Muonium Atoms in Liquid and Solid Neopentane

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Abstract

Relatively long-lived muonium atoms have been observed in neo-pentane (2,2-dimethylpropane). The yields of all muon states are found to be essentially the same in liquid and solid neopentane and the same as those in water. These results have bearings on three matters of current interest in muonium chemistry: the origin of the 'background' spin relaxation; the formation mechanism; and the change in yields at the liquid-solid phase transition. These data were obtained by the μSR technique (muon spin rotation) at the TRIUMF accelerator.

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Introduction

Muonium is the short-lived neutral atom (chemical symbol Mu) formed as the bound state of a positive muon with an electron. It has been established as a light isotope of hydrogen, and is particularly useful because it can be observed by nuclear physics counting techniques with great sensitivity and on short reaction timescales [1,2]. Most of the liquid phase studies have involved Mu in water, although it has been detected with reduced lifetime in alcohols [3] and saturated hydrocar-bons [4]. Its mechanism of formation is not yet settled, nor is it clear why there is always an apparent 'background' decay to the Mu signals - though a physical explanation based on the magnetic field has recently been offered [5].

In order to help resolve these problems we have studied purified neopentane in both condensed phases. This compound is of particular interest for three reasons. First, all of its hydrogen atoms are present in methyl groups, so Mu could be long-lived and thus easier to study than in hydrocarbons containing methylene hydrogens. Second, neopentane is known to have an unusually large free ion yield in radiolysis, despite its low dielectric constant. This is attributable to the enormous mo-bility of quasifree electrons in this medium due to the molecules being almost spherical [6]. Thus, if the spur model of muonium formation [7] is valid, the muonium yield in neopentane should differ markedly from both water and hexane. Third, neopentane has a convenient melting point and a simple solid structure. Therefore it is a suitable medium in which to study the effect of phase transitions on the muon yields.

Experimental

μSR facilities at the TRIUMF accelerator in Vancouver were used in this study. The technique is described in detail elsewhere [1,2] and the apparatus used is sketched in Fig. 1. A high energy positive muon strikes the sample under study, stops in it, associates chemically with it, then decays to a positron in 2.2 μs on average. The time between the muon's arrival and its decay (when observed by a positron detector) gives one point in a lifetime histogram. The sample is held in a trans-verse magnetic field, so that the spin of the muon (initially polarized) precesses with a Larmor frequency determined by the chemical state of

the muon. As the positron is emitted predominantly along the muon's spin direction, the lifetime histogram has the precession frequency superposed on it. Two types of muon state are readily observable - that of the free muonium atom and muons in diamagnetic environments (collectively grouped under D). The yields in these two states (A_M and A_D), plus the decay constant of Mu (λ), are obtained by computer-fitting the amplitudes in the time-histogram to Eq. [1],

$$N(t) = N_0\exp(-t/\tau_\mu)\{1 + A_D\cos(\omega_D t + \phi_D) + A_M\exp(-\lambda t)\cos(\omega_M t - \phi_M)\} + B_g \quad [1]$$

where N(t) is the signal amplitude at time t, ω_M and ω_D are the precession frequencies of Mu and diamagnetic muons, with ϕ_M and ϕ_D their initial phases. N_0 a normalization factor and B_g the background count rate. The yields are normalized to fractions of the incident muons (P) by use of $P_M = 2A_M/A_0$ and $P_D = A_D/A_0$, where A_0 is the diamagnetic amplitude under identical conditions in a medium, such as CCl_4 or Al, in which all muons are known to form diamagnetic states. The 2 appears in P_M because only that half of the total Mu ensemble with parallel muon and electron spins is observable in μSR. (In the antiparallel atom the muon spin is depolarized by rapid hyperfine oscillations.)

P_M, P_D and λ are the three parameters of interest obtained from the histograms modulated by the muon spin rotation. In these experiments there is no added solute so λ corresponds to the observed background decay constant in the pure solvent (λ_0). This could correspond to chemical reactions with the solvent, or with residual impurities, or it could be a physical or experimental artifact.

Neopentane was provided for us by Professor Ito, having been carefully purified by shaking with H_2SO_4, washing, drying and distilling. The sample was deoxygenated by freeze-pump-thaw cycles and vacuum-sealed in a 100 mL round-bottomed glass flask. About 10^7 events were collected on each of three positron counters for the sample held at four temperatures between 209 and 295K (melting point 253K). Temperature control was achieved in a closed styrofoam container through which cold helium gas was passed at a variable rate. The temperature was determined by a thermocouple in contact with the cell wall, and was monitored continuously throughout a μSR experiment.

Results and Discussion

Figure 2 shows typical μSR histograms for neopentane: in (a) only the high frequency diamagnetic Mu precession can be observed, in (b) only the low frequency diamagnetic muon signals are discernible. The lines represent the computer fits to Eq. [1] by a χ^2-minimization procedure (1,2). Best values were obtained from the fits for three independent histograms, and the average values of P_M, P_D and λ_0 are reported in Table I for four temperatures. P_L is the "missing fraction" equal to $1 - P_M - P_D$, the fraction of muons which are not observed. In unsaturated compounds some of this fraction appears as muonium radicals, but this is not expected in neopentane.

These results are of interest in three respects. First, they provide a measure of the yields in a hydrocarbon which has some physical properties intermediate between linear hydrocarbons and weakly polar alcohols and ethers - particularly with regard to the radiation chemical free ion yields (9). Neopentane provides a medium - attributed to the sphericity and non-polarizability of its molecules (6) - in which quasi-free electrons are exceptionally mobile (see Table II). In finding that the probability of muonium formation is essentially the same as that in water on the one hand, with its large free ion yield, and n-hexane on the other, with its minute free ion yield, leads us again (4) to the conclusion that the spur model (7) of muonium formation does not account for the yields in different liquids. This is underscored by the comparison provided in Table II, where the muon yields are seen to be essentially the same for solvents ranging from c-hexane to water, despite a complete change in the polarity, solvating power, and spur electron survival probabilities. Instead, one inclines to the view that Mu formation depends on the probability of hot Mu^* emerging from the epithermal stages of the track without having undergone a hot atom abstraction or substitution reaction. Perhaps the probability of such hot atom reactions occurring relative to thermalization is very similar for saturated molecules composed of fully hydrogenated C and O atoms.

The second major interest in these results lies in the fact that the yields barely change with temperature or phase over the range studied. Certainly there is no marked break at the melting point. This is in

marked contrast to water (7) and the condensed noble gases Ar and Kr (10), as indicated in Table III. Whether this is peculiar to neopentane or common to hydrocarbons remains to be seen. In these other media there was a complete absence of a missing fraction in the solid phase, with P_M increasing markedly as the material was solidified.

Third, the λ_o value found for neopentane approximately equals the smallest values found for any system at TRIUMF (4,11,12,13) or SIN (3,14,15). The implication is, therefore, that this 'background' decay rate of Mu is not a genuine chemical process but is an experimental or physical artifact. This has recently been emphasized by the fact that Nagamine et al. (5), using a pulsed muon beam with 50 ms between pulses, have obtained much smaller values of λ_o - down to 0.05×10^6 s^{-1}.

Indeed, Miyake et al. (16) have just found small λ_o values in neopentane and tetramethylsilane. The most probable explanation for the difference is suggested (5) to arise from a beating of the two-frequency precession of muonium and field inhomogeneities, even at ~8 G. This seems to be correct because by fitting the relaxation in ultrapure water over long lifetimes (8 µs gate) to a multifrequency equation rather than to [1] there was a significant reduction in the apparent value of λ_o (17). Our net conclusion is that Mu does not react with neopentane at a measurable rate: therefore, that the abstraction reaction [2]

$$Mu + C(CH_3)_4 \rightarrow MuH + C(CH_3)_3\dot{C}H_2 \qquad [2]$$

has a biomolecular rate constant, $k_M < \lambda_o$/[neat liquid], i.e. $k_M < 3\times10^4$ M^{-1}s^{-1}.

Acknowledgements

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Table I: Values of λ_0, P_M, P_D and P_L in neopentane in liquid and solid phases.

Phase	T/K	$\lambda_0/10^6 s^{-1}$	P_M	P_D	$P_L{}^a$
Liquid	295 ± 3	0.26 ± 0.03	0.18 ± 0.02	0.55 ± 0.02	0.27 ± 0.03
Liquid	259 ± 2	0.30 ± 0.07	0.14 ± 0.02	0.60 ± 0.02	0.26 ± 0.03
Solid	238 ± 2	0.17 ± 0.06	0.14 ± 0.01	0.59 ± 0.02	0.27 ± 0.03
Solid	209 ± 2	0.33 ± 0.13	0.19 ± 0.02	0.61 ± 0.02	0.20 ± 0.04

$^a P_L = 1 - P_M - P_D$

Table II: Physical properties affecting electron escape from spurs, and P_M, P_D and P_L values obtained for four pure liquids at 295 K.

Liquid	$G_{gi}/G_t{}^a$	μ^b	ε^c	$V_0{}^d$	P_M	P_D	P_L	Ref.
Neopentane	0.97	70	1.8	-0.39	0.18	0.55	0.27	This work
c-hexane	0.99	0.4	1.8	+0.01	0.20	0.69	0.11	4
Methanol	0.62	0.0006	33	NA	0.23	0.62	0.15	3,4
Water	0.38	0.002	78	NA	0.20	0.62	0.18	3,4

^{a} Fraction of total radiation-produced electrons (G_t = 4.5) which do not escape intraspur neutralization to become free ions.

^{b} Mobility in $cm^2 V^{-1} s^{-1}$ (A.O. Allen, NSRDS-NBS, 57, 1976).

^{c} Static dielectric constant.

^{d} Conduction band energies of electrons in the liquid at 295 K.

Table III: The effect of phase (and temperature) on the various muon yields in neopentane, water and argon.

Medium	Phase	T/K	P_M	P_D	P_L	Ref.
Neopentane	liquid	295	0.18	0.55	0.27	This work
Neopentane	solid	209	0.19	0.61	0.20	This work
Water	liquid	295	0.20	0.62	0.18	7
Water	solid	272	0.52	0.48	0	7
Argon	liquid	85	0.48	0.02	0.50	16
Argon	solid	77	0.91	0.008	0.08	16

Figure Captions

Fig. 1. Sketch of the apparatus used for a typical μSR measurement, showing only one set of positron counters. A is lead shielding; B a lead collimator; C and D are the muon 'start' counters; S is the sample sealed in glass bulb after deoxygenation; T is a styrofoam cryostat controlled by flowing cold gas at a controlled rate through it; H are the magnetic field coils giving a field out of the paper so that the longitudinally polarized muon precesses in the plane of the paper; E and K are the positron 'stop' counters. The start signal is registered by C.D.$\bar{E}$ and the stop by $\bar{D}.E.K$.

Fig. 2. μSR histograms (dots) and computer fits (lines) for liquid neopentane at 295 K. (a) showing the muonium precession with 8 G transverse magnetic field; (b) showing the diamagnetic muon precession at 80 G.
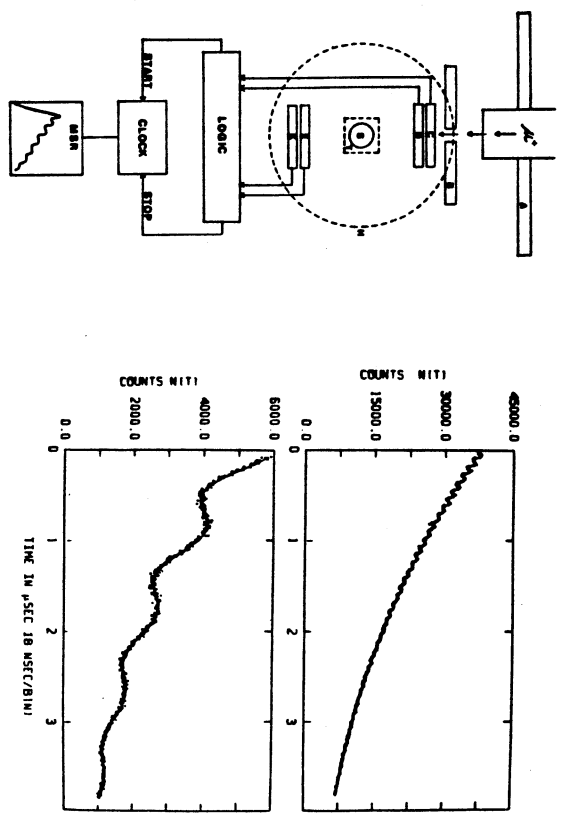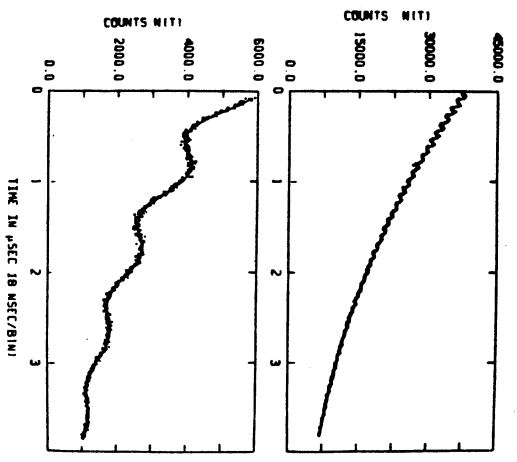

Fig. 1

Fig. 2