OH Radical in Water Studied by Quantum Beats on Positron Annihilation -The Effect of Water Liquid Structures-

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Abstract. Singlet radical pairs of ortho-positronium and hydroxyl (OH) radical were generated in positron radiolysis in water. Quantum beats on the energy distribution of positron annihilation γ-rays caused by the reaction of electron-spin-correlated pairs of ortho-positronium and OH radical were newly measured at 32°C by using positron annihilation age-momentum correlation (AMOC) measurement. The quantum beats can provide information of hyperfine coupling constants of the OH radical in water liquid structures, and hence can provide the information of change of the water liquid structures. The quantum beats appeared at 32°C could not be explained easily. The reason was continuous and slow change of water liquid structures at 32°C. The water liquid structures probably can be understood by using the positron annihilation quantum beat measurements.

1. Introduction
Positron that is anti-particle of electron has the same mass and the opposite charge of electron. Positronium (Ps) is a bound state of positron and electron. The Ps formation process in insulators is well-explained by the spur reaction model proposed by Mogensen in the case of positrons with energies of more than 100eV [1]. The model describes the Ps formation process as a combination of a thermalized positron and one of the excess electrons formed by the positron irradiation at the terminal spur of the positron track within about 1ps. A quarter of the Ps forms as para-Ps (p-Ps, singlet Ps), and three quarters form as ortho-Ps (o-Ps, triplet Ps).

Basically, in a vacuum, p-Ps annihilates with a lifetime of 125ps through the intrinsic annihilation of two annihilation γ-rays being emitted while o-Ps annihilate with an intrinsic annihilation lifetime of 142ns through three γ-rays being emitted. In condensed matter a positron in Ps can annihilate with one of the electrons from the surrounding molecules, which is known as “pick-off” annihilation. This mainly occurs with o-Ps because of its long intrinsic annihilation lifetime. Pick-off annihilation mainly provides two annihilation γ-rays. A positron that escapes the Ps formation, i.e. a free positron, can also annihilate with one of the electrons from the surrounding molecules. The lifetime of the free positrons is about 400ps, with free positron annihilation also mainly providing two annihilation γ-rays.

Because of Ps negative work functions in many materials, Ps is repelled by surrounding substance,

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and hence Ps can form a bubble in liquids. The size of the bubble is controlled by the zero point energy of Ps in the bubble and the energy of the bubble by the surface tension and the pressure. Therefore the bubble size should be larger with increasing temperature, for the less surface tension at higher temperatures. For the larger bubble size, the pick-off annihilation probability of Ps in the bubble is smaller because of the less overlapping of the positron in Ps and electrons on the wall of the bubble.

In water, o-Ps gave an opposite tendency, the shorter lifetimes at higher temperatures. [2] Stepanov suggested o-Ps reactions with spur reactants, such as hydroxyl (OH) radicals, H$_3$O$^+$ cations, and hydrated electrons to explain the temperature dependence observed in water. [3] In water these species form as indicated below within about 1ps.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^* + \cdot\text{e}^- \\
\cdot\text{e}^- + \text{e}^+ & \rightarrow \text{p-Ps}^* (25\%) \\
& \rightarrow \text{o-Ps}^* (75\%) \\
\text{H}_2\text{O}^* + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \cdot\text{OH} \\
\cdot\text{e}^- + n\text{H}_2\text{O} & \rightarrow \cdot\text{e}^-_{\text{aq}}
\end{align*}
\]

(1)

(2)

(3)

(4)

The expected o-Ps reactions with OH radicals, H$_3$O$^+$ cations, and hydrated electrons are as follows:

\[
\begin{align*}
\text{o-Ps}^* + \text{H}_2\text{O}^+ & \rightarrow \text{e}^+ + \text{H}_2\text{O} + \cdot\text{H} \\
\text{o-Ps}^* + \cdot\text{OH} & \rightarrow \text{PsOH} \\
& \rightarrow \text{e}^+ + \text{OH}^- \\
\text{o-Ps}^* + \cdot\text{OH}(\uparrow) & \rightarrow \text{p-Ps}^* + \cdot\text{OH}(\downarrow) \\
\text{o-Ps}^* + \cdot\text{e}^-_{\text{aq}}(\uparrow) & \rightarrow \text{p-Ps}^* + \cdot\text{e}^-_{\text{aq}}(\downarrow)
\end{align*}
\]

(5)

(6)

(7)

(8)

(9)

Here $\cdot$ indicates the presence of an unpaired electron.

Spin conversion reactions (8) and (9) can be easily observed using positron annihilation age-momentum correlation (AMOC) measurements [4]. Most of p-Ps annihilates intrinsically with the momentum of the electron and the positron cancelling each other out. Hence the energy of the annihilation $\gamma$-rays is very close to 511keV, which is the energy equivalent to the rest mass of an electron (or a positron). Conversely however o-Ps and free positrons annihilate by picking off one of the electrons from the surrounding molecules, which then means that the energy distribution of the annihilation $\gamma$-rays is wider because of the Doppler shift. With spin conversion reactions (8) and (9) the p-Ps annihilation increases and the distribution of the annihilation $\gamma$-ray energy becomes narrower. A shape parameter, $S$, is often used for easy comparison of the distribution of the annihilation $\gamma$-ray energy. The value of $S$ is the ratio between the counts appearing in the fixed central area and those in the overall peak area. The narrower the peak the larger the $S$ values. AMOC experiments can provide time resolved $S$-parameters and larger $S$ values at the older positron age region can indicate the existence of the spin conversion of o-Ps. [4]

The radical reaction depends on the spin state of the radicals. The radical reaction of the o-Ps and the OH radical, reactions (6) and (7), can just occur when the spin state of the radical pair is a singlet. The reactions between the o-Ps and the OH radical, (6), (7) and (8), are diffusion controlled and the spin conversion reaction or the radical reaction occur when they meet each other. Hence quantum
beats in the annihilation γ-ray energy distribution were expected to result from the singlet-state probability of the geminate pair of o-Ps and OH radical formed by one ionization process as indicated in (1). [5] Indeed, the hyperfine coupling constant of Ps is very large and then the oscillation between singlet state and triplet state is very fast, probably 15-20ps in water. This oscillation is too fast to detect by AMOC because of the time resolution of 240ps. However, we do not know the spin direction of the proton in OH radical and then there will be two oscillation frequencies, sum and difference of the Larmor frequencies of electrons in Ps and OH radical, making swells which frequency can indicate the hyperfine coupling constant of the OH radical because the Larmor frequency of the electron in the OH radical is much slower than that in the Ps. The probability of the radical reaction of the geminate pair of the o-Ps and the OH radical is more at the swells than between the swells because the spin state can be in a singlet state every 15-20ps. Hence, the probability of the spin conversion reaction is more between the swells and high S(t) values appear as quantum beats. The quantum beats observed here can give the information of the hyperfine coupling constant of OH radicals. [5]

Hirade indicated that there existed reactions of o-Ps and cation radicals in n-hexane. [6] The reactions between geminate pairs should be possible. It means that the quantum beats are also expected on S(t) for n-hexane. In the literatures, there have been many S(t) observed by AMOC even for liquids, and the S(t) for n-hexane was reported by Stoll. [7] The quantum beats were observed for n-hexane and the beat position can be well explained by the mechanism given here.

The quantum beats observed for water at 18°C and 25°C showing that there were two hyperfine coupling constants. [5] Here new results observed at 32°C will be introduced to provide more knowledge on the water liquid structures where OH radical formed.

2. Experimental

AMOC measurements [8] were performed using $^{22}$Na (about 400kBq) sealed in two 7.5μm Kapton foils as the positron source. About 10 % of the positrons annihilate within the foils. Ps does not form in Kapton foil and then there is just one lifetime component that gives about 382ps for the lifetime component from the source. Hence it does not affect the o-Ps reactions. A LOAX-51370/20-P (SEIKO EG&G) type semiconductor detector with an energy resolution (FWHM) of 1.28keV at 662keV was used to detect the annihilation γ-ray energy. The time resolution was about 240ps. Total counts appeared near the 511keV peak and in an about 10ns time range of the AMOC measurement reached about 1 million. The count rate was about 1.2 cps. Ultra-pure water supplied by Wako Pure Chemical Industries was used for the water samples. To remove any oxygen molecules nitrogen gas was bubbled through the samples before use in the experiments. The sample temperature was controlled by a water bath and then there is no magnetic field caused by the heater.

3. Results and Discussion

The positron age dependent S-parameters, S(t), obtained using AMOC in water at 32°C are provided in Fig.1(a). Large S values appeared in the earlier positron age region of up to 0.5ns, which was caused by the annihilation of the p-Ps formed in reaction (2). In the older age region than 1.5-2ns larger S values reappeared that must have been caused by the spin conversion of o-Ps. Moreover, the positron annihilation lifetime spectra constructed by the AMOC experiments for water did not show any beats or oscillations as expected by the mechanism explained above. [5]

The magnitude of the isotropic hyperfine coupling constant, i.e. the Fermi contact term, of the OH radical is 73.25MHz while that of the OH-H₂O complex is 155.3MHz [9]. Just one water molecule can enhance the hyperfine coupling constant to be more than twice the magnitude. The OH radical in liquid water can have OH-nH₂O complex states and hence the expected hyperfine coupling constant will be larger. The hyperfine coupling constant of the OH radicals in water was obtained by fitting the beat positions with the mechanism explained above. [5] The hyperfine coupling constants of OH radicals in the liquid structures as OH-nH₂O were observed here. The structure affects the hyperfine coupling constants making it possible to observe the change in the liquid structures of water using the quantum beats observed there.
It was reported that the hyperfine coupling constants were about 870MHz and 758MHz for 18°C and 810MHz and 678MHz for 25°C, respectively. [5] However, it might be expected to have more complicated liquid structures at higher temperatures. $S(t)$ at 32°C as shown in Fig.1 seems to have complicated structures than those at lower temperatures. It is almost impossible to explain beats in Fig.1 (a) by the mechanism explained above. The effect on the elapsed time of the measurement appeared in (b) and (c) that was obtained by the experiment for the $S(t)$ curve (a). (b) is the first half and (c) is the second half of the AMOC measurement shown in (a). (b) and (c) showed some beats and some of them can be explained by the proposed mechanism as indicated arrows in Fig.1. [5] The hyperfine coupling constants were about 709MHz and 580MHz estimated by the arrows indicated in (c) and (b) respectively. These are not all of the beats appeared here. It is indicating that there exist many water liquid structures where OH radicals formed. Moreover water is not just a simple mixture of all of water liquid structures. The fraction of every structure changes continuously and very slowly. It was reported that there were two hyperfine coupling constants observed at 18°C and 25°C and it was indicating that there could be two water liquid structures. [5] However, there seems to be more structures observed at 32°C and any structures are probably not stable. These things say that there are many water liquid structures and only some of them, probably mainly two structures, are more stable than others. That is the reason why two sets of beats were observed at lower temperatures such as 18°C. [5]

4. Conclusion

Quantum beats were detected in the reactions of electron-spin-correlated o-Ps and OH radical pairs in water at 32°C. These newly observed quantum beats in the annihilation $\gamma$-ray energy distribution caused by the o-Ps reactions provide the opportunity for new research to be undertaken. The changes in the beats can provide information on the change on the liquid structures of water. The $S(t)$ curve measured at 32°C for about 2 weeks did not show clear quantum beats expected by the mechanism of appearance of the quantum beats. It was caused by the change of the water liquid

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*Fig.1 $S(t)$ curve observed through AMOC in ultrapure water at 32°C. (a) was obtained through 2 weeks measurement. (b) was obtained by the first half and (c) was by the second half of the measurement.*
structures during measurement. The $S(t)$ curves obtained with the shorter measurement time could indicate the quantum beats. There probably exist many water liquid structures and only some of them are more stable than others. That is the reason why two sets of beats were observed at lower temperatures such as 18°C. Moreover the water liquid structures changed continuously and slowly.

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References
[1] Mogensen O E 1974 J. Chem. Phys. 60 998–1004
[2] Kotera K, Saito T, Yamanaka T 2005 Phys. Lett. A 345 184–190
[3] Stepanov S V, Byakov V M, Hirade T 2007 Radiat. Phys. Chem. 76 90–95
[4] Castellaz P, Major J, Mujica C, Schneider H, Seeger A, Siegle A, Stoll H, Billard I 1996 J. Radioanal. Nucl. Chem. 210 457–467
[5] Hirade T 2009 Chem. Phys. Lett. 480 132–135
[6] Hirade T and Mogensen O E 1994 Hyperfine Interact. 84, 491-498
[7] Stoll H, Koch M, Lauff U, Maier K, Major J, Schneider H, Seeger A, Siegle A 1995 Appl. Surf. Sci. 85 17–21
[8] Suzuki N, Nagai Y, Hyodo Y 2000 Radiat. Phys. Chem. 58 777–780
[9] Brauer C S, Sedo G, Grumstrup E M, Leopold K R, Marshall M D, Leung H O 2004 Chem. Phys. Lett. 401 420–425