The Study of the Electron–Positron Pair in CS_2

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Ole E. Mogensen reported that CS_2 was the only liquid which showed large decrease of the Ps intensity with lowering the temperature, even though electron and positron could encounter with each other at low temperatures such as -100 °C. The intensity change by the positron annihilation lifetime was observed at a little lower temperature by the positron annihilation angular correlation. Here I measured the change of intensity and lifetime of the longest lifetime component caused by varying the surface tension, the dielectric constant, and the temperature, to clarify the positron state in CS_2. These experimental results confirm the ideas of the "fourth positron state" and the "squeezed positronium state" which were proposed by Ole E. Mogensen.

Positronium (Ps) is a bound state of an electron and a positron. There are two different Ps states because of the different spin states. One is para-Ps which has about 125 ps lifetime, and the other is ortho-Ps which annihilates in 140 ns in vacuum and in 2—10 ns by pick-off annihilation in liquids, i.e. the annihilation of the positron in Ps and the electron in molecules. It is commonly said that the ratio of formation of para-Ps and ortho-Ps is 1 : 3.

According to the spur model,[1—3] Ps is formed by the reaction of a positron and one of the excess electrons in the positron spur, the terminal spur of positron track. If a positron can not react with one of the excess electrons to form Ps, in other words, if the positron is in the free positron state, it will annihilate in about 400 ps with an electron of the surrounding molecules. If excess electrons and/or a positron are scavenged by isolated molecules, they will not form Ps either.

Ps is repelled by the molecules, because of its negative work function. Hence Ps creates a bubble in liquids. The size of the bubble is controlled by the balance of the zero point energy of Ps, the surface tension of matrix and the pressure.[4] Then a model which applied the square potential for Ps can estimate the size of the bubble from the lifetime of ortho-Ps.

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+R_0}\right]^{-1} \quad (1)$$

τ_3 is the ortho-Ps lifetime, R is the size of the hole and R_0 is an empirical parameter. The best-fitted value of R_0 for all known data is 1.656 Å.[5]

Ps intensity, which in pure hexane was about 42%, decreased with increasing the concentration of CS_2 in hydrocarbons such as hexane just the same as other scavengers, CCl_4 or SF_6. However it increased at higher concentration than 0.1 M,[6] because of the high electron mobility.[7] In pure CS_2, electron mobility was high because of the tunneling between molecules, even though electrons were trapped on the molecules.[8] Ortho-Ps intensity in pure CS_2 at room temperature was about 46%.

CS_2 showed a quite strange phenomenon at low temperature region, -40 °C to melting point, -110.8 °C. Ps intensity decreased with decreasing the temperature.[9] This phenomena could be observed in the angular correlation (AC) measurement of two annihilation γ-rays. The same phenomenon could be seen in some aromatic solids, such as naphthalene,[10] biphenyl, *p*-terphenyl, and quaterphenyl,[11] but CS_2 was the only liquid which showed this phenomena.

O. E. Mogensen mentioned as follows in the previous paper.[9] Ps was squeezed so much even at room temperature, because three times of para-Ps intensity obtained by angular correlation measurement was so much lower than the ortho-Ps intensity. Ps bubble state was not the lowest energy state at the melting point $=-110.8$ °C, because rather large energy was needed to form the bubble and both the positron and the electron were strongly bound to the CS_2 molecules. Even at -110 °C, positron and electron were still bound by their mutual Coulomb attraction, as the dielectric constant was low. Such a state had been called the "fourth positron state"; the three other states were the free positron, para-Ps and ortho-Ps states. The detailed structure of the "fourth positron state" had been unknown.

It was mentioned that the fwhm of the narrowest component of the angular correlation spectra and the lifetime of ortho-Ps had a correlation, and CS_2 showed smaller value than other 30 liquids.[12] The correlation might be based on $\Delta p \times \Delta x = h$, Δp and Δx are uncertainty of momentum and position, and h is "Plank's constant". Δp $\left(=\frac{\Delta E}{c}\right)$ and Δx might be proportional to $\frac{511\ \mathrm{keV}\times(\mathrm{fwhm_1})\ \mathrm{mrad}}{3.00\times10^8\ \mathrm{m\,s^{-1}}}$ and $R(\tau_3)$, respectively, where ΔE is uncertainty of energy, c is the velocity of light, $\mathrm{fwhm_1}$ is from the narrowest component on AC measurement, τ_3 is the longest lifetime on LT measurement and $R(\tau_3)$ is estimated size of bubble from the ortho-Ps lifetime τ_3 with Eq. 1. There were 33 results of fwhm of the narrowest component and the lifetime of ortho-Ps.[12]

$\frac{511\ \text{keV}\times(\text{fwhm}_1)\ \text{mrad}}{3.00\times10^8\ \text{m s}^{-1}}\times R(\tau_3)$ is calculated with those results and the values are shown in Fig. 1. The number means the number in Table 1 in the paper.[12] Only the value for CS_2 is obtained from Table 2 in the paper, because the value for CS_2 in Table 1 was not obtained with the method as applied for other liquids, three free term fit. The last and lowest one is the value of CS_2.

Y. Kobayashi indicated the correlation between the lifetime of ortho-Ps and surface tension with more than 30 liquids. The results of CS_2 are out of the correlation.[13] The lifetime was too small for the surface tension of CS_2.

In this paper, I discuss the effect of hexane and methanol in CS_2 on the electron-positron state. The purpose of adding hexane is reducing the surface tension, i.e. reducing the Ps zero point energy. That of adding methanol is increasing the dielectric constant, i.e., making the trap on CS_2 molecule for electron and positron deeper with the arrangement of the dipoles of methanol molecules.

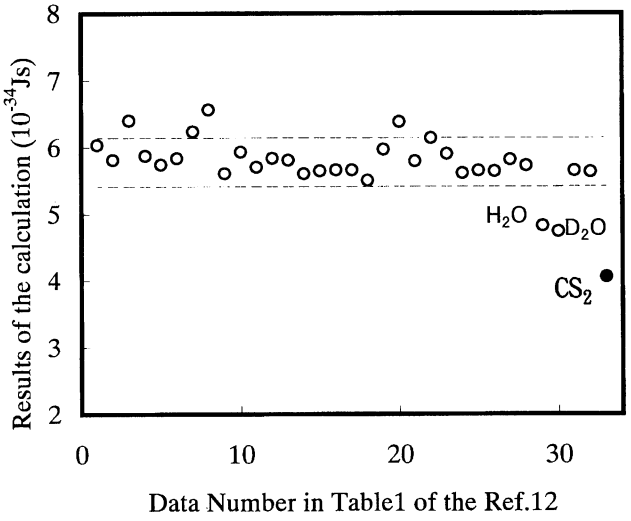


Fig. 1. Calculated values of $\frac{511\ \text{keV}\times(\text{fwhm}_1)\ \text{mrad}}{3.00\times10^8\ \text{m s}^{-1}}\times R(\tau_3)$ in liquids from Table 1 of Ref. 12. The value, fwhm_1, for CS_2 was obtained from the Table 2 of Ref. 12. The lines in the figure mean the standard deviation of all results.

Table 1. Results of Analysis of Pure CS_2 with POSITRONFIT

Temp/°C	τ_1/ns	I_1/%	τ_2/ns	I_2/%	τ_3/ns	I_3/%	Variance
25	0.125F[a)]	14.0	0.387	42.1	2.11	43.9	0.843
10	0.125F	13.6	0.376	42.2	2.03	44.2	0.997
0	0.125F	13.5	0.374	42.8	1.99	43.7	1.132
−10	0.125F	13.6	0.371	43.0	1.92	43.3	1.025
−20	0.125F	13.7	0.374	43.8	1.87	42.5	1.075
−30	0.125F	14.5	0.368	43.8	1.80	41.7	1.016
−40	0.125F	13.3	0.349	44.8	1.67	41.9	0.962
−50	0.125F	11.9	0.330	47.9	1.54	40.2	0.634
−60	0.125F	10.1	0.314	53.0	1.44	37.0	0.945
−70	0.125F	4.5	0.306	64.4	1.33	31.1	0.932
−80	0.125F	−4.6	0.299	79.8	1.18	24.8	0.709
−90	0.125F	−2.9	0.323	87.3	1.08	15.6	0.634
−100	0.125F	−2.8	0.338	92.9	0.92	9.9	1.014

a) F means that the value was fixed on the analysis.

Experimental

Each lifetime measurement was performed by the use of the usual γ spectroscopy technique. Both of the scintillators for start and stop were plastic ones (Pilot-U). ^{22}Na was used for the positron emitter. It emits a 1.3 MeV γ-ray and a positron simultaneously. The emitted positron annihilates with an electron and almost all annihilations emit two 511 keV γ-rays in liquids or solids. Then the time between 1.3 MeV γ-ray and 511 keV γ-rays, i.e. the lifetime of positron, is observed by normal fast-fast coincidence apparatus. If you use stronger source, count rate can be higher; however, random background will also be higher. We usually use a weak source as 150 kBq. On the other hand, one must measure for a long time, like 10 hours, so the drift of zero time should be corrected. We use the method of software stabilizer instead of the hardware stabilizer. At first, 5 or 10 spectra were measured and were summed up while correcting the drift of time zero. It can correct the drift to less than one channel; then, linear interpolation was used for summing up the spectra. Hence, the variance of the fit becomes smaller.[14] The resolution of the apparatus is about 200 ps (FWHM) with ^{22}Na source. Kapton was used for the standard, because it has only one lifetime component. Analysis was performed by the use of RESOLUTION and POSITRONFIT.[15,16] For the resolution curve of the lifetime analysis, the sum of three gaussians was used.

All samples were used without any purification and were degassed by the freeze-thaw method to avoid the effect of oxygen gas.

The stability of the temperature during measurement was less than 1 °C.

Results

Figure 2 shows the temperature dependence of the longest lifetime component intensities at several concentrations of hexane in CS_2. Some examples of fit of lifetime spectra are shown in Table 1. Even at 7.52 M (M = mol dm^{-3}), there exists the decrease of the longest lifetime component. The temperature region of the drastic change was a little shifted to lower temperature at higher concentration. Figure 3 shows

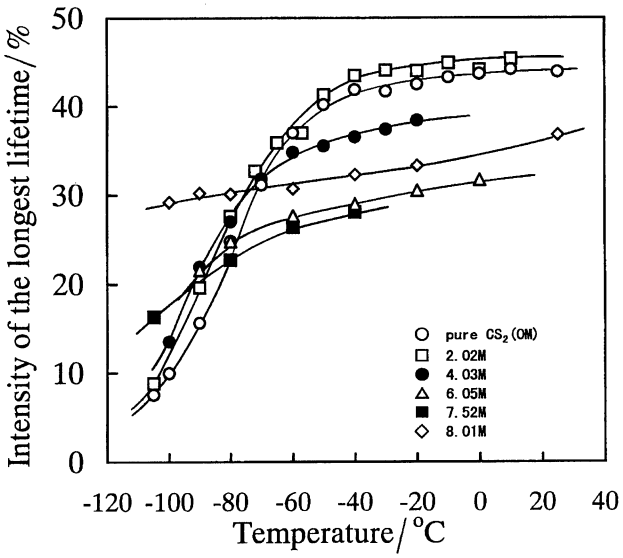


Fig. 2. The temperature dependence on the intensity of the longest lifetime component at several concentration of hexane in CS_2.

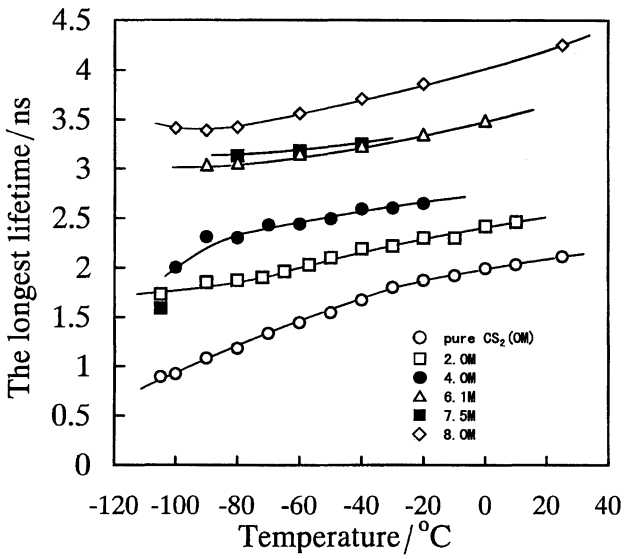


Fig. 3. The temperature dependence of the longest lifetime at several concentration of hexane in CS_2.

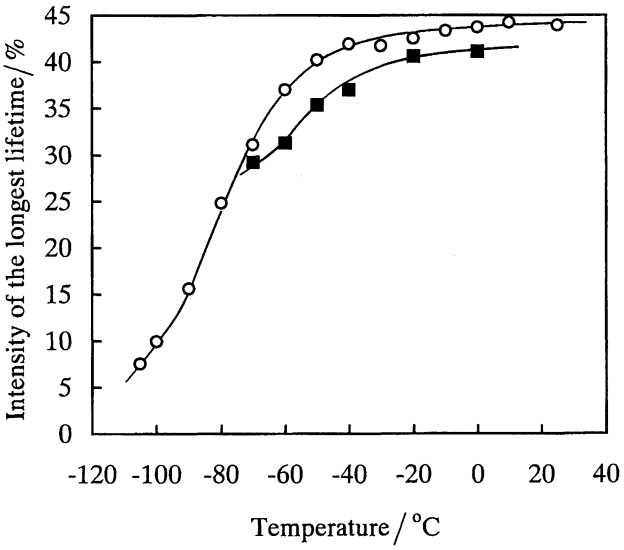


Fig. 5. The temperature dependence of the longest lifetime component intensity on pure CS_2 (○) and 1 M methanol in CS_2 (■).

the temperature dependence of the longest lifetime. The lifetime tends to be longer at higher concentration.

The intensities of ortho-Ps at several concentrations of methanol in CS_2 at room temperature are shown in Fig. 4. The intensity decreased at low concentration region and increased again at high concentration region. Figure 5 shows the temperature dependence of the longest lifetime component intensities at the concentration of 1 M methanol in CS_2 and those in pure CS_2. The change of the intensity shifts to higher temperature with adding methanol.

Discussion

The decrease of the intensity of the longest lifetime component starts around −40 °C, as shown in Fig. 2. The lifetime is about 1.5 ns at the temperature, and the change of the lifetime is not as drastic as that of the intensity. Then this large decrease can not be explained by problems in the analysis like, mixing of the second component and the longest one. Although the decrease of the intensity occurred at a little higher temperature on the AC measurement, the tendency of the decrease is almost the same. These things indicate that this decrease must be caused by nature.

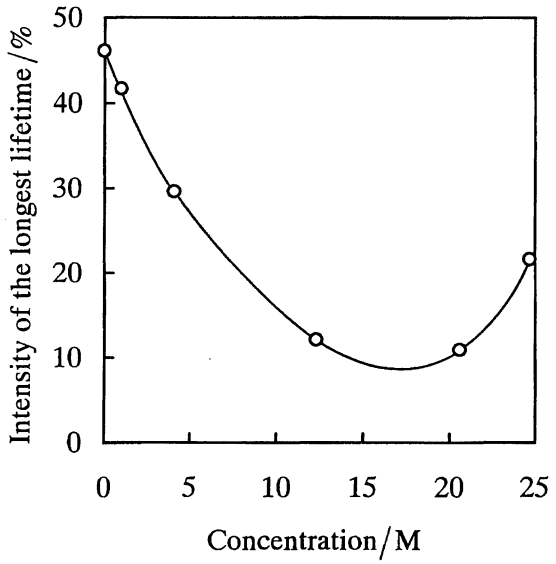
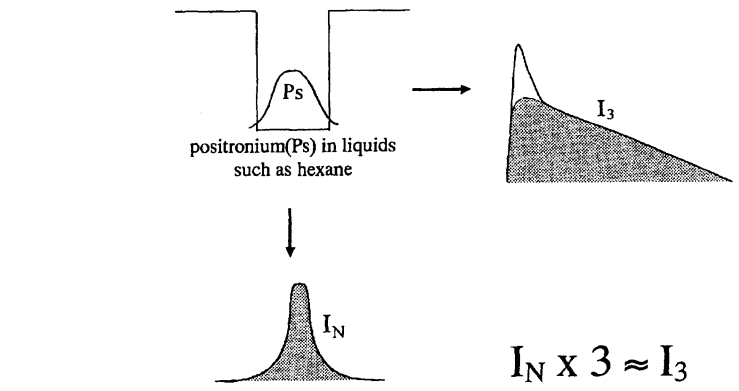


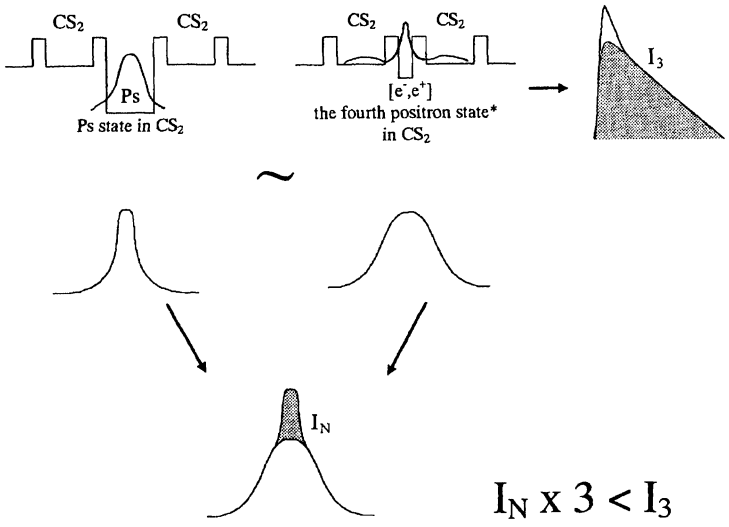
Fig. 4. The concentration dependence of methanol in CS_2 on the intensity of the longest lifetime component.

The wave function of the electron–positron pair state is probably smeared out on the CS_2 molecules as shown in Fig. 6, because it is squeezed by large surface tension and electron and positron can be localized on CS_2. Moreover, the electron–positron pair state might be distributed with the motion of surrounding molecules as indicated in Fig. 6, since the longest lifetime is one simple lifetime component. The lifetime of a positron on CS_2 molecules might be about 400 ps. Hence the lifetime of the electron–positron pair state is shorter than that of the Ps bubble state. This is the reason why CS_2 was out of the correlation of the surface tension and the lifetime as Kobayashi indicated.[13] Moreover the electron–positron pair state should give a broader curve which is not a simple gaussian in angular correlation. Therefore the narrowest component, I_N, might be just part of the electron–positron pair state, and the longest lifetime component might be due to all of the electron–positron pair state. It is the reason why three times of the intensity of the narrowest component measured by AC is much lower than that of the longest lifetime component by LT. Besides, these two results can explain the fact that the value of $\frac{511\ \mathrm{keV}\times(\mathrm{fwhm_l})\ \mathrm{mrad}}{3.00\times10^8\ \mathrm{m\,s^{-1}}}\times R(\tau_3)$ for CS_2 is so much lower than values for others.

CS_2/Hexane Mixture. Adding hexane must reduce the surface tension, hence the longest lifetime became longer, but the shift of the transition region to lower temperature was small. If the change of the lifetime is caused by the bubble size directly, the zero-point energy should be smaller in the mixture than in pure CS_2. This would mean that the decrease



Positronium state in liquids such as hexane



The electron-positron pair state in CS_2

Fig. 6. The mechanism of the electron–positron pair state in CS_2. I_N is the intensity of the narrowest component of angular correlation measurement and I_3 is the intensity of the longest lifetime component of lifetime measurement. (* The indicated wave function is just for easy-understanding, the real wave functions of electron and positron must be separated in this state.)

of the intensity at low temperature should not be seen at high concentration. However, it was. In pure CS_2, electrons seem to be trapped in the cluster of CS_2 molecules.[8] Probably, the electron–positron pair state is mainly formed in CS_2 clusters in the mixture of CS_2 and hexane, then the electron–positron pair may move to the place where the surface tension is reduced by the hexane molecules, and finally this state shifts to Ps bubble state. It is the reason why there is so little change in the intensity but a great change in the lifetime.

On the other hand, the lifetime at −105 °C in 2 M hexane is about 1.7 ns which is more than two times larger than that in pure CS_2. It might be the lifetime of the ortho-Ps bubble state. These phenomena strongly indicates that the "fourth positron state" is the electron–positron pair which cannot make the final transition to the Ps bubble state as O. E. Mogensen suggested.[9]

CS_2/Methanol Mixture. Methanol has a high dielectric constant (32.63 at 25 °C), which is much higher than that of CS_2 (2.64 at 20 °C). Then the energy difference, ΔG, of scavenged electrons on CS_2 molecules in pure CS_2 and in 1 M methanol in CS_2 can be calculated by Born's formula:

$$\Delta G = -\frac{L(ze)^2}{8\pi\varepsilon_0 r}\left(1 - \frac{1}{\varepsilon}\right),$$

where L is Avogadro's constant, ze is the charge, ε_0 is the dielectric constant in vacuum, r is the effective radius in Å and ε is the dielectric constant of the matrix. Now, I applied 4 Å as the effective radius; then the difference of ΔG in pure CS_2 and in 1 M methanol in CS_2 is about 0.21 eV. Indeed, this effect can be expected just on the trapped electron and positron. Probably, though 1 M is not a low concentration, the electron–positron pair state may not be affected by methanol, because an electron–positron pair has no charge. Then, the effect of methanol in CS_2 is expected just on the transition from the free positron state to the electron–positron pair state, in other words, the drastic change of the intensity

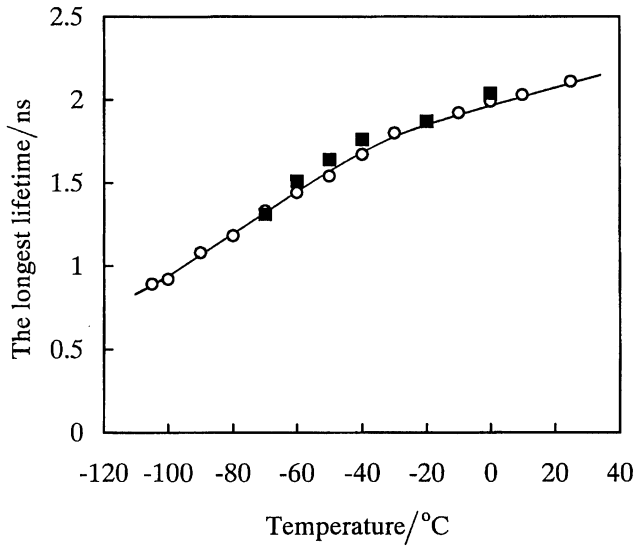


Fig. 7. The temperature dependence of the longest lifetime on pure CS_2 (○) and 1 M methanol in CS_2 (■).

of the longest lifetime component should happen at higher temperature than that in pure CS_2. The results is shown in Fig. 4 and it happened at the higher region, as expected. On the other hand, the change of the lifetime would be small, although 1 M concentration is not low, because the decrease of the surface tension should not be so much. The lifetimes of pure CS_2 and 1 M methanol in CS_2 at several temperatures are shown in Fig. 7. The lifetime was almost the same at every temperature.

It confirms that the transition from the bubble state to the mainly non-Ps state takes place between −40 and −110 °C and the Ps bubble state is not the lowest energy state at −110.8 °C.[9)]

Conclusion

In hexane/CS_2 mixture, Ps might be formed in the cluster of CS_2 molecules and move to the site where the surface tension is lower because of the hexane molecules. Even if the longest lifetime is 1.7 ns in 2 M hexane, the decrease of the intensity of the longest lifetime component can be seen. This phenomena confirms the model of the "fourth positron state".

The intensity of the longest lifetime component decreased at higher temperature in methanol/CS_2 mixture than in pure CS_2. It confirms that the transition from the bubble state to the mainly non-Ps state occurs at low temperature in CS_2.

This study was started by an argument with Dr. O. E. Mogensen. I thank him so much for his honest discussion, and am very sorry that I can not discuss the results and the interpretation with him. I also thank members of the Positron Club, the group of the young positron scientists in Japan, for their useful suggestions.

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