12.5th International Workshop on Positron and Positronium Chemistry

30 August – 3 September 2021, Internet

AMOC measurement for OH radical study in water

Japan Atomic Energy Agency, Ibaraki University

Tetsuya Hirade

This research is partially supported by a Ministry of Education, Culture, Sports, Science and Technology Grant-in-Aid for Scientific Research (C), 20K12501, 2020–2022.

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Positron annihilation age-momentum correlation (AMOC) measurement is a strong tool to investigate chemical reactions of positron and positronium (Ps). However, the count rate of AMOC measurement is usually very low because AMOC is a triple coincidence method. We succeeded to make the AMOC count rate higher than 10 cps, which is almost one million counts a day, by use of four scintillation detectors for 1.27MeV start signal from ^{22}Na.

AMOC measurements on OH radical in water show one more interesting phenomenon on the reaction of OH and ortho-Ps because there are two kinds of OH radical. One of them has a spin correlation on the electrons in the ortho-Ps and the OH radical. The other has no spin correlation. The spin conversion reaction between the spin-correlated pair gives 33% more yield of para-Ps. Hence, it is possible to study OH radical behavior in water by AMOC.

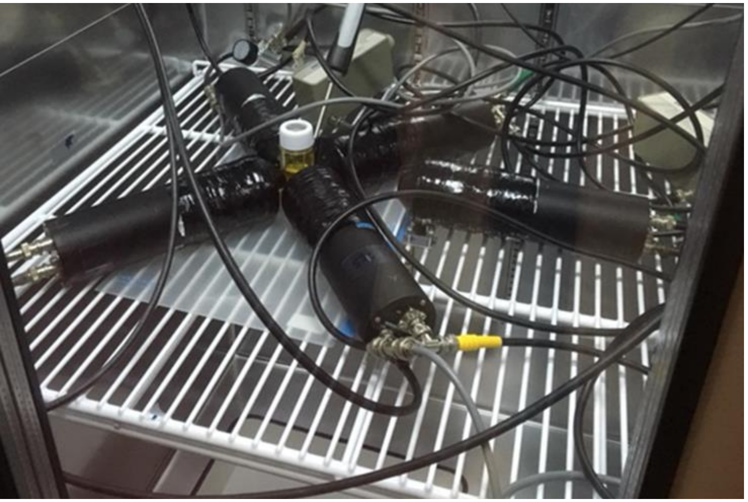
This research is partially supported by a Ministry of Education, Culture, Sports, Science and Technology Grant-in-Aid for Scientific Research (C), 20K12501, 2020–2022.

I am going to show

AMOC with 4 start detectors

and some results of water measurements.

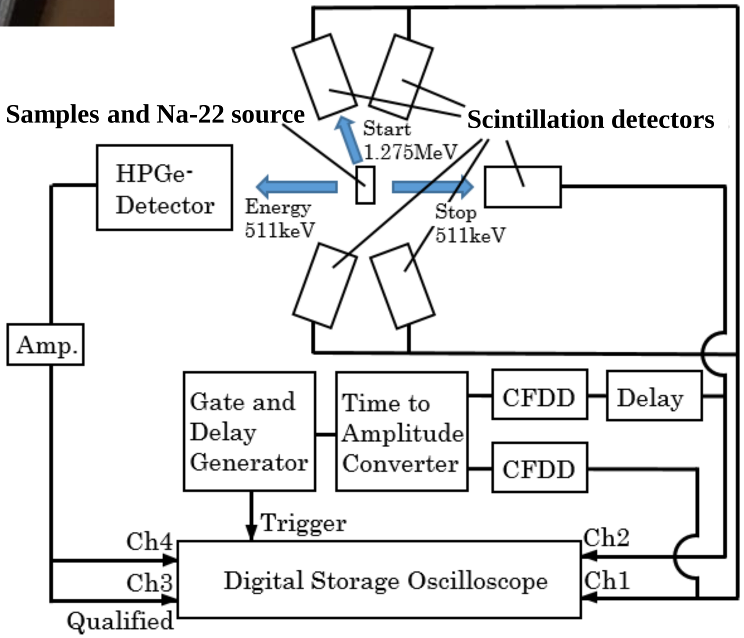
We need to overcome this difficulty.



Triple coincidence method = low counting rate

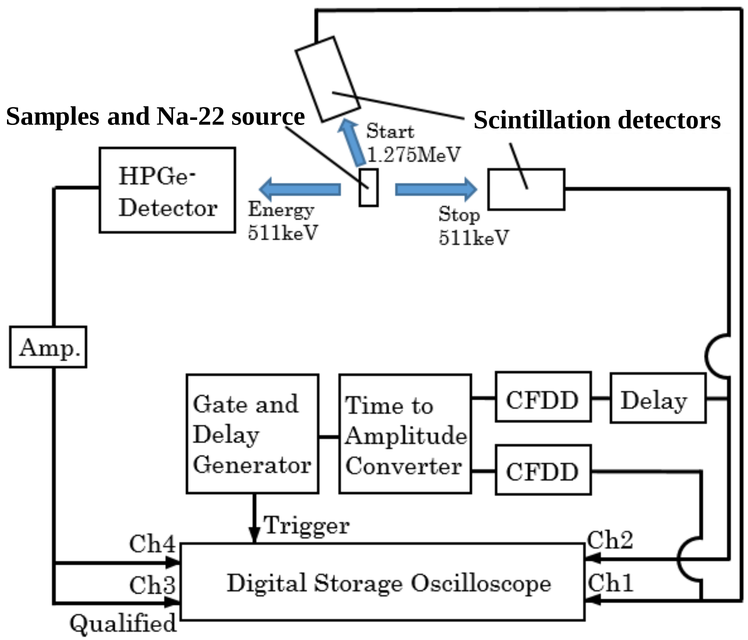
1 week for 1 million counts

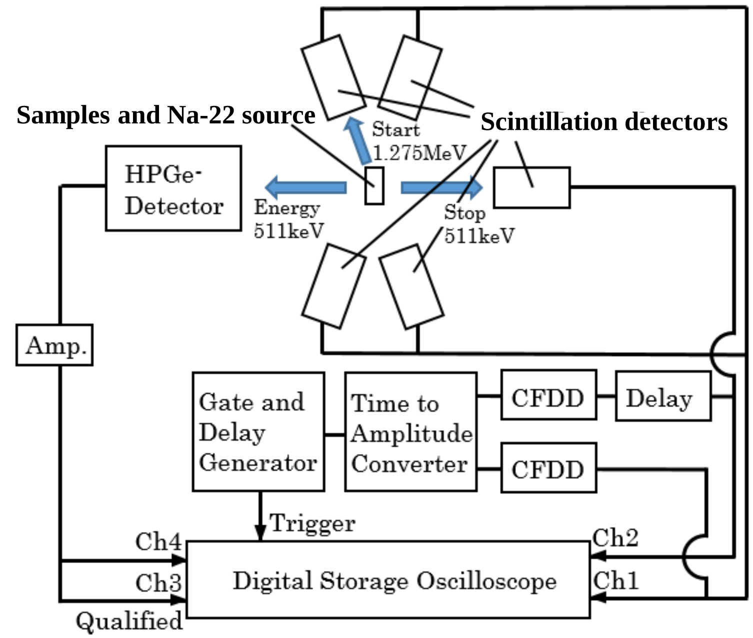
4x counts with 4 start detectors



However,
There is a serious
problem.

T. Hirade et al. , Nuclear Inst. and Methods in Physics Research, A 931 (2019) 100–104


Samples and Na-22 source
Scintillation detectors
Start
1.275MeV
Stop
511keV
Energy
511keV
HPGe-
Detector
Amp.
Gate and
Delay
Generator
Time to
Amplitude
Converter
CFDD
Delay
CFDD
Trigger
Ch4
Ch3
Qualified
Digital Storage Oscilloscope
Ch2
Ch1


Samples and Na-22 source
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Start
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Detector
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Time to
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CFDD
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CFDD
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Ch3
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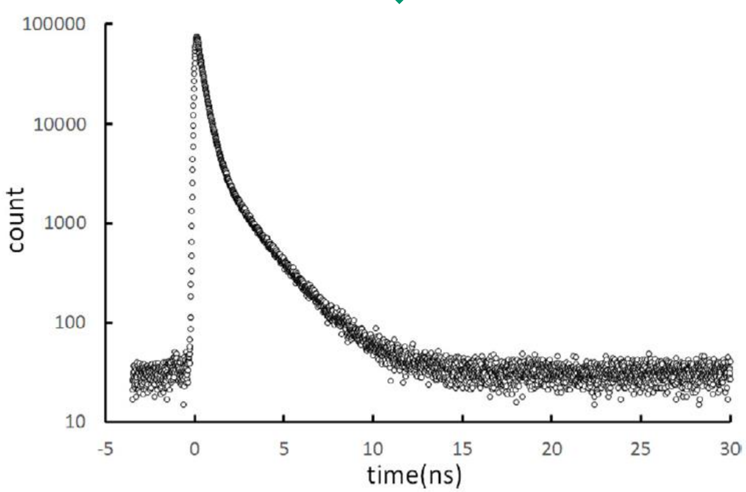
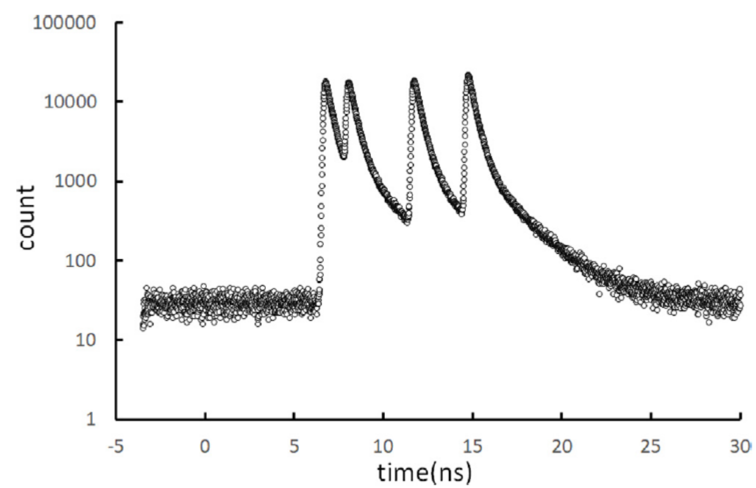
Ch2
Ch1

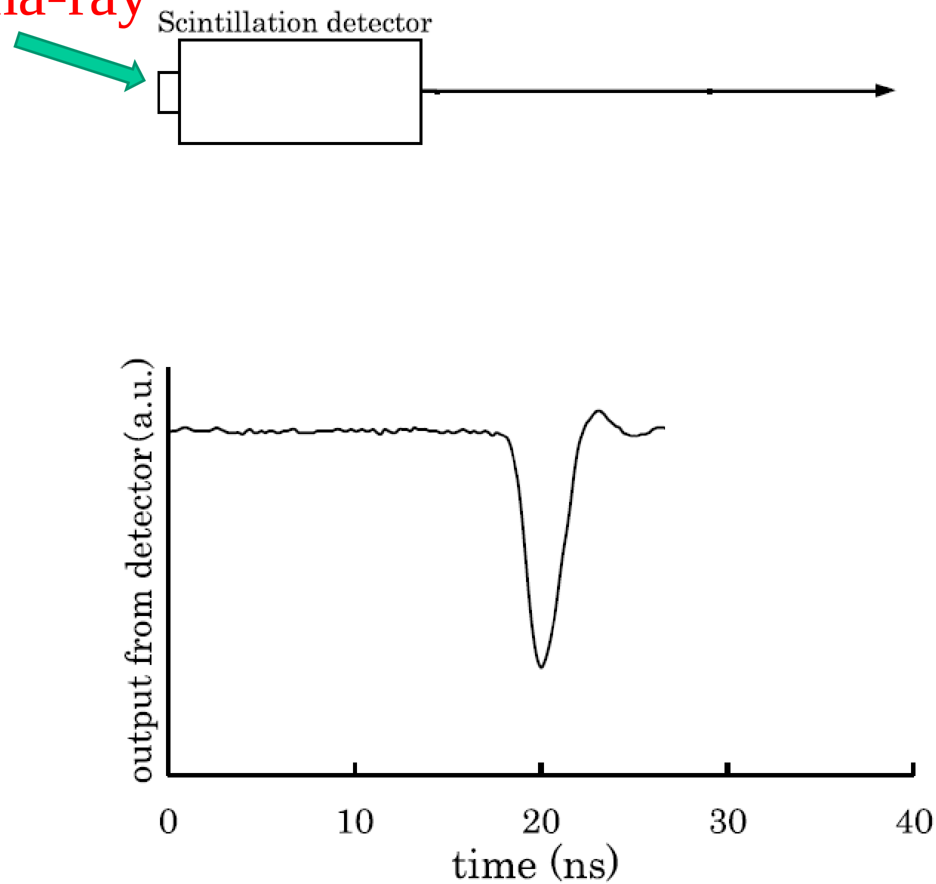

100000
10000
1000
100
10
count
-5
0
5
10
15
20
25
30
time(ns)


100000
10000
1000
100
10
1
count
-5
0
5
10
15
20
25
30
time(ns)

How to solve this problem.

We need detector (sensor) identification technique

Gamma-ray



T. Hirade et al. , Nuclear Inst. and Methods in Physics Research, A 931 (2019) 100–104

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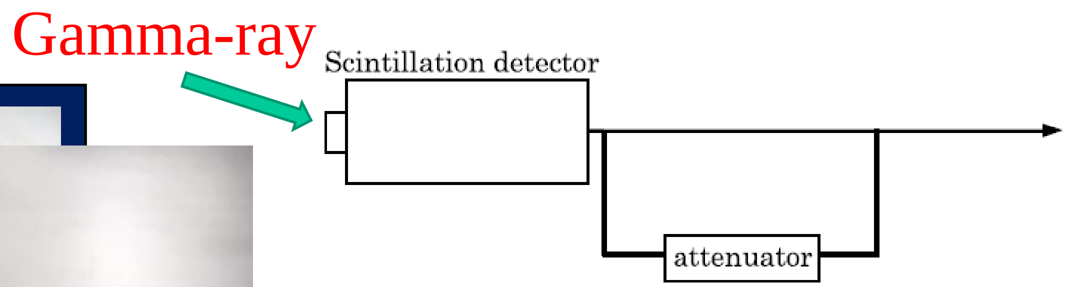
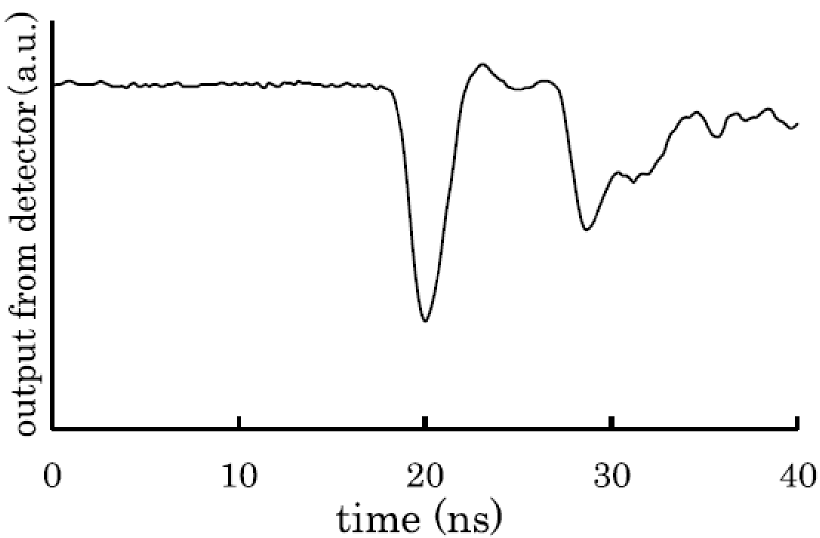
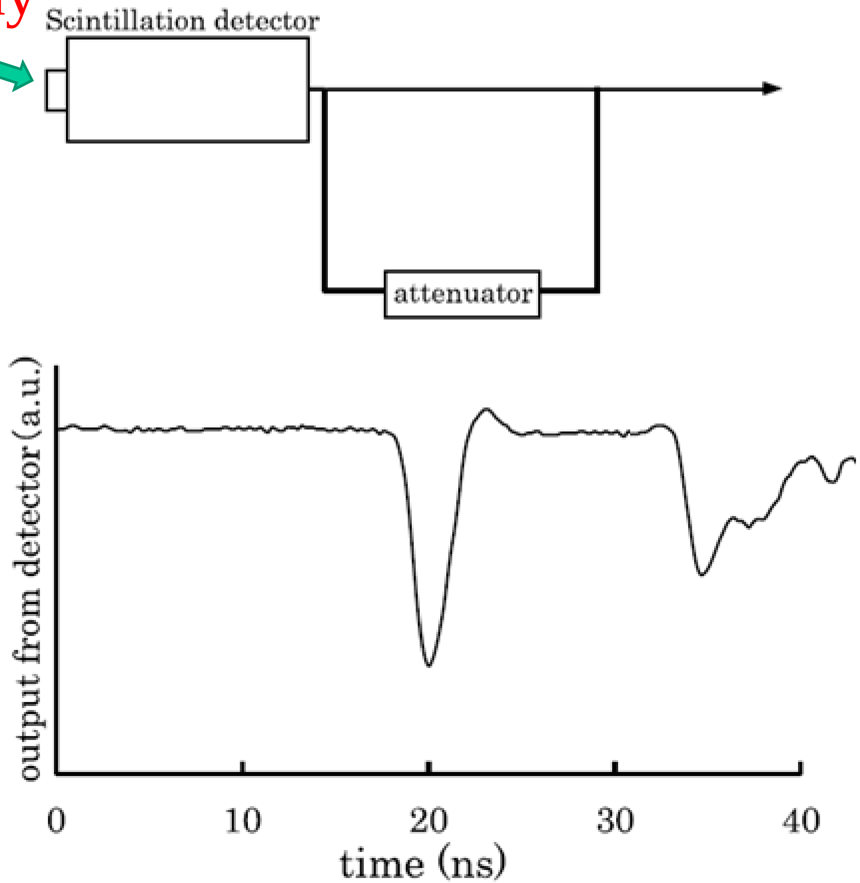




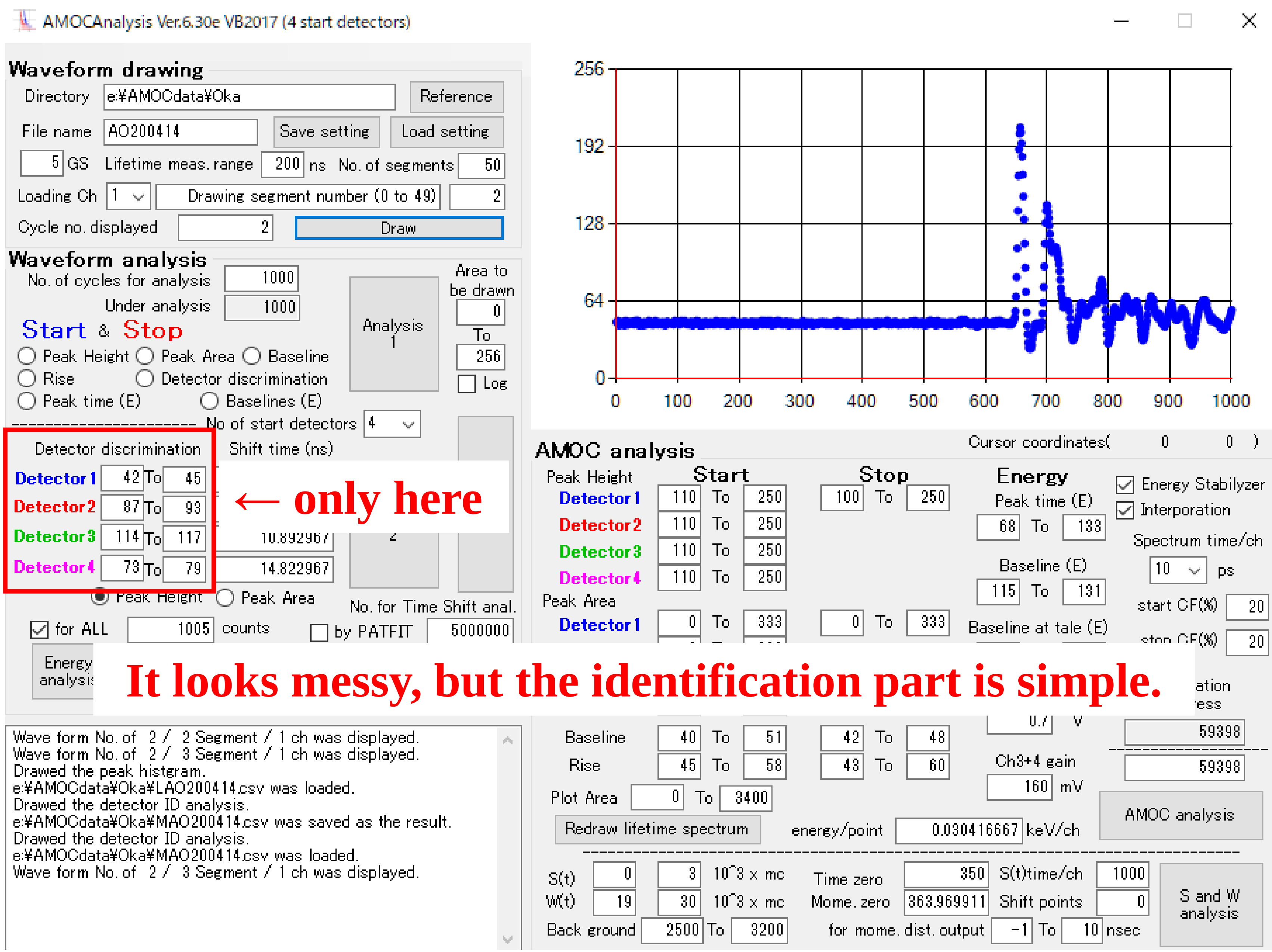
How to solve this problem.

We need detector (sensor) identification technique

Gamma-ray

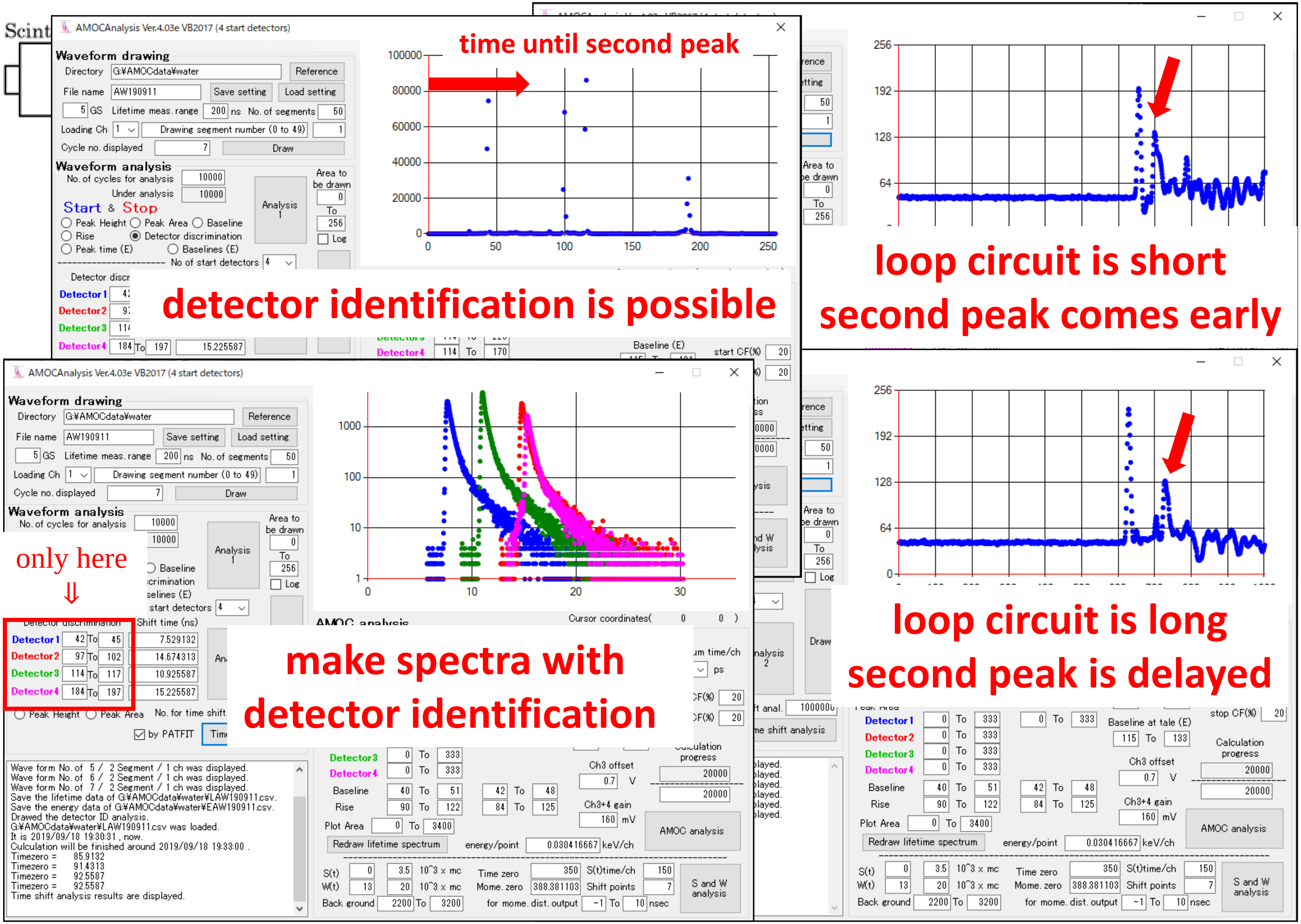


T. Hirade et al. , Nuclear Inst. and Methods in Physics Research, A 931 (2019) 100–104

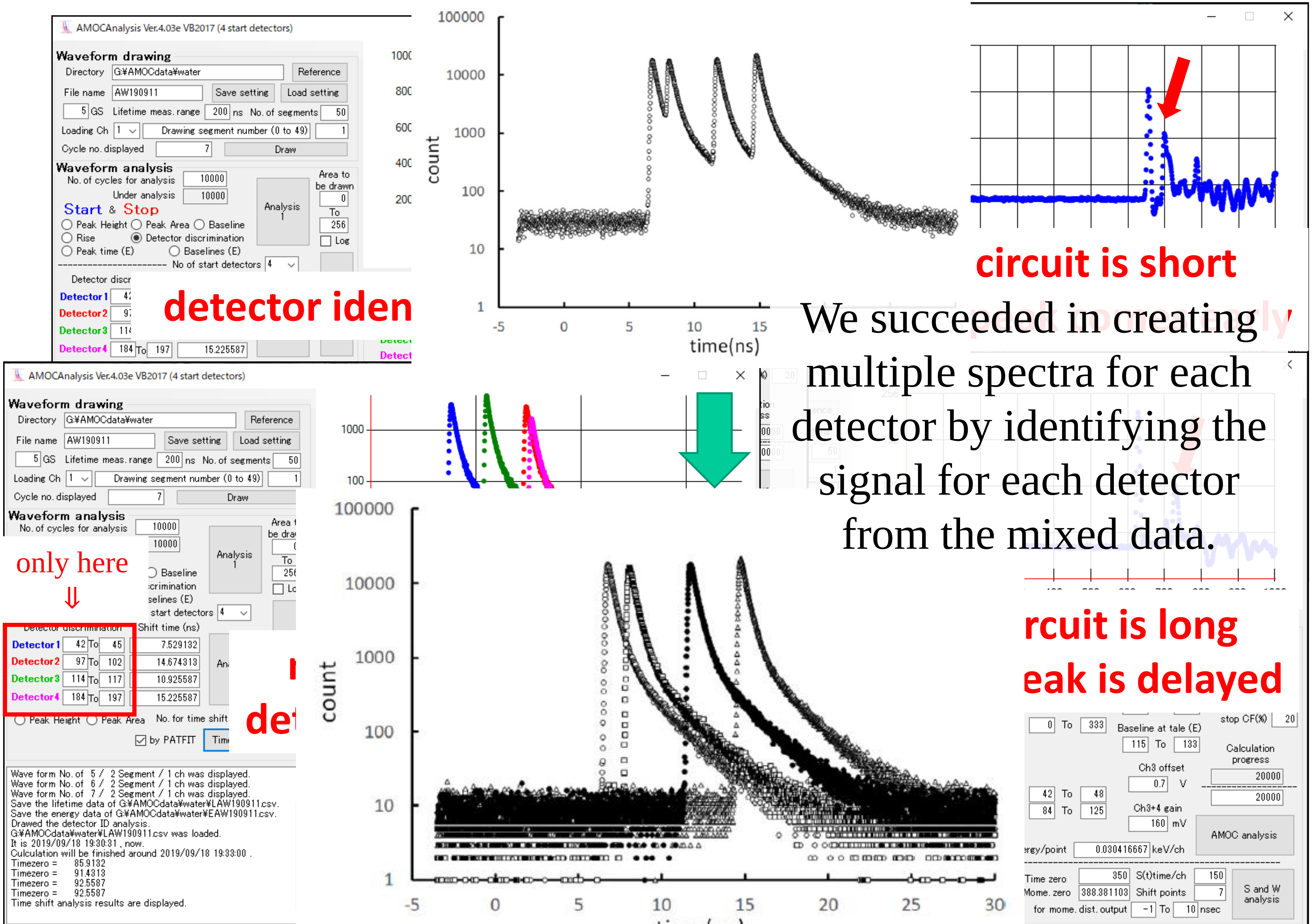


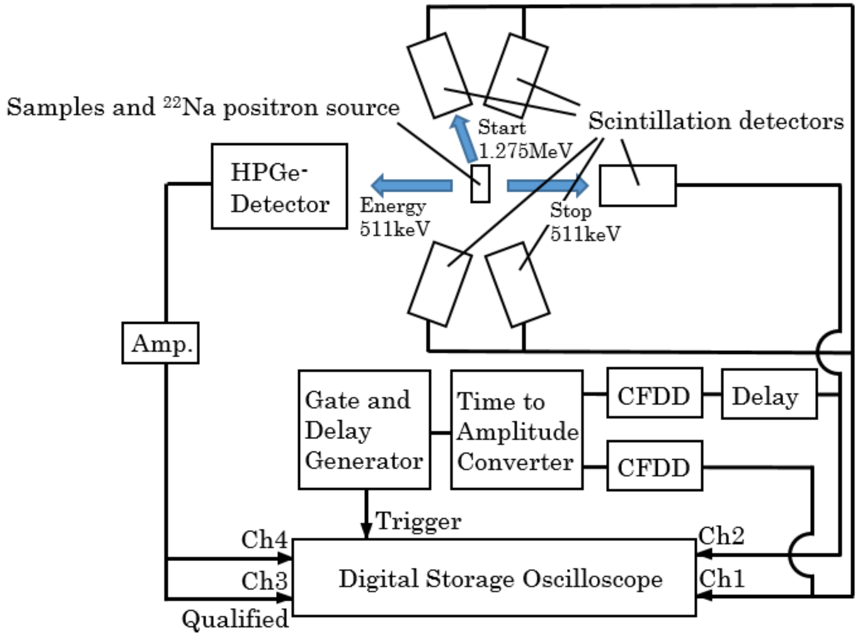
← only here

It looks messy, but the identification part is simple.


time until second peak
detector identification is possible
loop circuit is short
second peak comes early
only here
⇓
make spectra with
detector identification
loop circuit is long
second peak is delayed

We succeeded in creating multiple spectra for each detector by identifying the signal for each detector from the mixed data.





Time resolution：166 ps(fwhm)
Count rate：2.5 cps

↓

Time resolution：230 ps(fwhm)
Count rate：more than 10 cps
0.8 million counts / day

Nuclear Inst. and Methods in Physics Research, A 931 (2019) 100–104

T. Hirade [a,e,*], H. Ando [b], K. Manabe [c], D. Ueda [d]

[a] Nuclear Science and Engineering Centre, Japan Atomic Energy Agency, Tokai, 319-1195, Japan
[b] Osaka Prefecture University, 1-2 Gakuen-cho, Naka-ku, Sakai City, Osaka 599-8570, Japan
[c] Department of Chemistry, Tohoku University, Sendai 980-8578, Japan
[d] Quantum Science and Engineering Centre, Kyoto University, Uji 611-0011, Japan
[e] Institute of Quantum Beam Science, Ibaraki University, 4-12-1 Narusawa, Hitachi, Ibaraki, 316-8511, Japan

Temperature dependence of τ_3 in water

Chemical Physics 55 (1981) 177–182
North-Holland Publishing Company

TEMPERATURE DEPENDENCE OF POSITRON LIFETIMES IN WATER AND ETHANOL

F.A. SMITH and C.D. BELING
Department of Physics, St. Bartholomew's Medical College, London EC1M 6BQ, UK

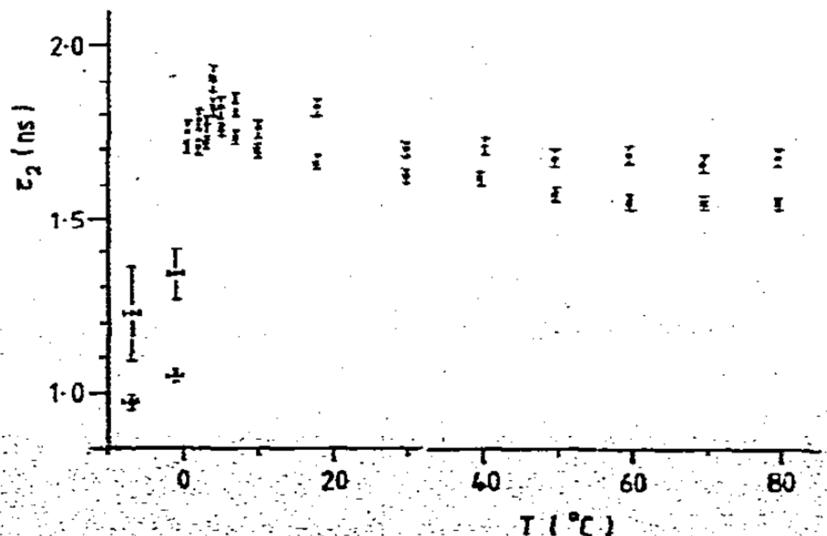


Fig. 1. Lifetimes and intensities of *o*-Ps in water from two-lifetime (X) and three-lifetime (•) fix.

Physics Letters A 345 (2005) 184–190

Measurement of positron lifetime to probe the mixed molecular states of liquid water

Katsushige Kotera [a,*], Tadashi Saito [b], Taku Yamanaka [a]
[a] *Physics Department, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan*
[b] *Radioisotope Research Center, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan*

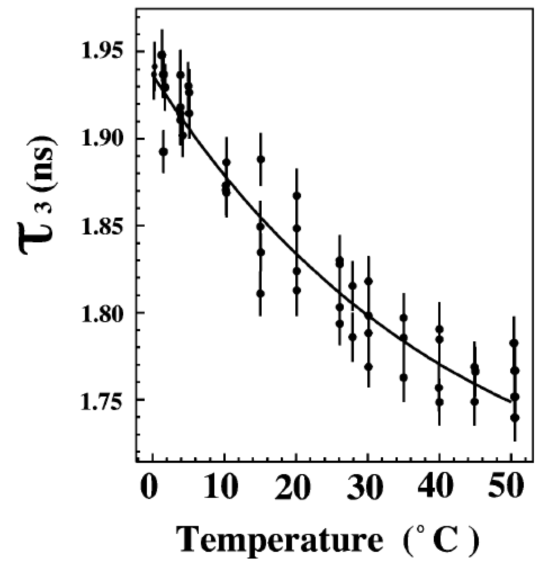


Fig. 3. τ_3 in water as a function of temperature. Dots show data. Vertical lines show errors. The solid line shows a fitting result by Ps-bubble model combined with the two-state model.

Radiation Physics and Chemistry 76 (2007) 90–95

To the theory of Ps formation. New interpretation of the e+ lifetime spectrum in water

Sergey V. Stepanov[a,*], Vsevolod M. Byakov[a], Tetsuya Hirade[b]

[a]Institute of Theoretical and Experimental Physics, Moscow 117218, Russia
[b]Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

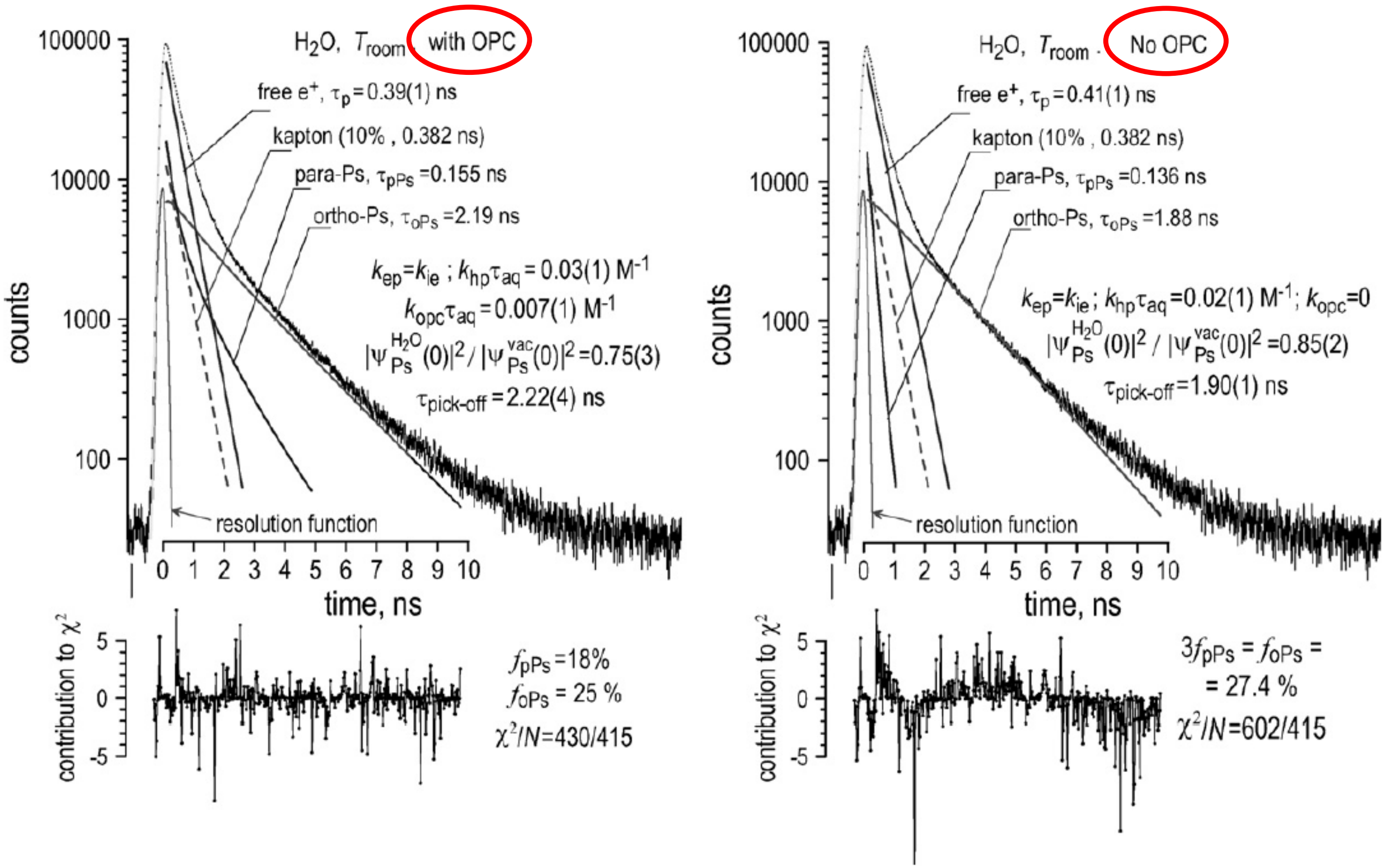


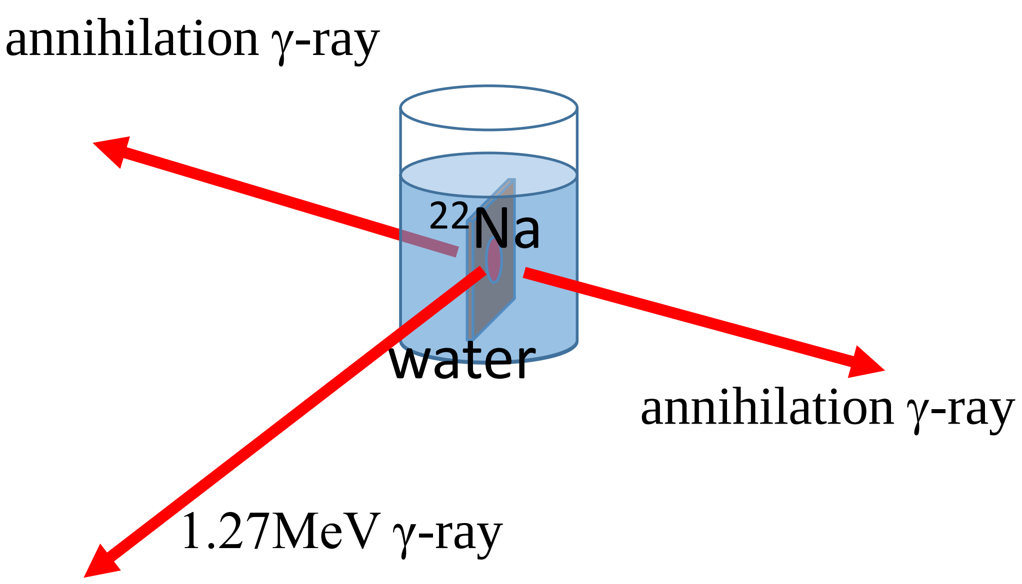
Fig. 2. Fitting of the LT annihilation spectrum in water at room temperature based on the white blob model. Left: ortho–para conversion is taken into account. Right: no ortho–para conversion. $\tau_{aq} \approx 0.3$ ps is the electron hydration time. On the bottom the contributions to χ^2 are shown.

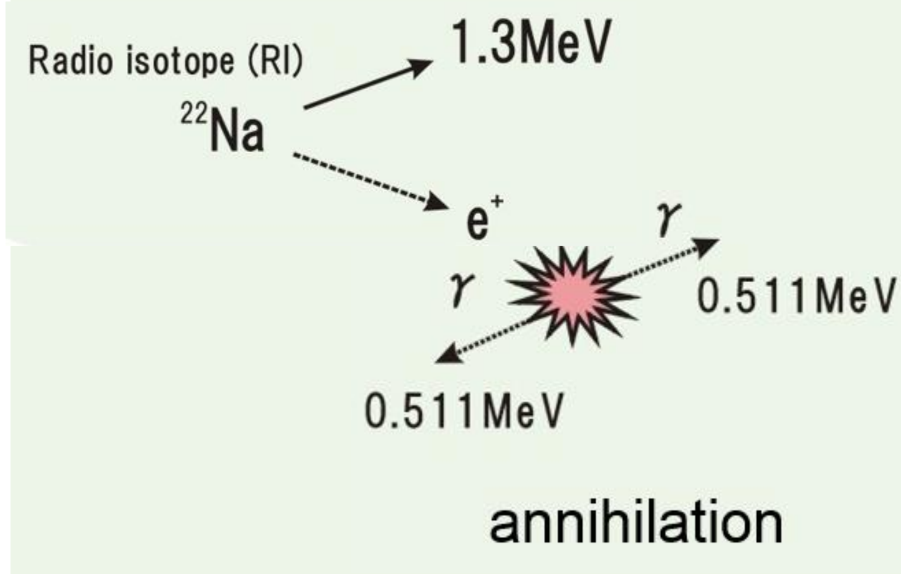
Reactions after ionization of a water molecule at the end part of the positron track

$$H_2O \rightsquigarrow H_2O^{\cdot +} + {}^{\cdot}e^- \qquad \text{(ionization)} \qquad (1)$$

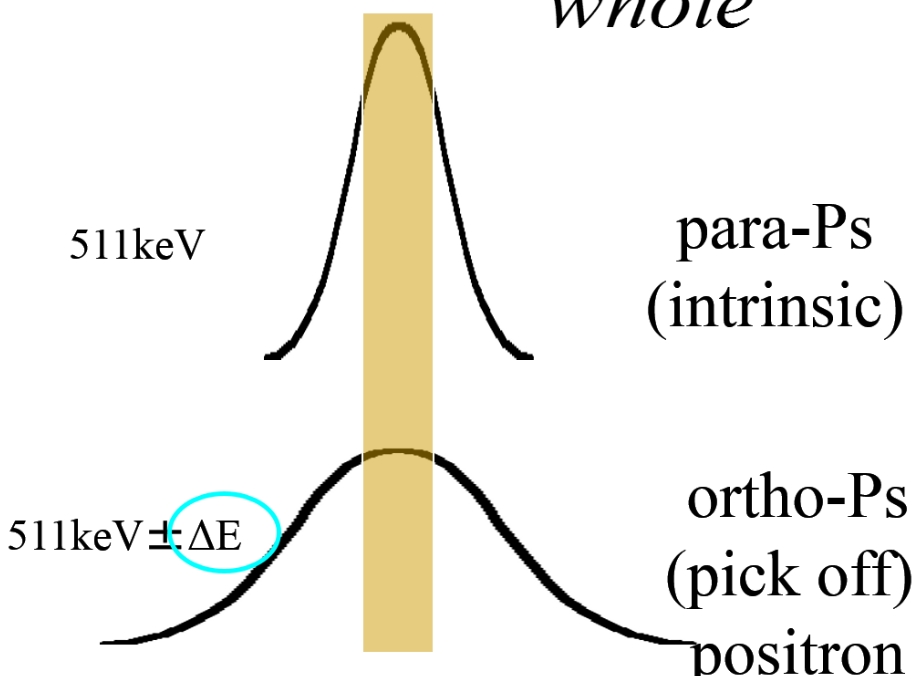
$$\begin{aligned} {}^{\cdot}e^- + e^+ &\rightarrow \text{p-Ps}^{\cdot}\ (25\%) \\ &\rightarrow \text{o-Ps}^{\cdot}\ (75\%) \end{aligned} \qquad \text{(Ps formation)} \qquad (2)$$

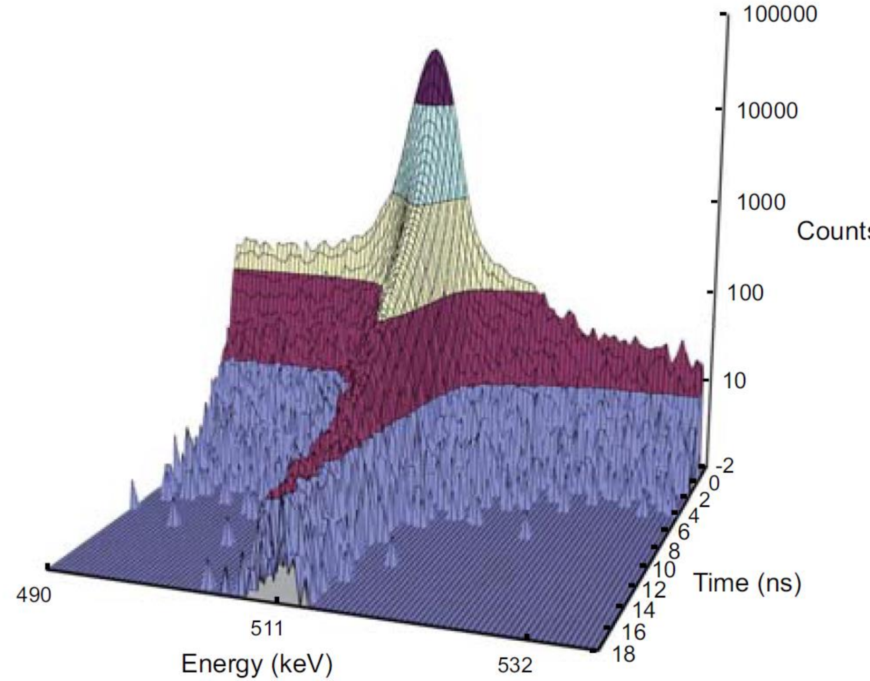
$$H_2O^{\cdot +} + H_2O \rightarrow H_3O^+ + {}^{\cdot}OH \qquad \text{(hydroxyl radical formation)} \qquad (3)$$

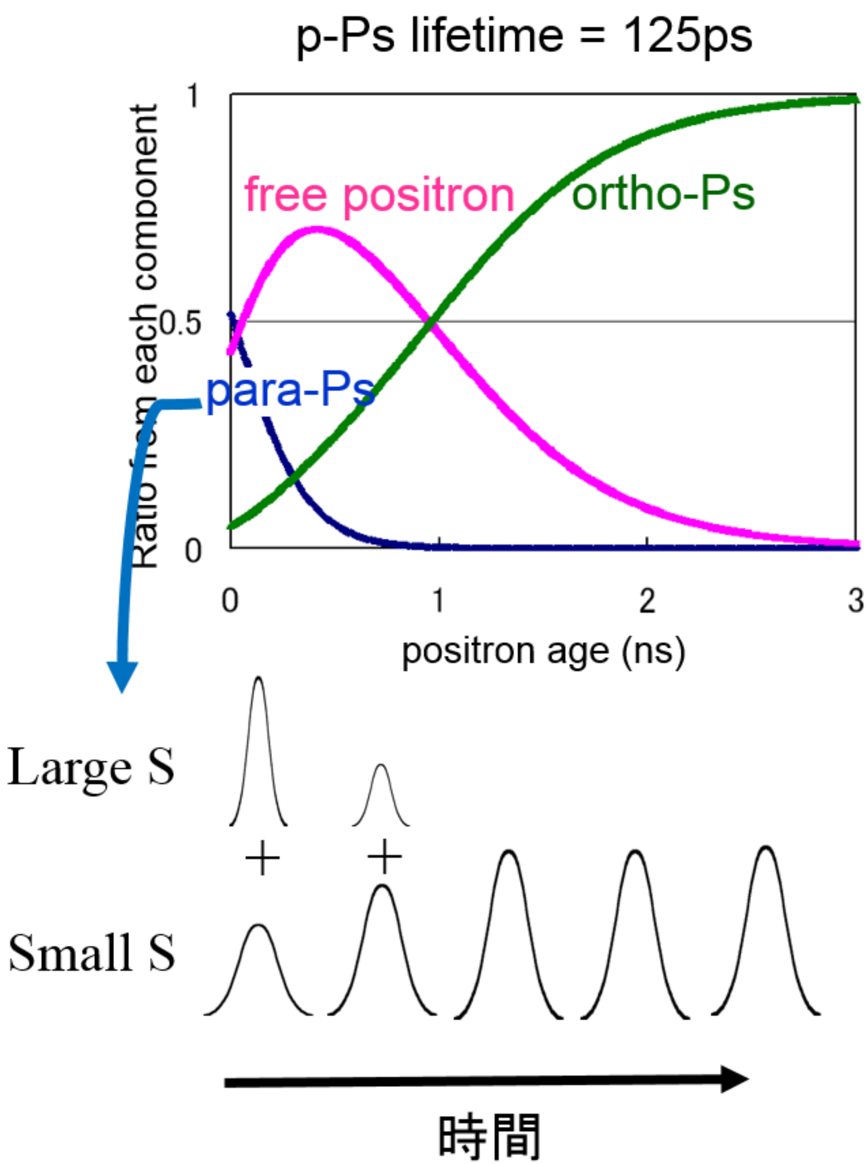


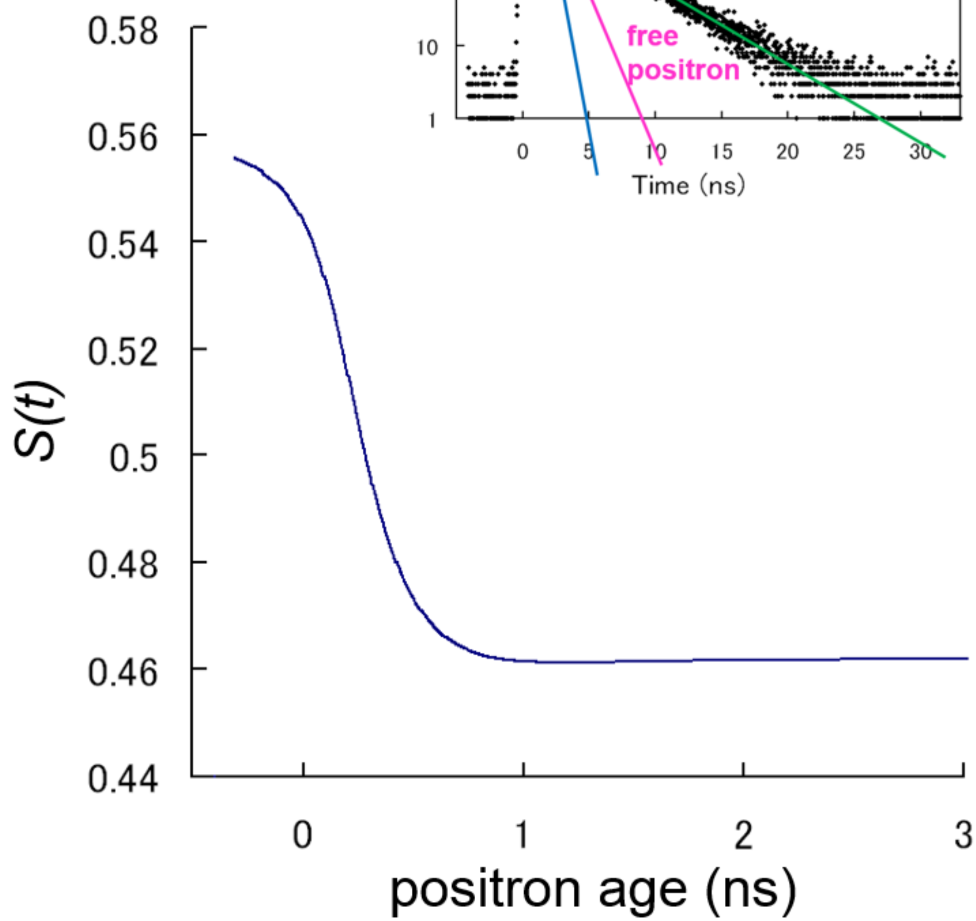


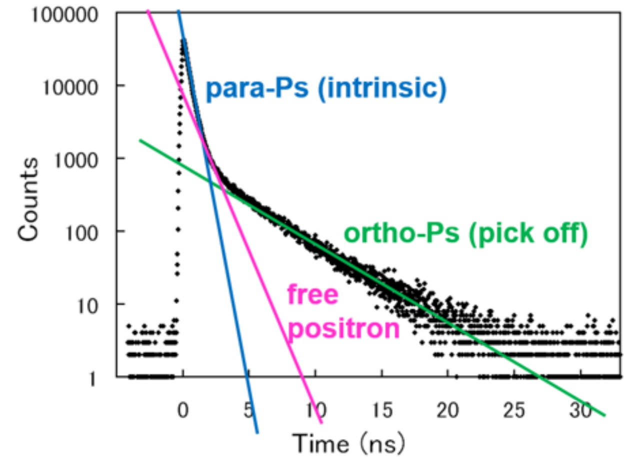
$$S = \frac{central}{whole}$$







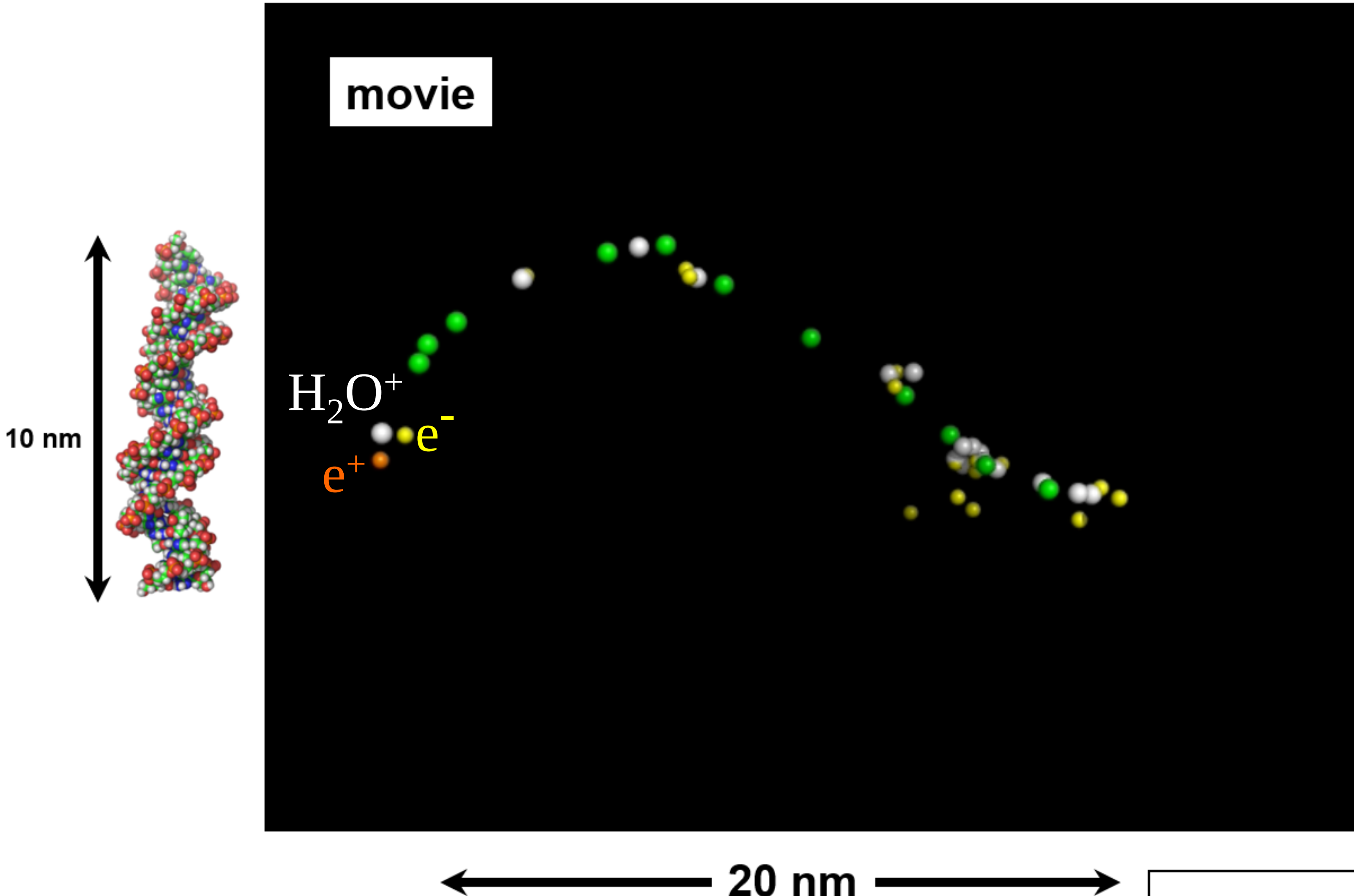




S(t) change can indicate the para-Ps annihilation!!

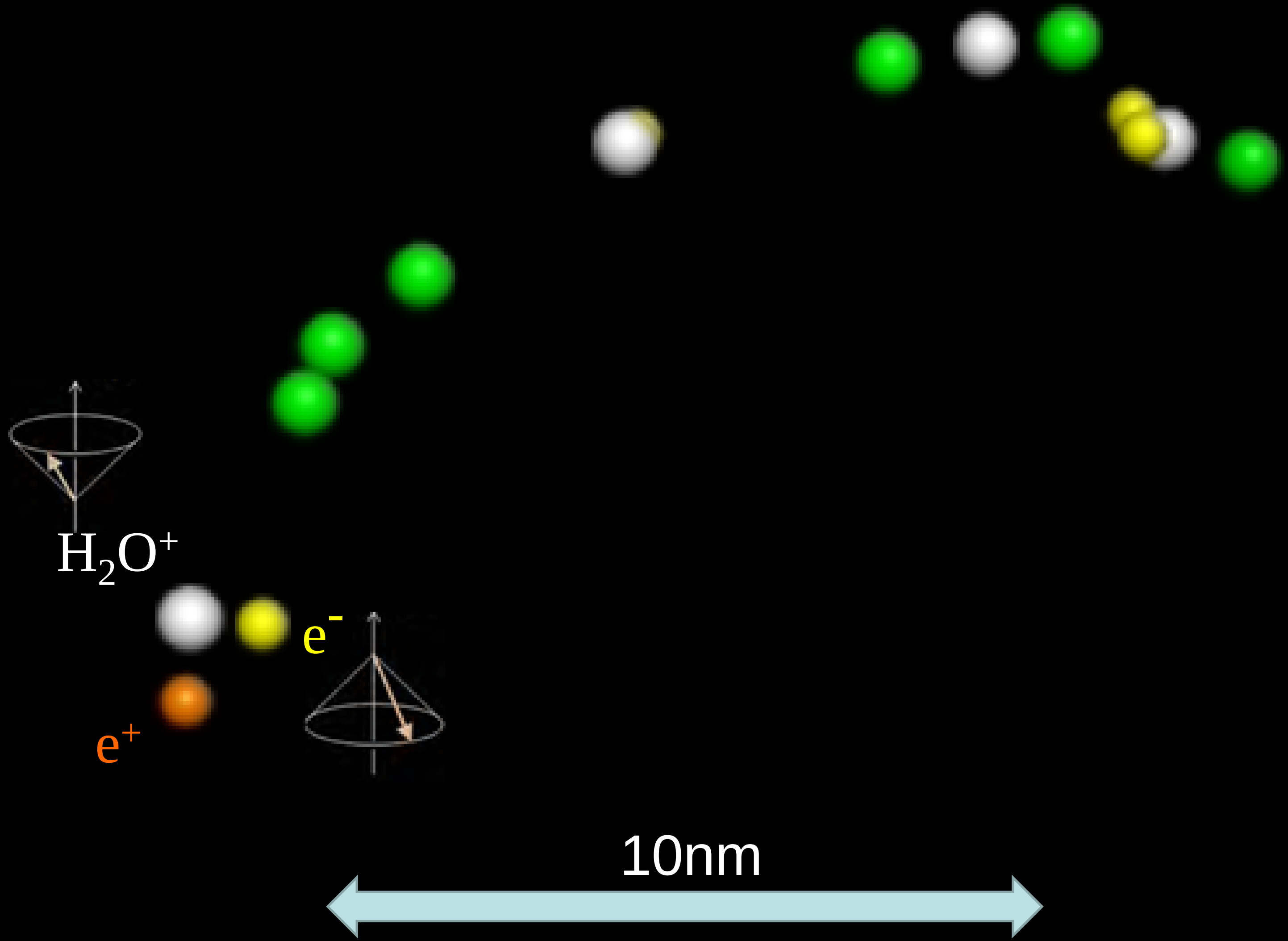
We demonstrate electron dynamics in liquid water within 10 fs

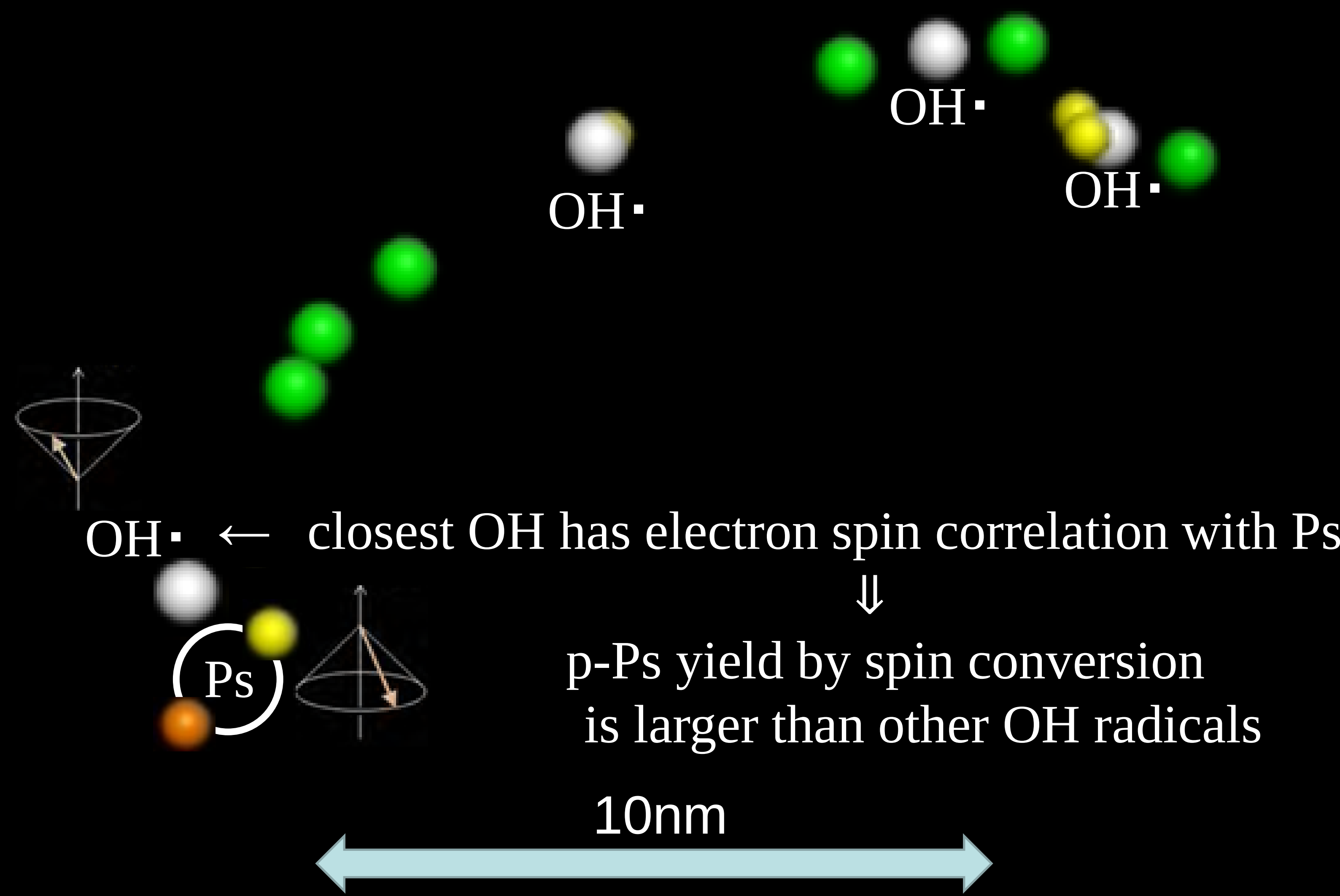
Orange : Auger electron (500eV), Yellow : SE, White : ION, Green : EXC

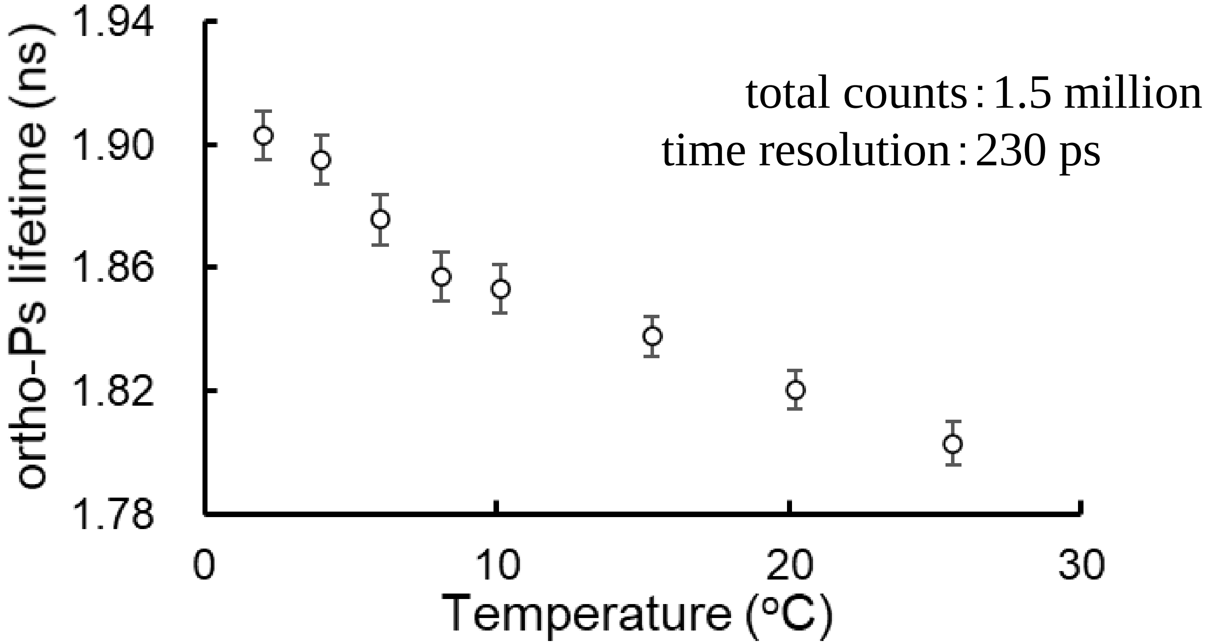


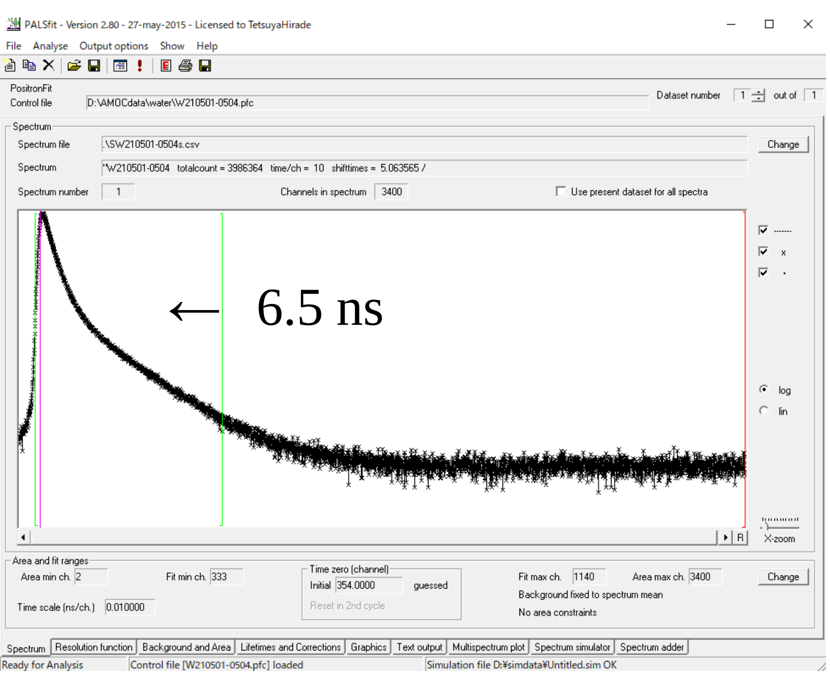
Some secondary electrons are recaptured
by ionization sites

Supplied by
Takeshi Kai (JAEA)


H_2O^+
e^-
e^+
10nm

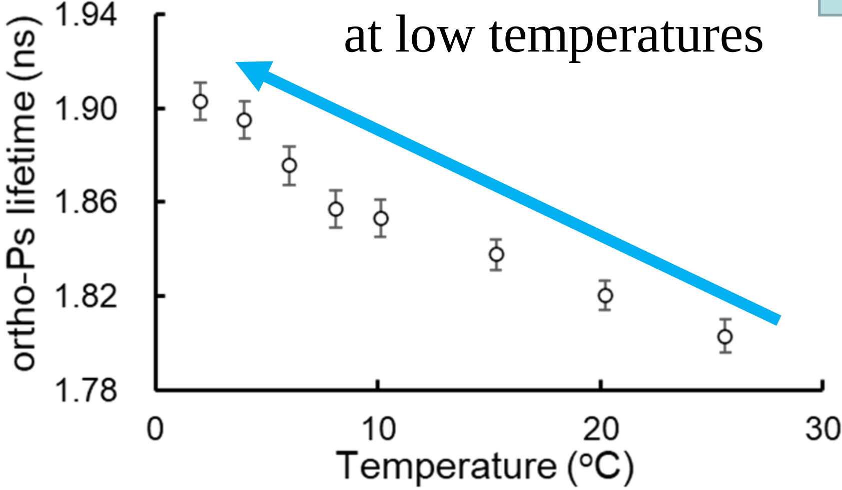

OH·
OH·
OH·
OH· ← closest OH has electron spin correlation with Ps
⇓
p-Ps yield by spin conversion
is larger than other OH radicals
Ps
10nm

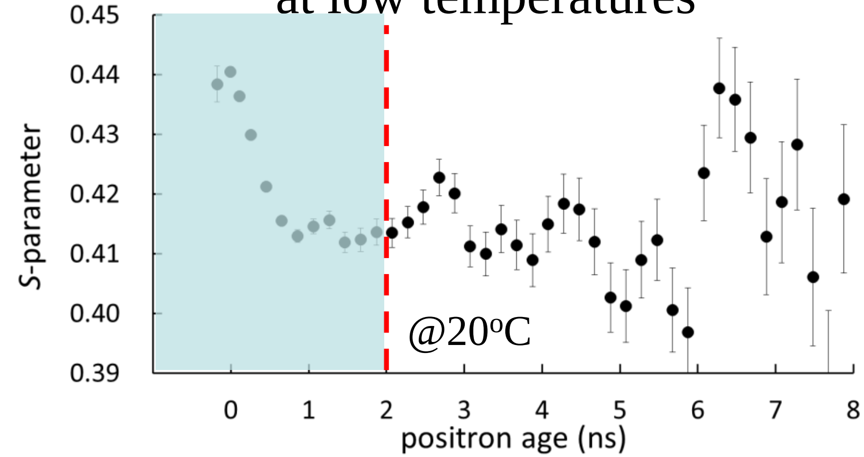


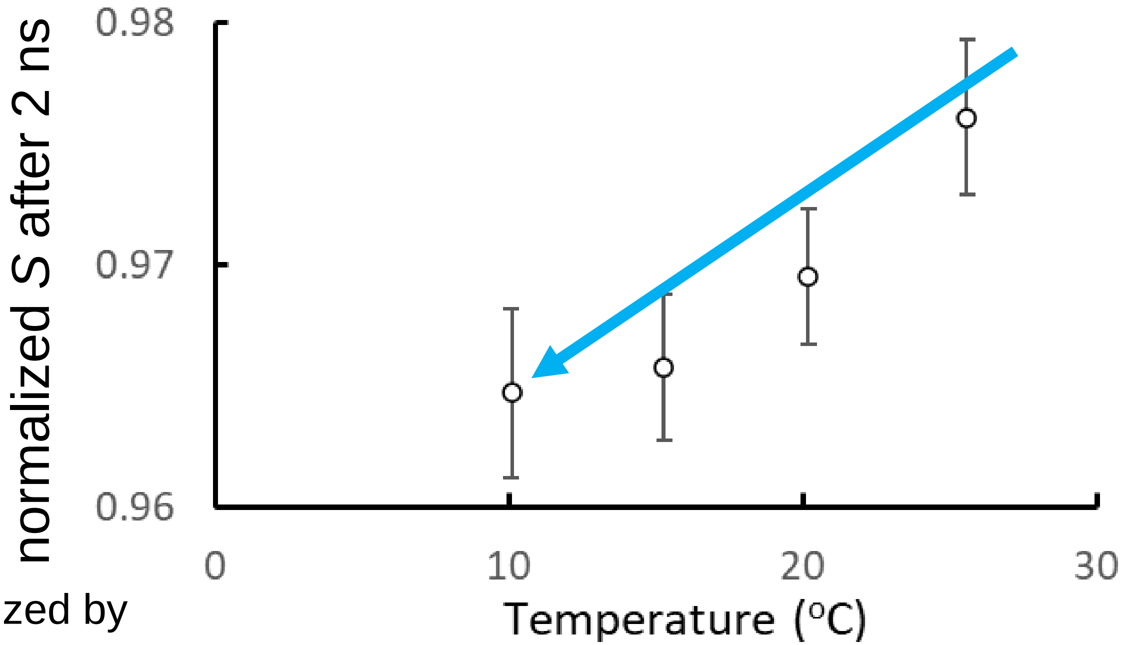



```
######################## F i n a l   R e s u l t s ########################
Data set 1                                                         L T I B Z A G
                                                                   3 1 0 1 0 0 2
Convergence obtained after 4 additional iterations
Chi-square =      934.01  with 802 degrees of freedom
Reduced chi-square = Chi-square/dof =    1.165  with std deviation 0.050
Significance of imperfect model =  99.92 %

             Lifetimes (ns)   :    0.1282     0.3900     1.9128
             Std deviations   :    0.0034      Fixed     0.0048

             Intensities (%)  :    9.9160    63.2561    26.8278
             Std deviations   :    0.1749     0.2281     0.0735

Background   Counts/channel   :   24.7391
             Std deviations   :      mean

Time-zero    Channel number   :  351.7868
             Std deviations   :    0.0339
Total-area   From fit         : 3.39377E+06     From table : 3.40227E+06
```

o-Ps reaction is less at low temperatures → p-Ps formation is less at low temperatures

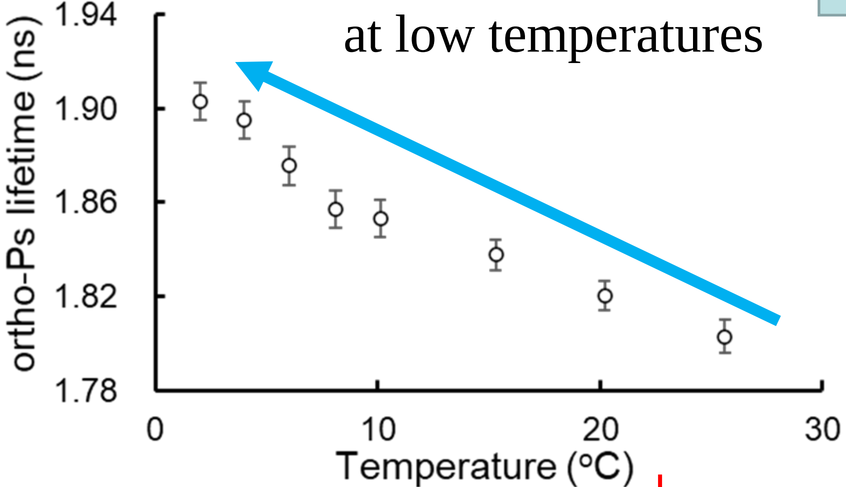




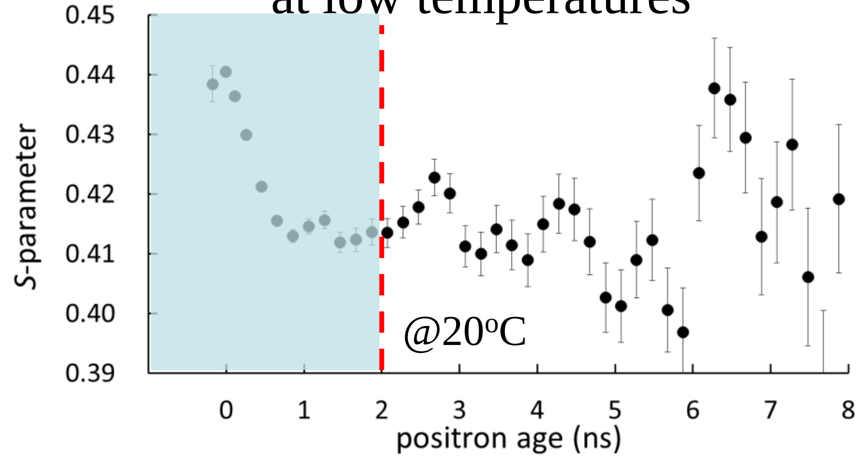


normalized by
S at - 0.3～1ns

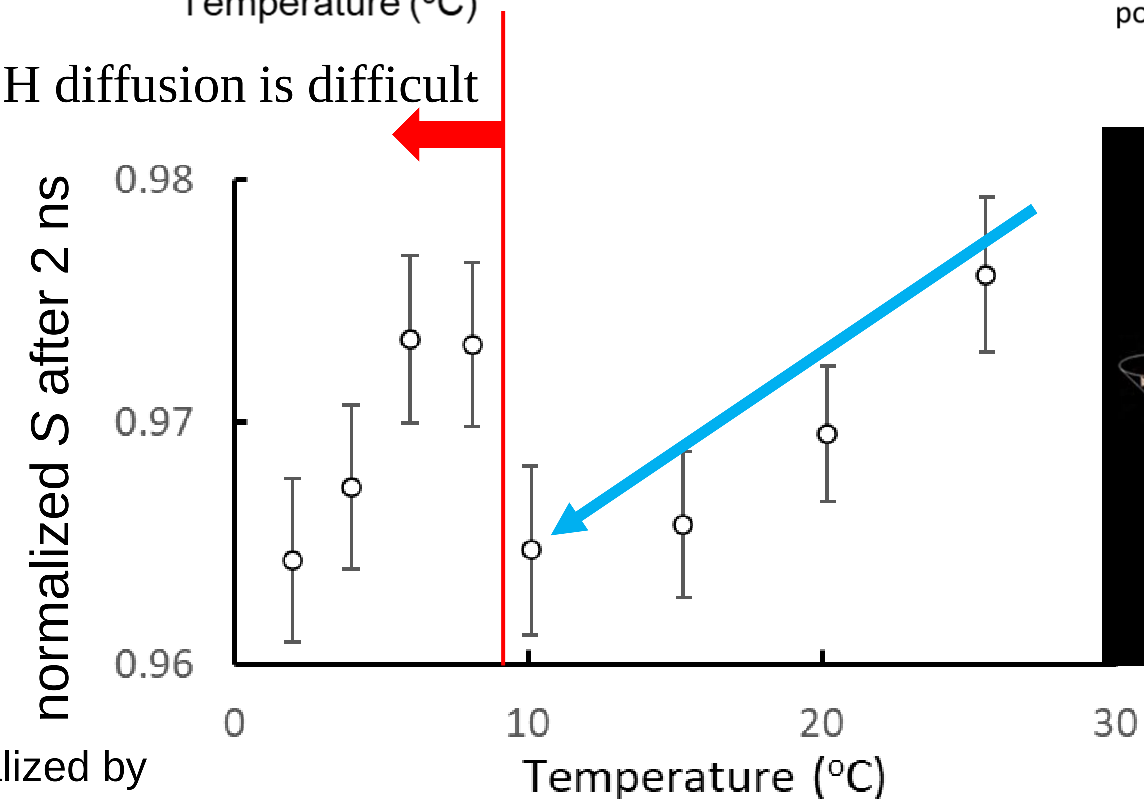
o-Ps reaction is less at low temperatures

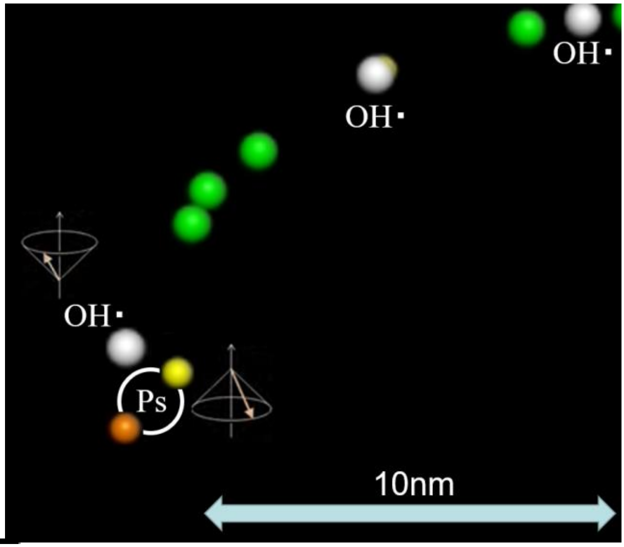


p-Ps formation is less at low temperatures



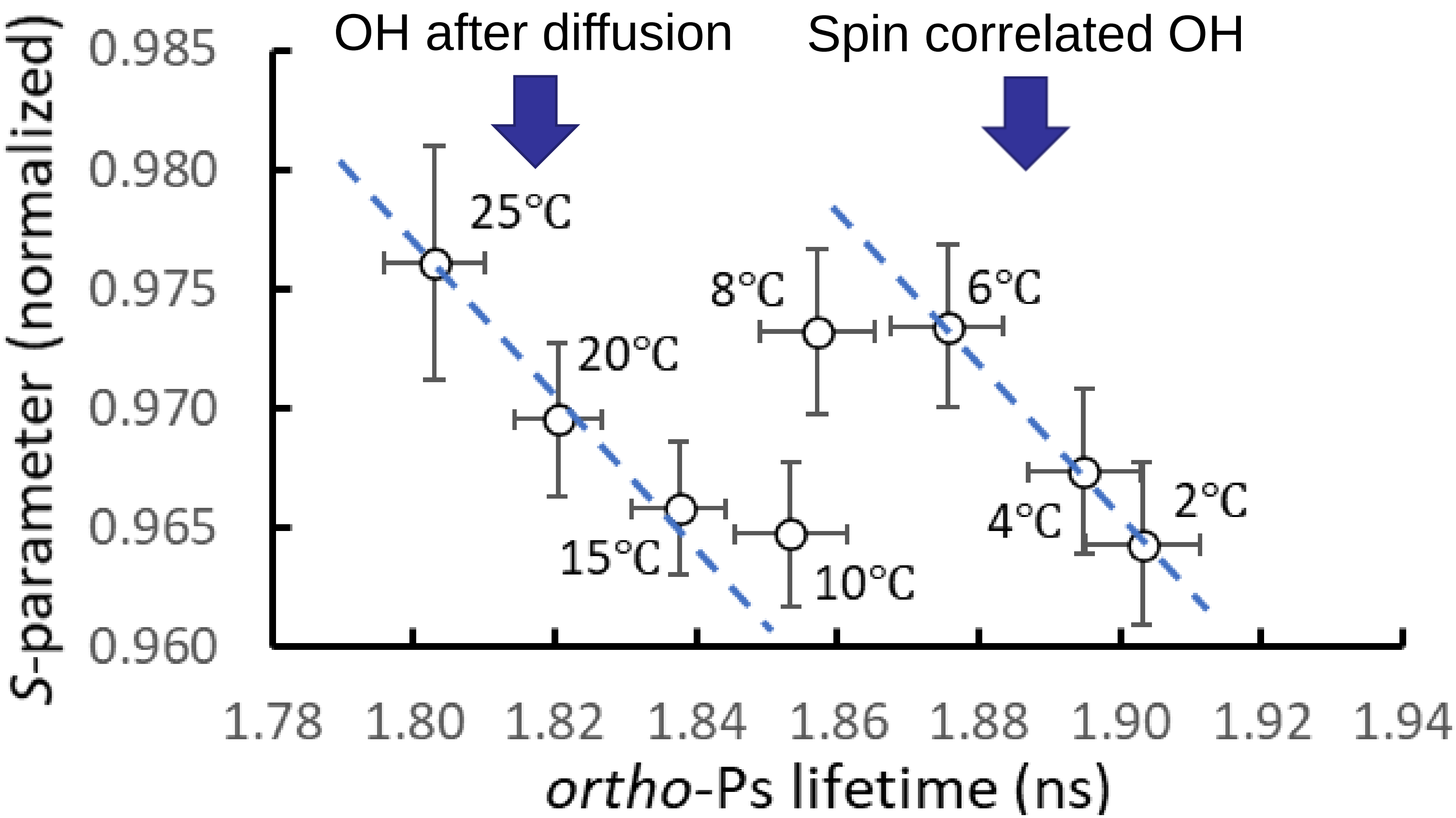
OH diffusion is difficult





normalized by
S at - 0.3〜1ns

Relation between o-Ps lifetime and *S*



Chemical Physics Letters 480 (2009) 132–135

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Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Age–momentum correlation measurements of positron annihilation in water: Possibility of quantum beats on ortho-positronium reactions

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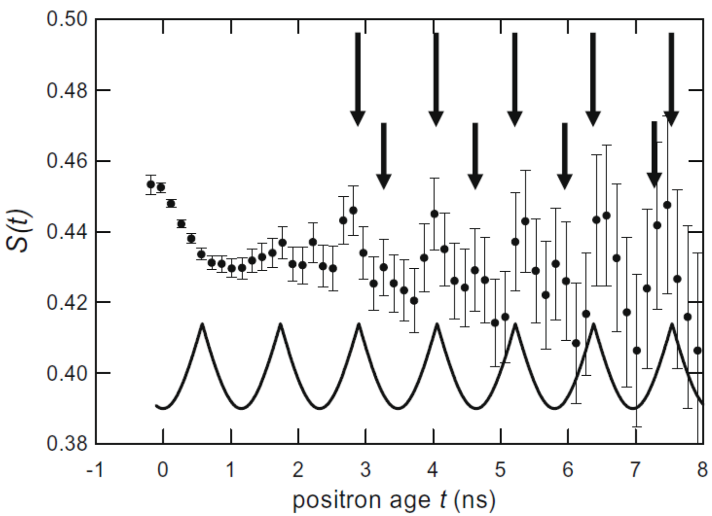


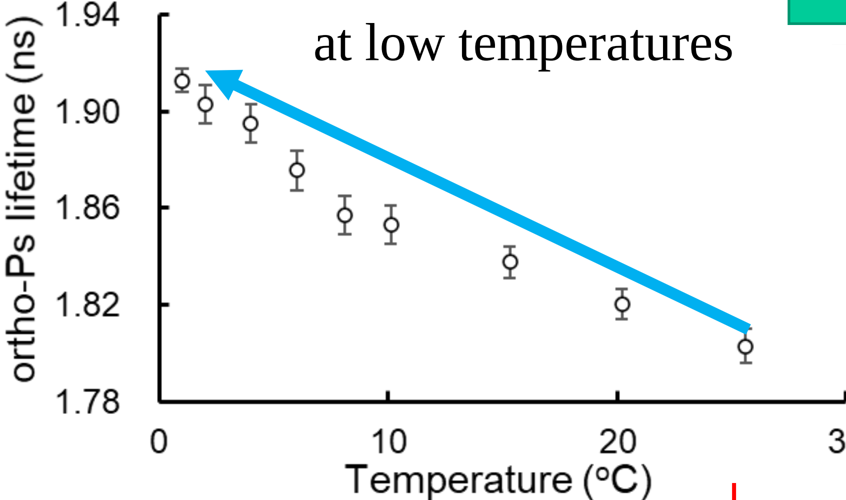
Fig. 1. $S(t)$ curve observed through positron annihilation age–momentum correlation (AMOC) in ultra-pure water at 18 °C. The arrows give the $S(t)$ beats. The long arrows are at about 1.15 ns intervals while the short arrows are at about 1.32 ns intervals. The solid line gives the expected beats indicated by the long arrows in $S(t)$ with the mechanism proposed here. The minimum should appear at the positron age of zero according to the mechanism.

A B S T R A C T

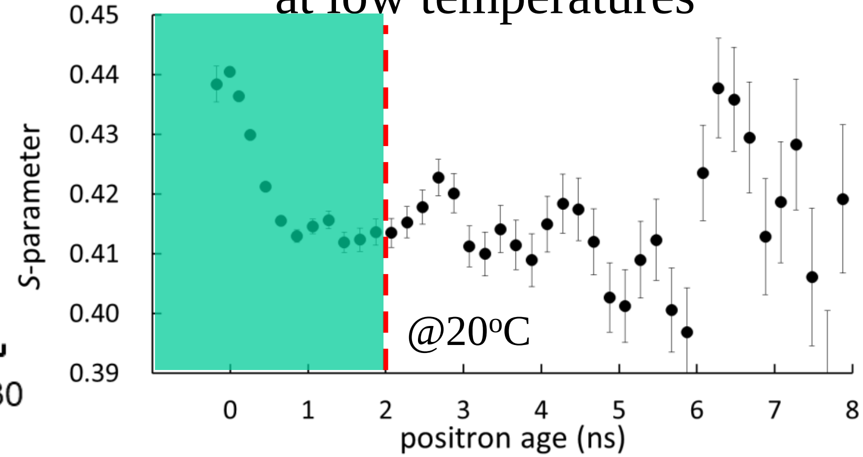
Quantum beats were detected in the reaction of electron-spin-correlated pairs of ortho-positronium and hydroxyl radical. Singlet ortho-positronium and hydroxyl radical pairs were generated in positron radiolysis of water molecules. The singlet–triplet transition caused via the hyperfine coupling of every radical affects the rate of the radical reaction, and then affects the rate of the competing reaction, the spin conversion reaction between ortho-positronium and hydroxyl radical. Spin conversion of ortho-positronium can possibly be detected using positron annihilation age–momentum correlation (AMOC) measurements, and time resolved annihilation gamma-ray energy distribution observed using AMOC measurements did successfully reveal quantum beats in water.

S peak positions can indicate
hyperfine coupling constant of OH radical

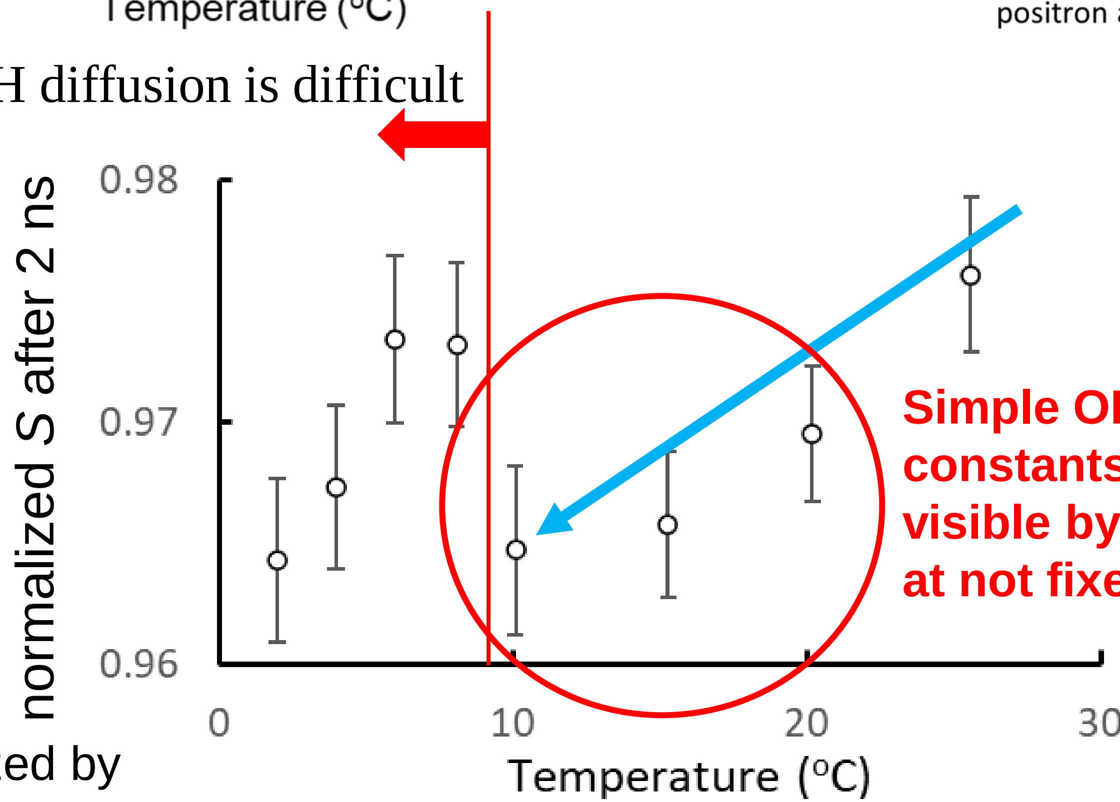
o-Ps reaction is less at low temperatures



p-Ps formation is less at low temperatures



OH diffusion is difficult



Simple OH hyperfine coupling constants (HFCCs)should be visible by measurement at not fixed temperature.

normalized by
S at - 0.3～1ns

AMOC at 10, 15 and 20ºC are measured to detect simple OH radicals present at all temperatures.

Chemical Physics Letters 401 (2005) 420–425

Effects of partially quenched orbital angular momentum on the microwave spectrum and magnetic hyperfine splitting in the OH–water complex

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Mark D. Marshall [b,*], Helen O. Leung [b]

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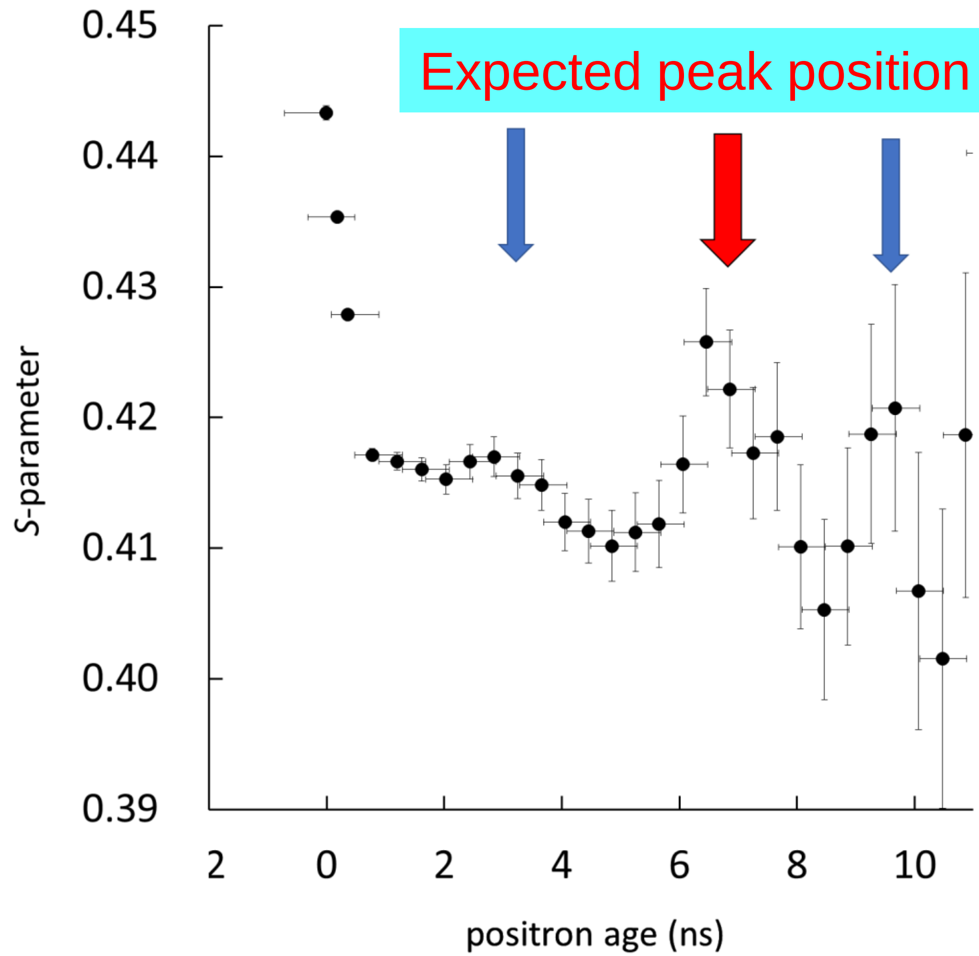
[b] Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000, US

Received 2 November 2004; in final form 9 November 2004
Available online 15 December 2004

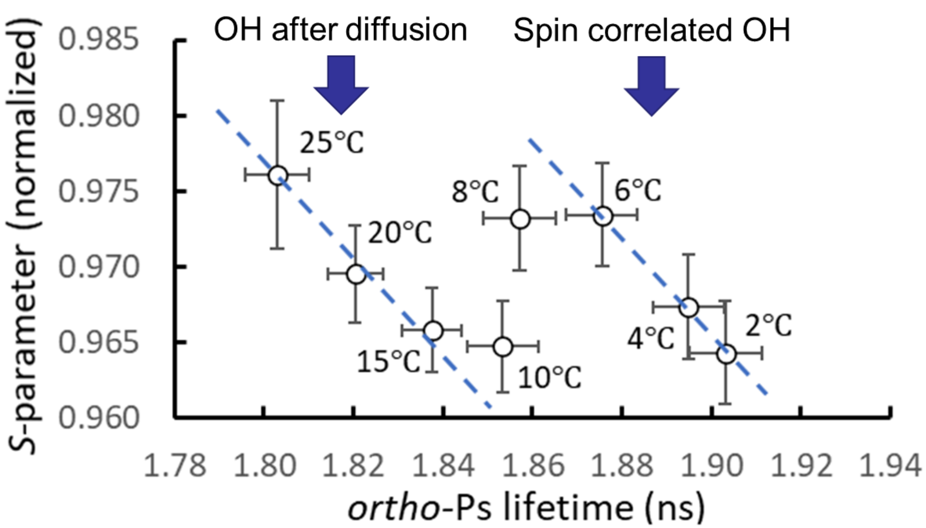
OH
73.25MHz

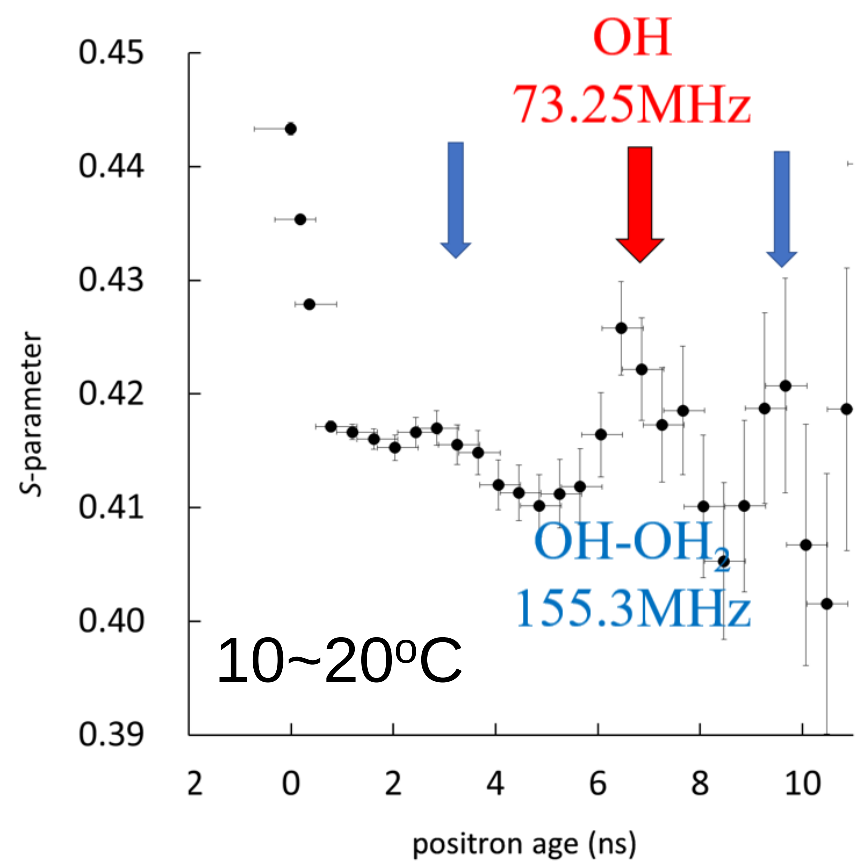
$OH\text{-}OH_2$
155.3MHz



Summary

1. By detector identification using the individuality of the signal, high count rate AMOC measurement becomes possible.
2. OH radical diffusion changed around 10^{o}C.
3. Expected beats with known HFCCs of OH were observed.
4. Results at lower temperatures also will be published soon.





This research was partially supported by a Ministry of Education, Culture, Sports, Science and Technology Grant-in-Aid for Scientific Research (C), 20K12501, 2020–2022.