where $\tau_3^{m=0}(B)$ and $\tau_3^{m=\pm 1}(B)$ are the lifetimes of *o*-Ps with m=0 and m=±1, respectively, a is the singlet-to-triplet mixing ratio of the Ps atom, $\lambda_{p-\text{Ps}}$ (=8 ns^{-1}) is the intrinsic annihilation rate of *p*-Ps and $\lambda_3(0)$ (=$\tau_3(0)^{-1}$) is the annihilation rate of *o*-Ps at B=0. The mixing ratio is given as

$$a = \{(1+x^2)^{1/2} - 1\}/x, \quad (3)$$

$$x = 4\mu_B B/\Delta E = B/3.64, \quad (4)$$

where μ_B is the Bohr magneton, B is the field strength in T and ΔE is 8.45×10^{-4} eV, the hyperfine splitting of the ground state of Ps in a vacuum.

As can be seen from Fig. 1, anomalously strong magnetic quenching is observed for solutions of nitrobenzene in isopentane, pentane, diethyl ether and heptane. The average *o*-Ps lifetimes in these solutions show pronounced minima at about 0.4—0.8 T; at higher fields they tend to return to the behavior of the normal Zeeman effect, as in the previous case of nitrobenzene in hexane and isooctane.[1—4)] The largest deviation from the theoretical curves is observed when iso-

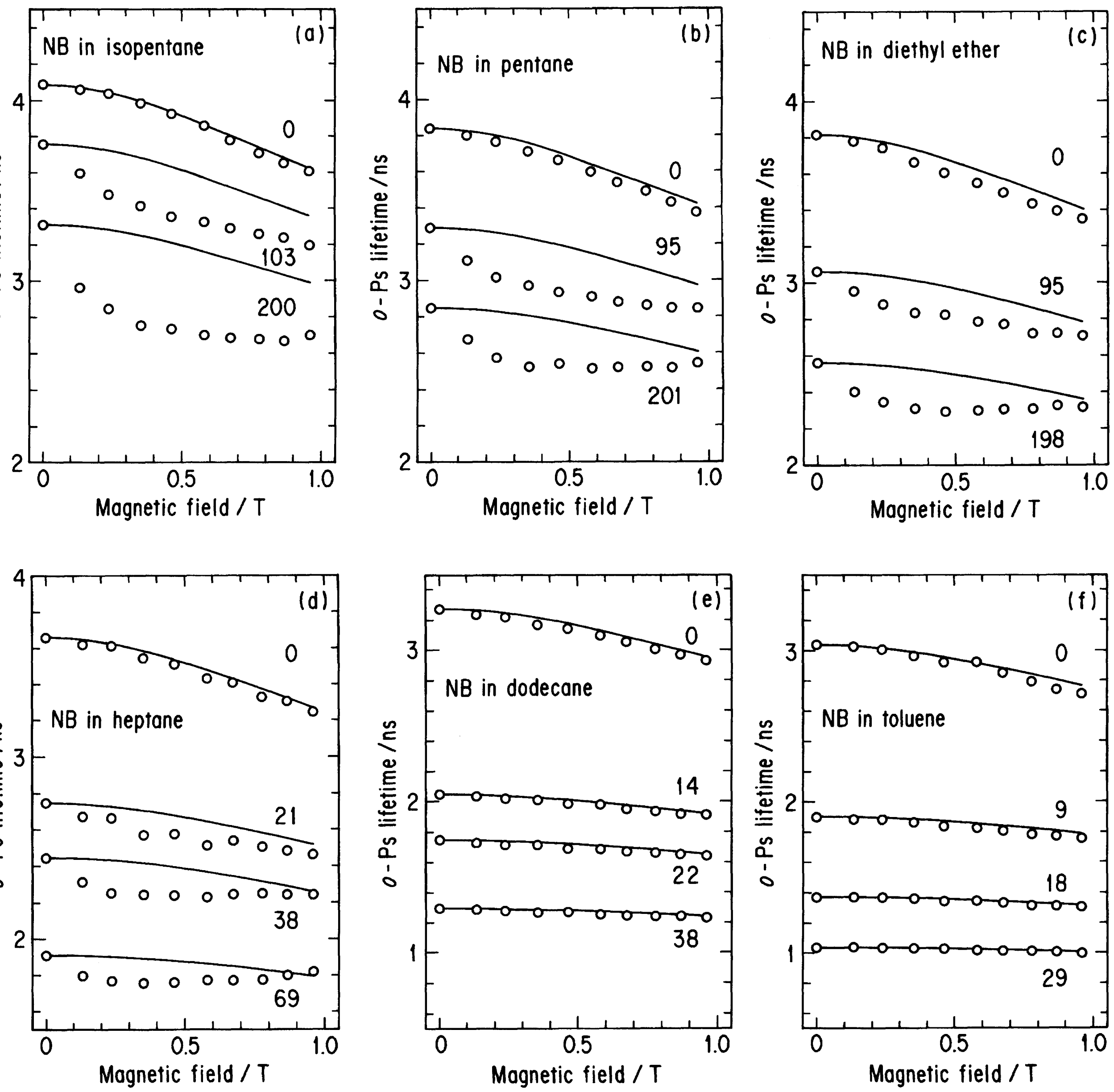

Fig. 1. Plots of the average *o*-Ps lifetime versus magnetic field for solutions of nitrobenzene (NB) in isopentane (2-methylbutane) (a), pentane (b), diethyl ether (c), heptane (d), dodecane (e) and toluene (f). Numbers are concentrations of nitrobenzene in units of mmol dm^{-3}. Solid lines are theoretical curves for the quadratic Zeeman effect.

pentane is used as a solvent. Interestingly, no anomalous effect has been observed for solutions of nitrobenzene in dodecane and toluene (see Fig. 1 (e) and (f)).

Table 1 summarizes the experimental results, including those reported by others,[1—4,7] on the magnetic quenching of *o*-Ps in various nitrobenzene solutions at room temperature. Also included in this table are the surface tensions (σ) of the solvents, together with the overall rate constants (k) of the reaction between Ps and nitrobenzene (NB):

$$\mathrm{Ps+NB} \rightleftharpoons [\mathrm{PsNB}].$$

As discussed by Kobayashi and Ujihira[9] and Kobayashi,[10] the relative stability of the Ps complex [PsNB] depends strongly on the surface tension of the solvent. In molecular liquids, Ps is trapped in a so-called bubble, which is a cavity created by Ps, itself, as the result of its large zero-point energy.[11] In a liquid with a high surface tension, such as toluene, Ps is localized in a small bubble with a large total energy. The encounter of such Ps with a nitrobenzene molecule results in the formation of a tightly bound Ps complex, followed by subsequent positron annihilation in the complex. On the other hand, in a solvent with a small surface tension, such as isopentane, Ps forms a large bubble with a small total energy. In this case, the reaction of Ps with nitrobenzene results in a weakly bound or unstable complex, which can easily decompose into Ps and nitrobenzene within its lifetime of about 0.4 ns by thermal activation.

It can be seen from Table 1 that anomalous magnetic quenching has been observed in many solvents with relatively low surface tension, where Ps forms a unstable complex with nitrobenzene, as is evidenced by the low quenching rate constants of 0.3—6.8 $\mathrm{dm^3\,mol^{-1}\,ns^{-1}}$. It should be noted that isopentane, giving the strongest effect, has the lowest surface tension among the various solvents listed in Table 1. In solvents with a higher surface tension, such as toluene and dodecane, where the Ps complex is supposed to be tightly bound, no anomalous effect has been observed.

A calculation of the positron and electron distributions in the Ps complex with nitrobenzene shows that the majority of Ps is localized on the nitro group.[12] The two particles are not equally distributed over the nitrogen and oxygen atoms, however, and the distance of the positron–electron pair in the Ps complex may be expanded. It is conceivable that in low surface-tension liquids some of the Ps detached from the once-formed Ps complex is located in the vicinity of the nitrobenzene molecule, and preserves the expanded state of the Ps complex. Such a Ps should have a smaller hyperfine interaction compared with free Ps and should give rise to strong quenching at low fields. For example, our result for the 200 $\mathrm{mmol\,dm^{-3}}$ nitrobenzene solution of isopentane in Fig. 1 (a) can be reproduced if we assume that 50% of Ps is in the expanded state with a hyperfine interaction of only 5% of its vacuum value, $\Delta E=8.45\times10^{-4}$ eV, and the rest of the Ps is in the normal state. In high surface tension solutions, since the positron in the Ps complex annihilates with a lifetime not much different from the saturated *o*-Ps lifetime at very high fields, the anomalous effect is not observed.

The average *o*-Ps lifetimes in solutions of 1,3-dimethyl-2-nitrobenzene (DMNB) in dodecane and toluene are given in Fig. 2. It is interesting to note that although solutions of nitrobenzene in these two solvents show normal behaviors, there is some anomaly in the magnetic-quenching data of the DMNB solutions. The Ps quenching rate constants of DMNB in dodecane and toluene, determined from the *o*-Ps lifetimes

Table 1. Magnetic Quenching of *o*-Ps in Various Solutions of Nitrobenzene (NB) at Room Temperature[a]

Solvent	C / $\mathrm{mmol\,dm^{-3}}$	σ / $\mathrm{mN\,m^{-1}}$	k / $\mathrm{dm^3\,mol^{-1}\,ns^{-1}}$	Magnetic quenching
Isopentane	103—200	14.97	0.30	Anomalous
Pentane	95—201	15.97	0.48	Anomalous
Diethyl ether	95—198	17.06	0.54	Anomalous
Hexane	10—100	18.42	1.6	Anomalous[1—3]
Isooctane	100—200	18.77	2.0	Anomalous[4]
Heptane	21—69	20.31	3.7	Anomalous
Octane	30	21.76	6.8	Anomalous[7]
Cyclohexane	Not given[1]	24.95	15	Normal[1]
Dodecane	14—38	25.44	13	Normal
Toluene	9—29	28.53	23	Normal
Benzene	Not given[1]	28.86	26	Normal[1]

a) C is the concentration range studied, σ is the solvent surface tension[8] and k is the rate constant of the reaction between Ps and NB.[10] The rate constant was determined from *o*-Ps lifetimes at B=0 based on the simple kinetic equation:

$$1/\tau_3^{\mathrm{solution}}(0) = 1/\tau_3^{\mathrm{solvent}}(0) + k[\mathrm{NB}],$$

where $\tau_3^{\mathrm{solution}}(0)$ and $\tau_3^{\mathrm{solvent}}(0)$ are the *o*-Ps lifetimes of the solution containing nitrobenzene and of the pure solvent, both at B=0, respectively and [NB] is the nitrobenzene concentration.

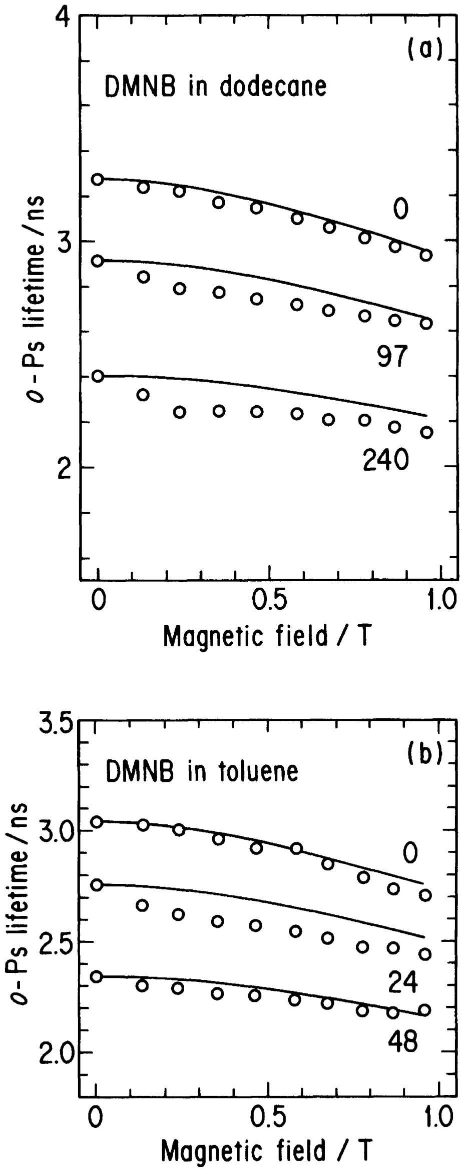

Fig. 2. Plots of the average *o*-Ps lifetime versus magnetic field for solutions of 1,3-dimethyl-2-nitrobenzene (DMNB) in dodecane (a) and toluene (b). Numbers are concentrations of 1,3-dimethyl-2-nitrobenzene in units of mmol dm^{-3}. Solid lines are theoretical curves for the quadratic Zeeman effect.

at B=0, are only 0.42 and 2.1 $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{ns}^{-1}$, respectively. This suggests that Ps forms a weakly bound complex with DMNB, in contrast to nitrobenzene, which has much higher rate constants and forms a tightly bound complex in these solvents. It is conceivable that electron donation from the methyl groups to the benzene ring makes the Ps affinity of DMNB somewhat smaller than that of nitrobenzene, and that the anomalous magentic quenching of DMNB in dodecane and toluene can be ascribed to the expanded Ps formed by detachment from the unstable complex.

Conclusions

The anomalous magnetic quenching of *o*-Ps is not specific to solutions of nitrobenzene in hexane and isooctane. In the present study we observed anomalous magnetic quenching for a number of solutions of nitrobenzene and 1,3-dimethyl-2-nitrobenzene: nitrobenzene in isopentane, pentane, diethyl ether and heptane, and 1,3-dimethyl-2-nitrobenzene in dodecane and toluene. The overall Ps quenching rate constants of nitrobenzene and 1,3-dimethyl-2-nitrobenzene in these solutions are small compared with the values expected for completely diffusion-controlled reactions, revealing that anomalous magnetic quenching is a rather common phenomenon, which appears when a weakly bound Ps complex is produced.

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