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Positronium Annihilation in Fluorinated Benzene Derivatives

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Positron lifetime measurements have been carried out to study formation and annihilation of *ortho*-positronium (*o*-Ps) in a series of fluorinated benzene derivatives. The *o*-Ps lifetimes (τ_3) are longer than those expected from Tao's empirical relationship for hydrocarbons, $\tau_3{}^{-1}$ (ns^{-1}) = $0.061\sigma^{0.5}$, where σ is the surface tension of the liquids in units of mN m^{-1}. It was found that there is a rather good correlation between the *o*-Ps intensity I_3 and the dipole moment for the fluorinated compounds.

It is known that the reactivity and stability of hydrocarbon molecules are dramatically changed by replacing hydrogen by fluorine. The fluorine–carbon bond is stronger than other halogen–carbon bonds or the hydrogen–carbon bond. The van der Waals radius of fluorine is small enough to produce a fluorocarbon structure around a carbon chain or ring system. There are other characteristic features in fluorocarbons. For example, surface tension and boiling point of fluorocarbons are appreciably lower than expected from their molecular weight. These characteristic features are mainly caused by the weak intermolecular force of fluorocarbons. Fluorine-containing substances are applied to many fields on the basis of their unique physical properties.[1,2]

A lifetime spectrum of positrons annihilating in molecular liquids is normally decomposed into three exponential components. The longest-lived component, with an average lifetime τ_3 and the corresponding relative intensity I_3, is attributed to pick-off annihilation of *ortho*-positronium (*o*-Ps), the spin-parallel bound state between a positron and an electron, in which the positron in *o*-Ps annihilates with one of the neighboring electrons with opposite spin. The pick-off annihilation lifetime is inversely proportional to the overlap of the positron and electron wavefunctions, and hence varies from one liquid to another.[3]

The main purpose of the present research was to clarify the effect of fluorination of hydrocarbon on the formation and annihilation of *o*-Ps. Positron lifetime measurements were conducted for a series of fluorinated benzene derivatives and the data were compared with those for benzene and other non-fluorinated compounds.

Experimental

Fluorinated benzene derivatives were purchased from Tokyo Chemical Industry, Ltd. and are listed in Table 1. The degree of fluorination ranged from 0 to 6.

Positron lifetime spectra were recorded with a fast–fast coincidence system. The time resolution of the system was ca. 180 ps FWHM. The positron source was ca. 1 MBq of ^{22}Na sealed between two thin Kapton foils. Oxygen dissolved in the liquids was removed by the vacuum freeze-thaw technique.

The lifetime spectra were resolved into three exponentially decaying components, a short-lived τ_1, an intermediate-lived τ_2, and the longest-lived τ_3 (with corresponding intensities I_1, I_2, and I_3), by the POSITRON FIT EXTENDED program.[4,5] In the course of the data analysis, the lifetime of the spin- antiparallel *para*-positronium (*p*-Ps) component, τ_1, was fixed to its intrinsic self-annihilation lifetime of 125 ps. All the measurements were performed at room temperature (293±2 K).

Table 1. *Ortho*-Ps Intensities and Lifetimes for the Fluorinated Benzene Derivatives

Liquid	τ_3	I_3	Dipole moment
	ns	%	D
Benzene	3.10	41.1	0
Fluorobenzene (C_6H_5F)	3.10	26.2	1.6
1,2-Difluorobenzene (1,2-$C_6H_4F_2$)	3.10	14.6	2.46
1,3-Difluorobenzene (1,3-$C_6H_4F_2$)	3.29	26.4	1.51
1,4-Difluorobenzene (1,4-$C_6H_4F_2$)	3.36	43.5	0
1,2,4-Trifluorobenzene (1,2,4-$C_6H_3F_3$)	3.36	19.6	1.39
1,3,5-Trifluorobenzene (1,3,5-$C_6H_3F_3$)	3.62	35.6	0
1,2,4,5-Tetrafluorobenzene (1,2,4,5-$C_6H_2F_4$)	3.46	37.0	0
Pentafluorobenzene (C_6HF_5)	3.59	28.5	1.44
Hexafluorobenzene (C_6F_6)	3.62	52.9	0

Results and Discussion

A. *Ortho*-Ps Lifetime in Fluorinated Benzene Derivatives. It is well known that Ps is highly localized in a cavity called a "bubble" in liquids.[3,6,7] A simple bubble model states that the size of the cavity is determined by the balance between the zero-point energy of the localized Ps and the energy required to make such a hole in a liquid. As the latter energy is governed by molecular cohesion of the liquids, surface tension has been used successfully to describe the bubble state of *o*-Ps atoms. According to Tao,[8] the relation between the *o*-Ps lifetime and the surface tension σ takes the simple form:

$$\tau_3{}^{-1} = a\sigma^b, \tag{1}$$

where a and b are constants. For *n*-alkanes, the equation is written as

$$\tau_3{}^{-1} = 0.061\sigma^{0.5}, \tag{2}$$

where τ_3 is the *o*-Ps lifetime in ns and σ is the surface tension in $\mathrm{mN\,m^{-1}}$ ($=\mathrm{dyn\,cm^{-1}}$).[8]

Figure 1 shows a plot of τ_3 vs. surface tension σ for the fluorinated benzene derivatives. Also included in this figure is the plot for several hydrocarbons (*n*-alkanes and benzene derivatives).[9] The numerical values of τ_3 and σ for the fluorinated compounds are listed in Table 1. It is seen in Fig. 1 that τ_3 for both the unfluorinated and fluorinated hydrocarbons increases with decreasing σ. Interestingly, while Eq. 1 can reproduce the *o*-Ps lifetimes for hydrocarbons, upward deviations are observed for the fluorinated benzene derivatives, indicating that τ_3 values in the latter liquids are somewhat elongated.

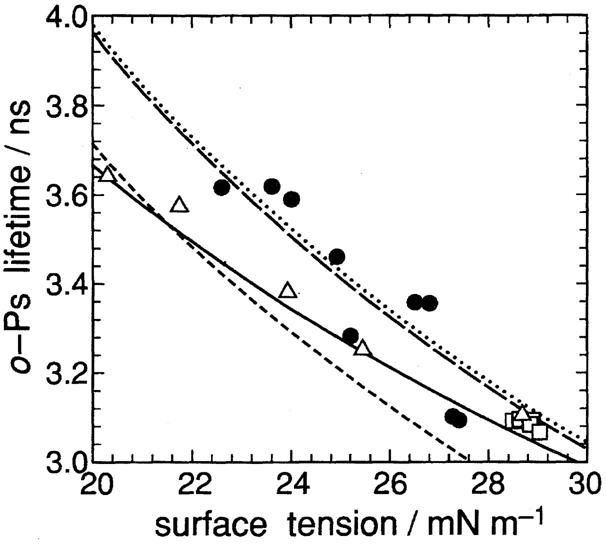

Fig. 1. Plot of *o*-Ps lifetimes vs. surface tensions for the fluorinated benzene derivatives measured by the Wilhelmy method (●). The data for several hydrocarbons are also included in this figure: (△) *n*-alkanes, (□) methyl substitute benzenes.[9] The solid line in this figure shows the empirical relationship of Tao for hydrocarbons.[8] The wide and narrow dashed lines are the predictions of Eqs. 4 and 5 with $\Delta R = 0.166$ nm and $\Delta R = 0.170$ nm, respectively, under the condition of $\lambda_a = 2\ \mathrm{ns^{-1}}$. The dotted line represents the prediction with $\Delta R = 0.170$ nm and $\lambda_a = 1.87\ \mathrm{ns^{-1}}$.

To derive Eq. 2, Tao considered not only the surface tension but the attractive force between the Ps atom and the surrounding molecules was taken into account as a factor reducing the bubble radius. He estimated that the attractive force contributed to a 0.9 Å reduction of the bubble radius for many liquids.[8] As characteristic features of fluorocarbon molecules such as lower surface tension and boiling point are mainly due to the weak intermolecular forces, it is likely that the attractive force between the Ps atom and the surrounding molecules is reduced in fluorocarbons. If the attractive force is really reduced, the Ps cavity should be enlarged and hence τ_3 becomes longer than that for hydrocarbons.

Meanwhile, the bubble model which does not take the attractive force between the Ps atom and the surrounding molecules into consideration has been used as well. On assuming that the Ps bubble can be represented by a spherical potential well with an infinitely high wall, the total energy of the Ps bubble state is given by

$$E = \pi^2\hbar^2/4mR^2 + 4\pi\sigma R^2 + 4\pi R^3P/3, \tag{3}$$

where R is the bubble radius, m is the electron mass, $\hbar$ is Plank's constant divided by 2π, σ is the surface tension and P is pressure.[3,10] The last term $4\pi R^3P/3$ is negligible in this study because it is very small in the present case of the liquids under saturated vapor pressure. As the total energy E assumes a minimum in equilibrium from the condition $\mathrm{d}E/\mathrm{d}R = 0$, we can obtain the following relationship between the bubble radius and the surface tension:[3,10]

$$R = 1.242\sigma^{-0.25}, \tag{4}$$

where R is given in units of nm.

Eldrup et al. assumed a uniform electron layer on the surface of the bubble and derived the following relation between the *o*-Ps lifetime and the bubble radius:[11]

$$\tau_3{}^{-1} = \lambda_a(\mathrm{ns}^{-1})[1 - \frac{(R-\Delta R)}{R} + \frac{1}{2\pi}\sin\frac{2\pi(R-\Delta R)}{R}], \tag{5}$$

where ΔR is the effective thickness of the electron layer. λ_a is the annihilation rate of the Ps atom in the electron layer and is often assumed to be $2\ \mathrm{ns^{-1}}$.[11] As is shown in Fig. 1, the experimental data in this study can be reproduced using $\Delta R = 0.170$ nm for the hydrocarbons and $\Delta R = 0.166$ nm for the fluorinated benzene derivatives, provided that λ_a is always equal to $2\ \mathrm{ns^{-1}}$. The experimental data for the fluorinated benzene derivatives can also be reproduced by using $\Delta R = 0.170$ nm and $\lambda_a = 1.87\ \mathrm{ns^{-1}}$ if we assume that $\Delta R = 0.170$ nm is unchanged by fluorination. The smaller ΔR or λ_a obtained above appears to indicate that the effective number of electrons, which contribute to the pick-off annihilation of *o*-Ps, is somehow reduced in fluorinated compounds.

B. *Ortho*-Ps Intensity in Fluorinated Benzene Derivatives. The *o*-Ps intensities for the fluorinated benzene derivatives are summarized in Table 1. We see in this table that there is no one-to-one correlation between the *o*-Ps intensity and the number of fluorine atoms in the molecules. For example, the *o*-Ps intensity for the three difluorobenzenes ($C_6H_4F_2$) ranges from 14.6 to 43.5% and increases in the order of 1,2-$C_6H_4F_2$, 1,3-$C_6H_4F_2$, and 1,4-$C_6H_4F_2$. Comparison of the I_3 values with dipole moments for the three difluorobenzenes reveals that the lower the dipole moment is, the larger the Ps formation probability is.

Figure 2 shows a plot of the *o*-Ps intensity vs. dipole moment for all the fluorinated benzene derivatives in Table 1. It is seen that the two quantities are rather well correlated with each other and the *o*-Ps intensity decreases with increasing dipole moment. A similar correlation is observed for other compounds as well; we see in Fig. 2 that the *o*-Ps intensity for hydrocarbons, alcohols, carbon disulfide, tetrahydrofuran, dioxane, acetonitrile, diethyl ether, and pyridine decreases with increasing dipole moment in a similar manner to the fluorinated benzene derivatives.

According to the spur reaction model, Ps is formed as the result of recombination of a thermalized positron-electron pair in the terminal positron spur.[7,21,22] Based on Onsager's model for the recombination of a charge-separated pair,[23] it has been considered that the Ps formation probability in nonpolar liquids is primarily determined by the ratio of the characteristic initial separation (r) of the pair to the Onsager radius (r_c); the smaller the ratio, the larger the recombination probability and hence Ps formation. Here the Onsager radius r_c is defined as $r_c = e^2/4\pi\varepsilon_0\varepsilon kT$, where e is the electric charge, ε_0 is the dielectric constant in vacuum, ε is the relative dielectric constant, k is the Bolzmann constant and T is the absolute temperature.

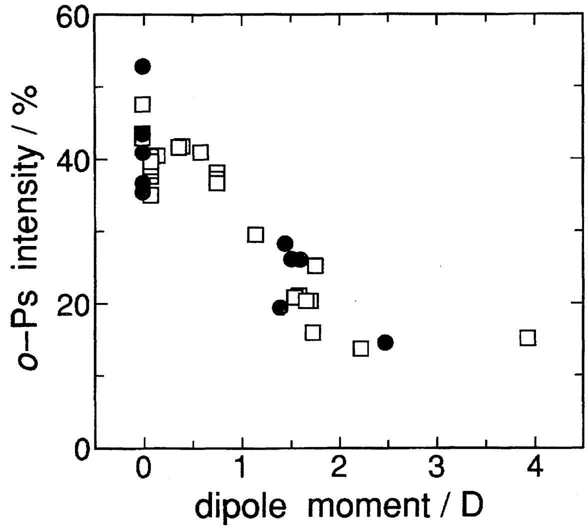

Fig. 2. Variation of the *o*-Ps intensity I_3 with the dipole moment (1 D = 3.33564×10^{-30} C m) in the fluorinated benzene derivatives (●). The plot for the other molecules such as hydrocarbons, alcohols etc. is also included in this figure (□).[7,12] Data of dipole moment are taken from Refs. 13, 14, 15, 16, 17, and 18. Dipole moment for symmetrical molecular configuration is assumed to be zero. Other halogenated, such as chlorinated, brominated, liquids are not included in this figure because the *o*-Ps yield is considerably reduced in these liquids as a result of dissociative electron capture.[19,20]

Recently, we studied the effect of a polar additive on Ps formation in polyethylene (PE).[24] It was found that the presence of polar species can cause trapping of Ps precursors. A similar trapping effect has to be present in polar liquids; one can expect that, with increase in the dipole moment, the trapping rate of the positron and/or the electron is increased. This may be the reason why the intensity I_3 decreases with increasing dipole moment in Table 1 and Fig. 2. However, even in the liquids with high dipole moments, some positron-electron pairs with a short initial separation may escape from trapping[24] and a certain fraction of Ps formation remains uninhibited. This is in qualitative agreement with the data in Fig. 2, where the Ps formation is not totally inhibited in liquids with very high dipole moments.

In Fig. 2 and Table 1, we can see that, even among the nonpolar liquids with no dipole moment, there is a fairly large scatter in the I_3 data. For example, the *o*-Ps intensity for C_6F_6 is higher than the value for another nonpolar liquid, benzene, by 12%. The characteristic initial separations of the positron-electron pairs were estimated to be 8 nm for hexafluorobenzene and 18 nm for benzene based on an assumption that the distribution of the initial separation can be described by an exponential function,[25,26] suggesting that the different ratios of the initial separation to the Onsager radius are mainly responsible for the different values of I_3, because the Onsager radii are very similar to each other in the two liquids. No data of the characteristic initial separations and dielectric constants are available for the other compounds in Table 1, but we expect that the ratio of the characteristic initial separation of the positron-electron pairs to the Onsager radius may be different in different compounds and their recombination probability may vary from one compound to another. In spite of the correlation in Fig. 2, the fairly large scattering in the I_3 data among the nonpolar liquids indicates that the *o*-Ps intensity in the fluorinated benzene derivatives is not solely determined by dipole moment.

Summary. The *o*-Ps lifetime for the fluorinated compounds tended to be longer than expected from surface tension. In light of the unique properties of the fluorinated compounds, it is not surprising that the *o*-Ps lifetimes in fluorobenzenes are somewhat different from those in hydrocarbons. The effective number of electrons, which contribute to pick-off annihilation of *o*-Ps, was supposed to be reduced in the fluorinated compounds. One should note that the relation between τ_3 and the surface tension depends on chemical structure, and this effect has to be properly taken into consideration when interpreting *o*-Ps lifetime data in liquids. On the other hand, no clear change by fluorination was observed in the *o*-Ps intensity. A rather good correlation between the *o*-Ps intensity and dipole moment was found for fluorinated and non-fluorinated compounds, and discussed within the framework of the spur model of Ps formation.

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