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Defects in the rotator and liquid phases of *n*-alkanes: a study using FTIR and positron annihilation

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Abstract. Fourier transform infra-red (FTIR) and positron lifetime spectroscopy (PLS) techniques have been used to quantify end-*gauche*, double-*gauche* and kink conformer concentrations in a number of the higher *n*-alkanes over a temperature range which includes crystalline, rotator and liquid phases. These have been correlated with *ortho*-positronium (*o*-Ps) lifetimes and intensities in identically prepared samples of dodecane (C₁₂), hexadecane (C₁₆), eicosane (C₂₀), tetracosane (C₂₄), octacosane (C₂₈) and dotriacontane (C₃₂). Consideration was given to the importance of sample preparation and the presence of impurities and free oxygen in determining the correct *o*-Ps lifetimes in the liquid phase. It was found that *o*-Ps lifetimes and intensities correlate well with the appearance of conformer defects which arise when the system leaves the all-*trans* configuration of the crystalline phase and approaches the rotator and liquid phases. The important volume in the determination of *o*-Ps lifetime was found to be the defect volume per molecule, and together with the behaviour of the *o*-Ps intensity as a function of temperature in the liquid phase this suggests that either the positron or positronium is trapped in the conformer defects.

1. Introduction

A recognition of the importance of alkane chains C_{*n*}H_{2*n*+2}, in fields as diverse as polymer technology, biomembranes, biomaterial development and molecular electronics, has resulted in their study by many chemical and physical methods. Structural determinations using x-rays [1, 2] and neutrons [3] have been supplemented by infra-red [4, 5, 6, 7], Raman [8, 9, 10] and NMR [11] spectroscopy. In addition, theoretical work has considered the influence of defects on the melting transition [12] and on the simulation of molecular motion in the rotator phase [13].

Recent results from positron annihilation spectroscopy have also been shown to be extremely sensitive to phase transitions [14, 15] and to the presence of structural defects [16] which appear in long chain molecular systems. The work of Lévy *et al* [14] used both lifetime and Doppler broadening spectroscopy over a wide temperature range on just two paraffins, C₃₂H₆₆ and C₃₃H₆₈, while Serna *et al* [16] used lifetime measurements at one temperature only on a range of polyethylene samples having well characterized crystalline and defect structures.

A number of questions arise as a result of these investigations which bear not only on the nature of the system being studied, but also on the processes which precede positron annihilation. Foremost amongst these is the precise definition of a free volume, which has been generally acknowledged to be of prime importance in determining the quenching of *o*-Ps. It is not clear whether this is provided simply by subtracting the inherent molecular

volume from the unit cell volume in all cases, or whether there are additional components which arise from changes in molecular shape. Furthermore there is abundant evidence that differences in sample preparation (such as heat treatment and the use of different solvents in the re-crystallization procedure) as well as the purity of the starting material can have significant effects on the positron parameters. Although the presence of free molecular oxygen is known to strongly affect the quenching of *o*-Ps in certain systems it is not clear that it will do so in the highly viscous alkane samples studied in this work.

This paper sets out to investigate the dependence of the lifetime and intensity of the *o*-Ps bound state on the concentration of conformers which form as the alkane system changes from crystalline, through the rotator to the liquid state. The latter were determined by FTIR spectroscopy using identical sample preparation and temperature control as in the case of the positron lifetime measurements. Positron lifetime and FTIR data have therefore been taken in the even *n*-alkanes C₁₂H₂₆, C₁₆H₃₄, C₂₀H₄₂, C₂₄H₅₀, C₂₈H₅₈ and C₃₂H₆₆ over the range 15–80 °C in order to try to quantify the significance of the free volume in determining *o*-Ps formation and quenching. It has been considered essential to extend both sets of measurements well into the liquid region in order to establish the sensitivity of the *o*-Ps data to conformer concentration.

2. Experimental details

Samples of C₁₂H₂₆, C₁₆H₃₄, C₂₀H₄₂, C₂₈H₅₈ and C₃₂H₆₆ were obtained from Sigma Chemicals Ltd (stated purity 99%), with an additional sample of C₂₀H₄₂ from Koch-Light Laboratories Ltd (purity ~ 98%). The sample of C₂₄H₅₀ (purity 99%) came from Aldrich Chemicals. All samples had been crystallized from the solvent by the manufacturers and were used for the main experiments in the as-received state without any further purification, by being allowed to slowly crystallize from the melt, at ~ 4 °C min⁻¹, directly into the sample cell (except C₁₂H₂₆ and C₁₆H₃₄ which are liquid at room temperature) in order to avoid the non-reproducible occurrence of air bubbles during the temperature cycling.

2.1. Positron lifetime measurements

All lifetime spectra were analysed using a three-component fit, with the shortest two components constrained to 0.125 ns (*p*-Ps) and 0.395 ns (free positron). Although satisfactory four-component fits could be made to data from the rotator phase of the higher chain lengths, to give a marginally lower χ^2 per channel, this was not possible from either the crystalline or liquid phases. The identification of Ps trapping processes would therefore have been made difficult, as the temperature increased through the phase transitions, if different fitting procedures had been used. It was considered more appropriate therefore to interpret the data in terms of a single *o*-Ps lifetime and intensity only.

The main component (99.88%) of the resolution function had an FWHM of 0.372 ns, while the correction for annihilations within the source holder contained only a 1% contribution at a lifetime (2.383 ns) near that of *o*-Ps. Because of the need to take data at temperatures up to 80 °C, the Kapton foils used to seal the ²²Na source were separated from the foils which enclosed the sample by an air gap of 2 mm. This resulted in a total source annihilation correction factor of 30%, made up of 22.05% at 0.395 ns and 7.66% at 0.100 ns.

The effect that such a large source correction factor might have on the precision of the experiment was determined by measuring the positionium parameters in water over the same temperature range as used for the alkane systems. Using modified versions of POSITRONFIT

EXTENDED [17] to fit these water data, the *o*-Ps lifetimes and intensities showed excellent agreement with literature values, confirming that reliable determinations could be made of the *o*-Ps parameters in alkane systems.

2.2. FTIR measurements

Methylene wagging modes were observed in the spectral region 1325–1400 cm^{-1} in $\text{C}_{12}\text{H}_{26}$, $\text{C}_{16}\text{H}_{34}$, $\text{C}_{20}\text{H}_{42}$, $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{28}\text{H}_{58}$. The intensities of the individual bands at 1341, 1353 and 1368 cm^{-1} were assumed to be proportional to the occurrence of end-*gauche*, double-*gauche* and kink conformers respectively and were normalized to the intensity of the CH_3 bending mode at 1378 cm^{-1} .

Films of approximate thickness 200 μm were prepared between BaF_2 windows by heating a sample above its melting point and allowing it to cool slowly as in the case of the positron measurements. Temperature control of the samples was achieved using the same calibrated thermistor and thermostatted circulator so that the temperature could be regulated to ± 0.5 $^\circ\text{C}$ with an estimated overall accuracy of ± 1.0 $^\circ\text{C}$. A high-temperature limit of 70 $^\circ\text{C}$ for the FTIR measurements had to be imposed for experimental reasons. Approximately 20 min was allowed for temperature equilibration between each spectrum.

Measurements were made on a Mattson FTIR spectrometer on which the operating parameters were chosen to give a resolution of 1 cm^{-1} by co-addition of 32 interferograms. Data were apodized with a triangular function and Fourier transformed to yield data encoded every 0.5 cm^{-1} . A linear baseline was selected to connect observed minima in the spectra between 1325 and 1400 cm^{-1} .

Spectra were analysed using a number of Lorentzian functions in the multiparameter fitting routine MINUIT [18]. All line widths, intensities and peak positions were allowed to vary during the least-square fitting in which the difference between the simulated sub-bands and the experimental spectrum was minimized. Figure 1 shows a typical fit for the liquid phase of $\text{C}_{20}\text{H}_{42}$.

3. Conformer states

The extensive investigations by Snyder [19] on the infra-red spectra of *n*-alkanes resulted in the tabulation of frequencies for a large number of vibrations, including some that are specific to the localized structures that contain *gauche* bonds. Intensities of the various C–H stretching, scissoring, rocking and wagging modes can be used to obtain quantitative information on defect structures within the chains that contribute to the overall disorder of the system. The bands chosen in this work are the C–H bending modes for segments of the chain containing specific *trans-gauche* sequences. The peak at 1341 cm^{-1} indicates a penultimate bond oriented such that the terminal methyl group is in a *gauche* configuration relative to the methylene group three carbon atoms away (end *gauche*). The peak at 1353 cm^{-1} is due to two adjacent *gauche* bonds along the carbon back bone (double *gauche*) while the peak at 1368 cm^{-1} arises from a *gauche-trans-gauche* GTG sequence (kink). Close to these sub-bands there appears the peak at 1378 cm^{-1} which is due to the symmetrical bending of the terminal CH_3 group and which is insensitive to conformation and chain length. This intensity was therefore used as an internal standard against which to normalize the intensities of the conformation-sensitive CH_2 modes [20]. Since the above wagging vibrations are localized they can be assumed to be unaffected by chain length or conformational changes elsewhere in the chain. The band intensities could therefore be considered linearly dependent on conformer concentration [21].

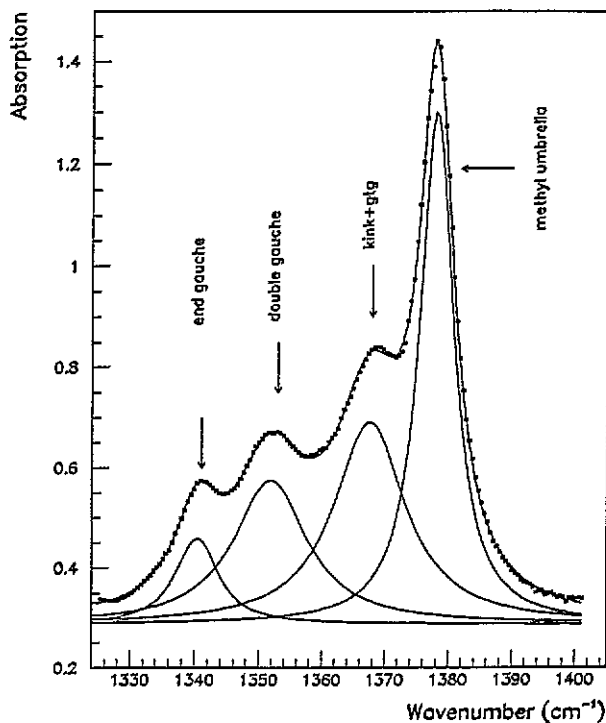


Figure 1. Lorentzian curve fit of the conformer peaks at 1341, 1353, 1368 and 1378 cm^{-1} for the liquid phase of $\text{C}_{20}\text{H}_{42}$. The experimental data points are the closed squares and the solid lines come from the MINUIT multiparameter fitting routine [18].

Confirmation that these infra-red bands are most likely to be associated with the defect structures which appear when long chain molecular systems undergo melting has come from other investigations.

The onset of melting in $n\text{-C}_{33}\text{H}_{68}$ was shown by Ewen *et al* [22], using small-angle x-ray, neutron and Raman scattering, to involve a succession of at least three distinct phase transitions rather than progressing via a single step in which orientational disorder was achieved through rotational jumps about the long molecular axis [23]. Ewen *et al* furthermore provided indirect evidence that the so-called rotator phase had as many as 40–70% of the molecules in non-planar configurations. Three types of non-planar defect were also identified by Maroncelli *et al* [24] using differential scanning calorimetry and infra-red spectroscopy in the rotator phases of the odd n -alkanes from C_{17} to C_{29} , the concentrations of which were found to increase with chain length.

4. Results

4.1. Positron annihilation

4.1.1. Sample preparation, purity and oxygen content. Using the highest-purity samples of solvent-crystallized $\text{C}_{24}\text{H}_{50}$, $\text{C}_{28}\text{H}_{58}$ and $\text{C}_{32}\text{H}_{66}$ in the as-received state from the suppliers, all of which exist in the crystalline phase at 22 °C, o -Ps lifetimes and intensities were

compared for samples which had been mechanically compressed into the sample chamber, and those which had been slowly cooled from the liquid phase. The slight but significant increase in both *o*-Ps lifetime and intensity values in the melt-crystallized samples is consistent with the x-ray results from Davis *et al* [25] who found an increase in the unit cell volume in melt-crystallized over solvent-crystallized polyethylene samples. With the additional evidence from Raman data in even *n*-alkanes [26], which suggested that melt-crystallized samples possessed a more rigid crystal structure than those used directly from solvent growth, the samples used in the present work were all crystallized from the melt.

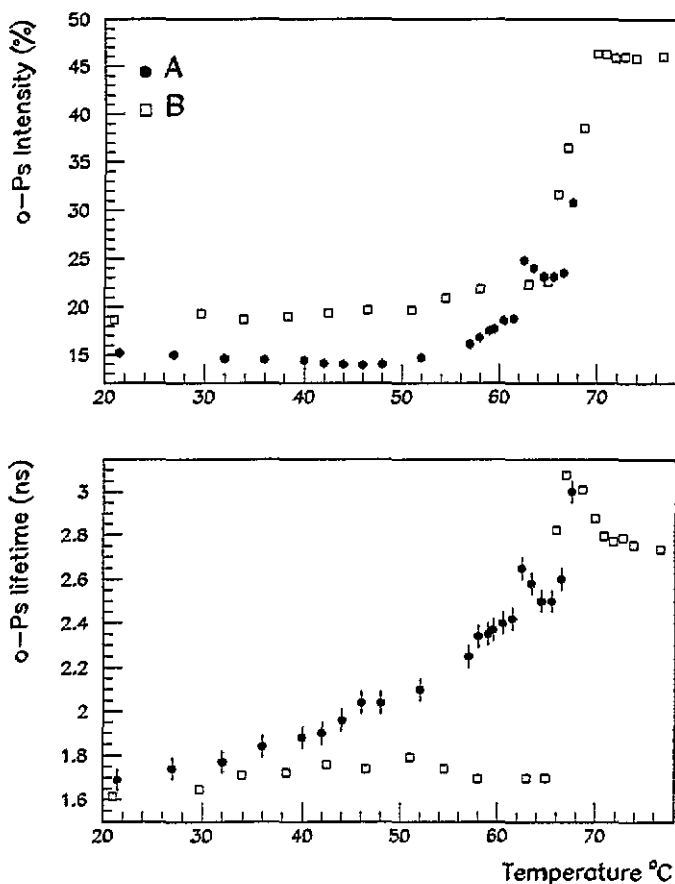


Figure 2. *o*-Ps lifetimes (ns) and intensities (%) in dotriacontane $C_{32}H_{66}$. (A) Lévy *et al* [14], (B) present work.

The as-received melt-crystallized samples gave transition temperatures which showed excellent and reproducible agreement with literature values. A comparison (figure 2) with the results of Lévy *et al* [14] from $C_{32}H_{66}$, over a much wider temperature range, shows differences in both the absolute values and in the temperature variation of *o*-Ps lifetimes and intensities. In particular it must be noted that the unexplained peak observed by Lévy *et al* at 336 K in $C_{32}H_{66}$ but not in $C_{33}H_{68}$ was tentatively assigned to the use of a polar solvent in the recrystallization procedure in the former case and a non-polar solvent in the latter case.

A determination of the free oxygen content in such samples cannot be made easily. Only by taking the sample to the liquid phase under vacuum, and then bubbling through oxygen-free nitrogen or by melting under a purged nitrogen atmosphere, can it be reasonably assumed that the oxygen content is zero. Otherwise it might be expected that any oxygen in the sample, whether in the crystalline or liquid phase, would exist in a concentration determined by the equilibrium conditions prevailing as the sample cooled from the liquid phase.

The effect of oxygen diffusion and its influence on the *o*-Ps lifetime as quantified by the quenching rate constant, k_q , has been studied in a number of liquid organic systems by Lee and Celitans [27]. They showed that at a constant temperature the oxygen quenching rate constant is inversely proportional to the viscosity. Our data for dodecane (C_{12}) and hexadecane (C_{16}) in figure, 3 which show a decrease in *o*-Ps lifetime with temperature, are in agreement with this trend. However, the extent of the likely reduction of *o*-Ps lifetime due to the diffusion of free oxygen is uncertain in liquid alkanes having chain lengths in the range 12–32 C atoms, because of the presence of the melting temperature and the consequent involvement of structural changes. Even if there were significant diffusion of molecular oxygen, the quenching rate constant would be expected to be small because of the high viscosity. There is therefore no *a priori* indication of whether the *o*-Ps lifetime will increase or decrease as the temperature is raised through the crystal–liquid transition. Indeed it might be expected that a sample saturated with atmospheric oxygen in the liquid phase would continue to show the same *relative* change in *o*-Ps lifetime either side of the transition temperatures as one which had been totally de-gassed.

4.1.2. *o*-Ps lifetimes and intensities for $12 \leq n \leq 32$. Figures 4 and 5 show the temperature variation of *o*-Ps lifetimes and intensities in $C_{20}H_{42}$, $C_{24}H_{50}$, $C_{28}H_{58}$ and $C_{32}H_{66}$. In those cases where there is a hexagonal (rotator) phase existing between the monoclinic (crystalline) and liquid phases (C_{24} – C_{32}), a hysteresis of ~ 4 °C is observed at both transition temperatures. Furthermore, the *o*-Ps lifetime decreases as the system goes from the hexagonal to the liquid phase. Table 1 shows, however, that the free volume per molecule, $V - V_0$, where V is the molecular cell volume and V_0 is the inherent volume of each molecule, undergoes a corresponding increase. Although the mean *o*-Ps lifetimes and intensities are largely independent of chain length in all three phases, the total free volume shows a systematic increase as the number of C atoms increases, and this casts further doubt on the previously assumed positive correlation between *o*-Ps lifetime and free volume.

Table 1. Inherent, V_0 , and molecular cell, V , volumes and macroscopic density, ρ , for the crystalline, rotator and liquid phases of *n*-alkanes. $V - V_0$ is the free volume per molecule. Data compiled from Templin [38], Gerson *et al* [39] and Heyding *et al* [40].

<i>n</i>	V_0 (nm ³)	V			$V - V_0$			ρ		
		Crystal (nm ³)	Rotator (nm ³)	Liquid (nm ³)	Crystal (nm ³)	Rotator (nm ³)	Liquid (nm ³)	Crystal (nm ³)	Rotator (nm ³)	Liquid (nm ³)
12	0.2090	—	—	0.3778	0.1000	—	0.1688	—	—	0.7487
16	0.2754	—	—	0.4863	0.1300	—	0.2109	—	—	0.7733
20	0.3414	0.5055	—	0.6029	0.1641	—	0.2615	0.9280	—	0.7780
24	0.4074	0.6120	0.6512	0.7215	0.2046	0.2438	0.3141	0.9187	0.8634	0.7792
28	0.4734	0.6997	0.7523	0.8413	0.2263	0.2789	0.3679	0.9367	0.8712	0.7789
32	0.5394	0.8014	0.8561	0.9545	0.2620	0.3167	0.4151	0.9340	0.8745	0.7802

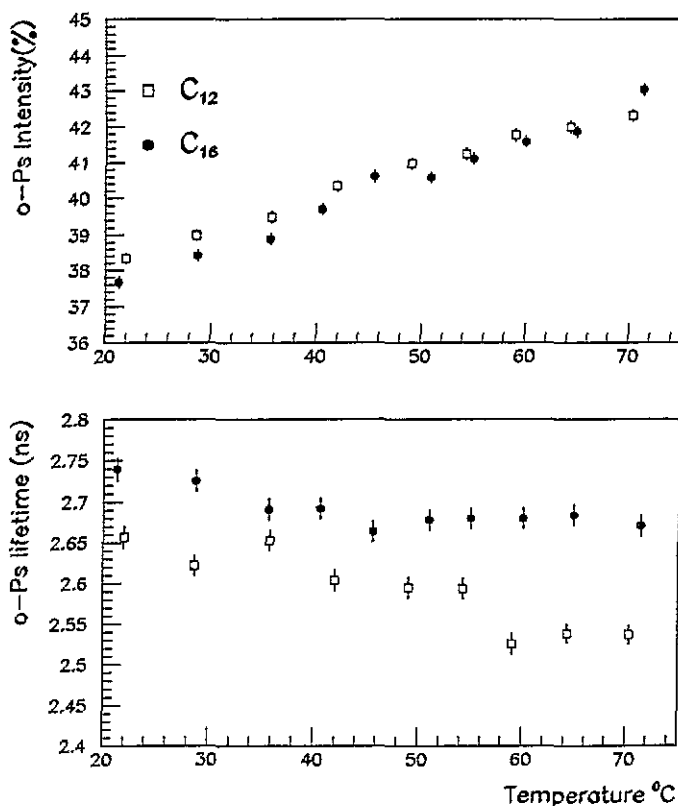


Figure 3. *o*-Ps lifetime (ns) and intensities (%) in the liquid phase of dodecane C₁₂H₂₆ and hexadecane C₁₆H₃₄.

4.2. FTIR

In the monoclinic (crystalline) state, infra-red absorption is observed only at 1378 cm⁻¹ which is the band corresponding to the CH₃ deformation mode. Liquid and hexagonal (rotator) phases, where they exist, all show additional absorption in the conformer bands at 1368 cm⁻¹ (CH₂ kink + GTG wagging), 1353 cm⁻¹ (CH₂ double-*gauche* wagging) and 1341 cm⁻¹ (CH₂ end-*gauche* wagging). With the exception of the end-*gauche* conformer in C₁₂, the intensities of all bands are seen to increase with chain length.

The normalized intensities over the complete temperature range for all samples are shown in figure 6, the most significant feature being the anomalous behaviour of C₂₈H₅₈ in the 4 °C immediately above the rotator-liquid phase transition. In this system the FTIR spectra show a tendency to split into sub-bands in the rotator phase (at 59 °C), which become more prominent in the first 4 °C of the liquid phase (from 61 °C to 65 °C) and even beyond (at 66 °C). Whereas the other FTIR spectra could be fitted with a χ^2 per channel of approximately unity with an error on the fitting parameters of $\sim 2\%$, these spectra in C₂₈H₅₈, when fitted with a single component in each of the three conformer states, produced χ^2 per channel values of approximately four with corresponding errors on the parameters of $\sim 10\%$.

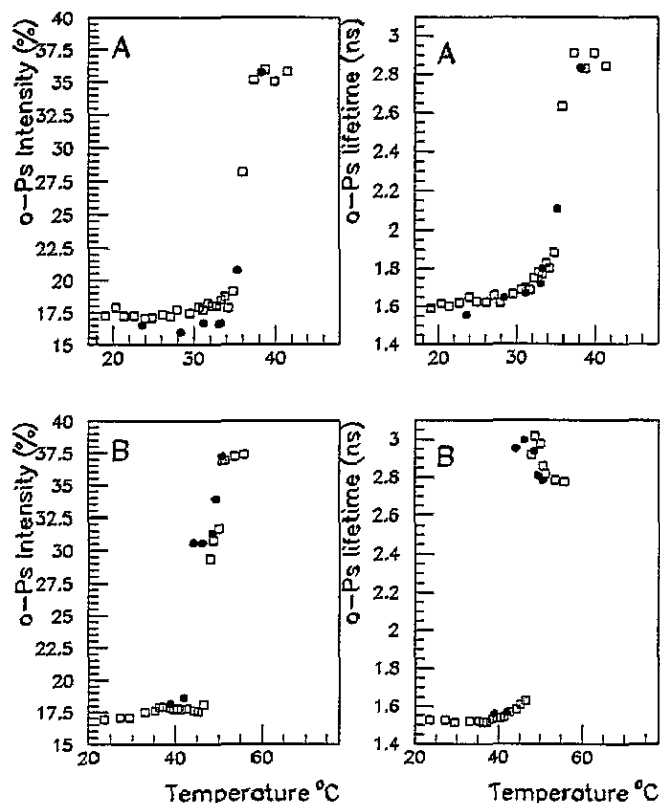


Figure 4. *o*-Ps lifetimes (ns) and intensities (%) in (A) *n*-eicosane C₂₀H₄₂ and (B) *n*-tetracosane C₂₄H₅₀. A hysteresis is observed in both parameters at the transitions which involve a rotator phase. Open squares correspond to temperature increase, closed circles to temperature decrease.

4.3. Correlation between FTIR and positron annihilation parameters

Figures 4, 5 and 6 show that *o*-Ps intensities and conformer concentrations (per CH₃ group) in the rotator phase of C₂₄ and C₂₈ are independent of both temperature and chain length. This is not the case in the liquid phase however, figure 7 showing the correlation for C₁₂, C₂₀, C₂₄ and C₂₈ between end-*gauche*, double-*gauche* and kink defects with the intensities and lifetimes of *o*-Ps.

A positive correlation is observed between *o*-Ps intensity and the double-*gauche* conformer concentration for *all* the systems studied. As the chain length increases, the conformer concentration increases and the effect it has on the *o*-Ps intensity decreases. For the shortest chain length, the *o*-Ps intensity is very sensitive to the small number of double-*gauche* defects, whereas in the longer chains the *o*-Ps intensity is relatively unaffected by the considerable increase in conformers with temperature. A similar correlation between *o*-Ps intensity and end-*gauche* and kink conformers only appears for the longer chains (C₂₄ and C₂₈). The total conformer concentration per CH₃ group is linearly related to the *o*-Ps intensity found for all chain lengths in the liquid phase, although with gradients which are widely different. For those alkanes which are liquid over the temperature range studied or have no rotator phase (C₁₂, C₁₆, C₂₀), the *o*-Ps intensity has little or no relation with conformer concentration, but when a rotator phase does exist (C₂₄, C₂₈) a definite correlation

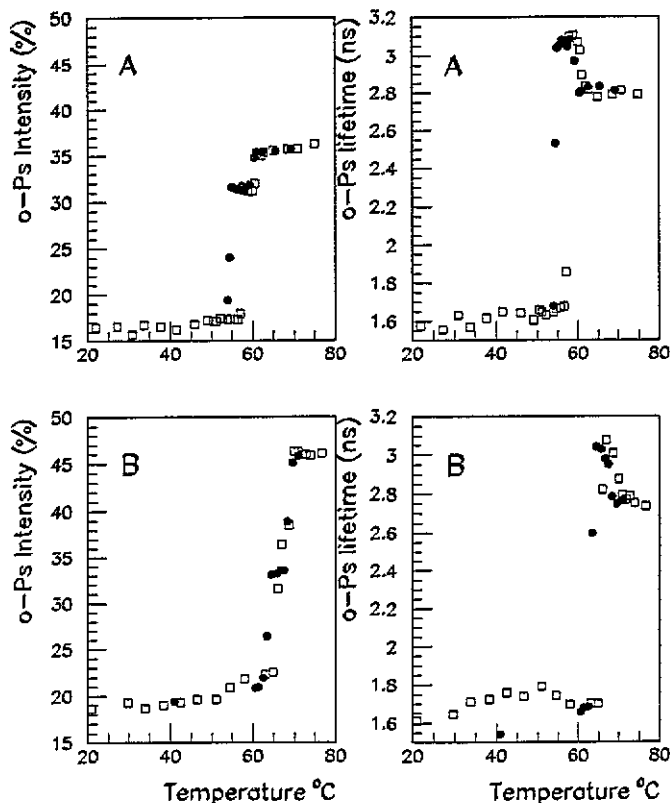


Figure 5. *o*-Ps lifetimes (ns) and intensities (%) in (A) *n*-octacosane C₂₈H₅₈ and (B) *n*-dotriacontane C₃₂H₆₆. A 4% hysteresis is observed in the lifetimes at both the crystalline-rotator and rotator-liquid transitions. The intensities show hysteresis only at the crystalline-rotator transition.

is observed.

The double-*gauche* defect is also the only one to consistently show a negative correlation with *o*-Ps lifetime, although with a rather anomalous behaviour in the case of C₂₄.

5. Discussion

Since the conformer concentrations are normalized to the number of CH₃ modes, the total conformers per molecule, Σ , will be twice this number

$$\Sigma = 2[I_{eg} + I_{dg} + I_k]$$

where I_{eg} , I_{dg} and I_k are the normalized intensities of the end-*gauche*, double-*gauche* and kink conformer peaks respectively. Evidence concerning the structural nature of *n*-alkanes in the rotator and liquid phases has come mainly from computer simulations of the molecular dynamics. In the rotator phase both *gauche*- and kink-type defects are found to occur near the chain ends [28, 29], whereas in the liquid phase a more uniform distribution would be expected because of the random network of the weakly bound chains [30, 31].

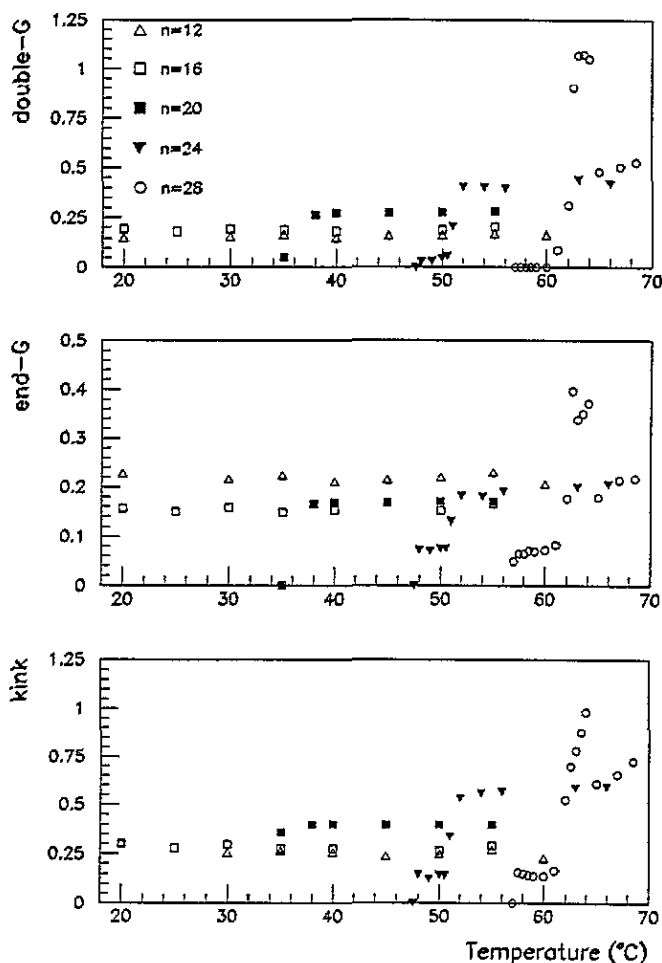


Figure 6. Normalized end-gauche (1341/1378), double-gauche (1353/1378) and kink intensities (1368/1378) as a function of temperature. Open triangles—C₁₂; open squares—C₁₆; closed squares—C₂₀; closed inverted triangles—C₂₄; open circles—C₂₈.

The quantity to be correlated with the *o*-Ps lifetime should therefore be a defect volume per molecule which reflects this expected change in distribution. As the system expands through a phase transition, the increase in free volume per molecule will be due to the combined effects of a reduction in the Van der Waal forces and the formation of defects. The assumption is made firstly, that all the molecules in the crystalline phase are in the all-*trans* configuration and secondly, that the Van der Waals increase can be obtained to a sufficient approximation by scaling up the free volume per molecule in the crystalline phase, $(V - V_0)_c$, by the appropriate density ratio. For phase *p*, this is $(V - V_0)_c \rho_c / \rho_p$ where ρ_c and ρ_p are the densities in the crystalline phase and phase *p* respectively.

This is subtracted from the experimental free volume per molecule, the latter being determined in the rotator phase from crystallographic data and in the liquid phase from macroscopic density data. The average additional volume per molecule which is due to defects is then

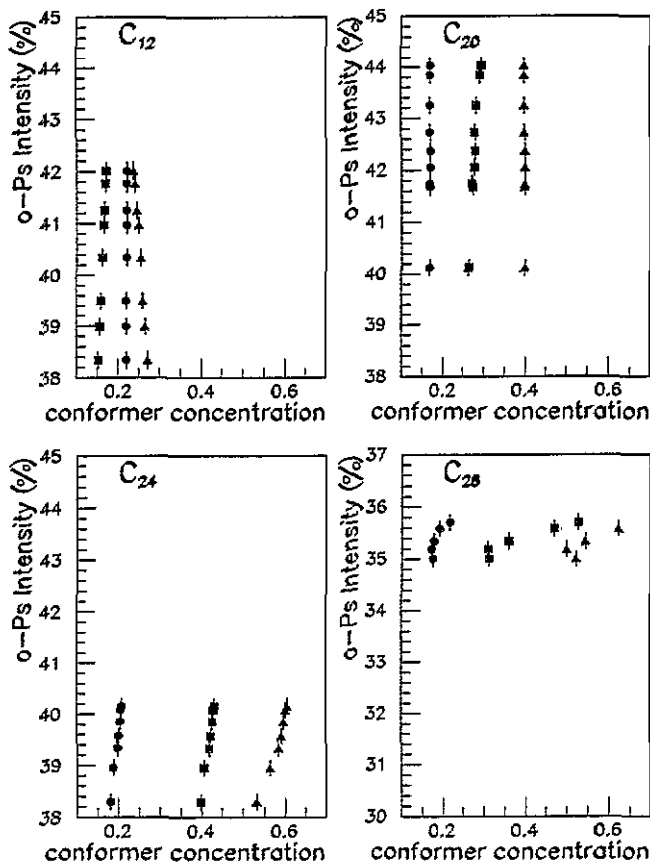


Figure 7. *o*-Ps intensities (%) versus conformer concentration per CH₃ group in the liquid phase of *n*-dodecane C₁₂H₂₆, *n*-eicosane C₂₀H₄₂, *n*-tetracosane C₂₄H₅₀ and *n*-octacosane C₂₈H₅₈: circles—end *gauche*; squares—double *gauche*; triangles—kink.

$$V_d = (V - V_0)_p - [(V - V_0)_c \rho_c / \rho_p]$$

being $\sim 25\%$ of the total free volume per molecule in the rotator phase and $\sim 12\%$ in the liquid phase. This average value arises from the different distributions of defects in the rotator and liquid phases. Since the concentration of conformers is known from the FTIR measurements, the average defect volume associated with each conformer, V_x , may be obtained from $V_d = \Sigma V_x$ where Σ is the mean number of defects per molecule.

Figure 8 shows the positive correlation between the defect volume per molecule, V_x , and the *o*-Ps lifetime for the rotator and liquid phases of C₂₀, C₂₄ and C₂₈. It should be noted that the only data point in figure 8 which does not conform to a monotonic increase of *o*-Ps lifetime with defect volume per molecule V_x , is the one for the liquid phase of C₂₀ for which no rotator phase exists.

This correlation is only obtained if the *o*-Ps lifetime decreases as the system goes from rotator to liquid phase, and is therefore at variance with the results of Goworek and Gorniak [15].

A number of points can be made regarding this disagreement.

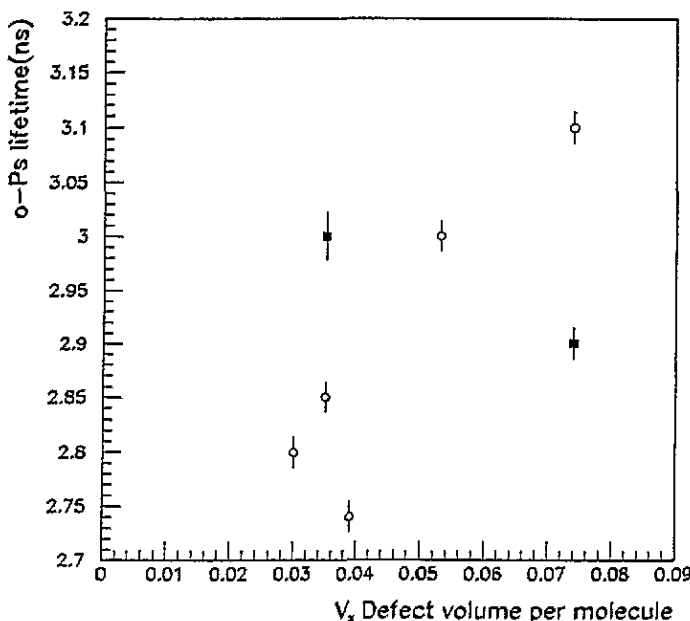


Figure 8. o -Ps lifetimes (ns) in the rotator and liquid phases of C_{20} , C_{24} and C_{28} versus defect volume per molecule, V_x (nm^3). Open circles—present work; closed squares—Goworek and Gorniak [15].

(i) The difference in o -Ps lifetime between the crystalline and rotator phases of C_{28} shown in figure 5 is the same as that reported by Goworek and Gorniak [15] (~ 1.5 ns).

(ii) The small increase in the o -Ps lifetime between the rotator and liquid phases observed in [15] (~ 0.1 ns) does not scale either with the very large increase in the average *free* volume per molecule (table 1), or with the average *total* volume per molecule (the parameter used by Eldrup *et al* [32]). If either of the latter were a variable on which the o -Ps lifetime depended linearly, the expected lifetimes in the liquid phase would be in excess of 5.5 ns, a value which is twice that which is observed.

(iii) Although no Ps quenching rate constants are available for the higher alkanes used in this work, an estimate of $\sim 10 \text{ M}^{-1} \text{ ns}^{-1}$ can be obtained for free oxygen from the dependence of rate constant on viscosity [27] in lower-molecular-weight organic systems. To explain an observed o -Ps lifetime of ~ 2.8 ns in the liquid phase would therefore require an oxygen concentration of $\sim 18 \text{ mM}$ —a value which is too high by over three orders of magnitude if it is assumed that the liquid alkane is saturated with air at STP.

(iv) Similarly, the o -Ps lifetimes in the rotator phases of C_{24} , C_{28} and C_{32} shown in figures 4 and 5 are the same (~ 3.0 – 3.1 ns) in spite of the large increases in free molecular volume (table 1). Eldrup *et al* [32] showed that there is a positive correlation between o -Ps lifetime (assumed to be the longest of four components fitted to their data) and the average total volume per molecule for a number of different organic systems. Since the o -Ps lifetime extrapolated to the rotator–liquid phase transition is constant (~ 2.8 ns) for all the chain lengths studied in the present work, there cannot be any such correlation for these alkanes.

(v) In the crystalline phase, the free volume per molecule increases with chain length, but the o -Ps lifetime remains constant at ~ 1.5 – 1.6 ns, again confirming that the free volume is not the most important parameter.

Table 2. Defect volume per molecule, V_x , and *o*-Ps lifetime in rotator and liquid phases of $n = 20, 24$ and 28 alkanes.

n	Phase	V_x (nm ³)	τ (ns)
20	Liquid	0.039	2.74
24	Rotator	0.053	3.00
24	Liquid	0.030	2.80
28	Rotator	0.079	3.10
28	Liquid	0.035	2.85

The above points therefore suggest that neither the free volume nor any likely free oxygen contamination are important factors in determining the *o*-Ps lifetime when defects, whether introduced by impurities or through the normal melting process, are present. The increase in the *o*-Ps lifetime, above the constant value that is observed in the crystalline phase, shows good correlation with the defect volume per molecule (figure 8) brought about by the melting process.

Apart from C₃₂, the *o*-Ps intensities show an increase with temperature in the liquid phase of all the alkanes studied in this work, strongly suggesting a correlation with the presence of one or more of the conformer defects. It has been argued that in liquids, the effectiveness of geminate recombination in preventing the electron from taking part in positronium formation is reduced when the electrons have a high mobility [33], and for a number of organic liquids a correlation between electron mobility and positronium yield has indeed been observed [34]. Electron mobility data in *n*-alkanes do not extend to chain lengths greater than $n=14$ [35], but has been used to confirm the trend in *n*-hexane [36] and *n*-dodecane in the present work although there does not appear to be any consistency between absolute values. For example, an *o*-Ps intensity of 40.3% corresponds to a mobility of $9.5 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in *n*-hexane, but only $3.0 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in dodecane. This may be attributed to conformational inhomogeneity which becomes increasingly probable as the chain length increases, evidence for which in *n*-alkanes comes from Raman measurements [37]. In the latter the longitudinal acoustic mode (LAM) band, which indicates the existence of an all-*trans* configuration, is prominent only for $n \leq 8$, after which there is a weaker, broader 'pseudo-LAM' band to indicate a more defected chain and a consequent drop in electron mobility at a constant temperature. This behaviour is consistent with the decrease of *o*-Ps intensity in the liquid phase (at the same temperature) as the chain length increases, but owing to the difficulty of extrapolating electron mobility values to the chain lengths used in the present work, no quantitative relation can be confirmed.

6. Conclusions

By means of Fourier transform infra-red and positron lifetime spectroscopy, the presence of defects and their influence on the formation and quenching of *ortho*-positronium has been studied in higher alkanes in the temperature regions corresponding to the rotator-liquid phase transition and beyond.

Using the FTIR data to provide the conformer concentrations, it was found that the *o*-Ps lifetime correlated well with the defect volume per molecule rather than the average free volume per molecule or the average total volume per molecule. Since the *o*-Ps intensities increase with temperature in the liquid phase and correlate with the presence of all three types of conformer, particularly the double *gauche*, the results imply either that the positron becomes preferentially localized at a defect and then forms the *o*-Ps atom, or that *o*-Ps

formed elsewhere becomes localized at a defect when the all-*trans* configuration of the crystalline phase is lessened as temperature rises towards the rotator and liquid phases. The presence of conformers is, however, a factor which strongly influences both the formation and quenching of *o*-Ps.

It was found that impurities, particularly those that might have been introduced during re-crystallization, can result in large changes in the positronium parameters. The optimum sample preparation was found to be a slow recrystallization from the melt using the highest-purity material as supplied by the manufacturer.

A consideration of the observed changes in *o*-Ps lifetime, the free volumes available in each of the different phases and systems and the known *o*-Ps quenching rate constant was used to argue against the importance of free molecular oxygen as a factor in reducing the *o*-Ps lifetime in the liquid phase of the longer-chain alkanes below that in the rotator phase.

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