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Resolved nuclear hyperfine structure of a muonated free radical using level-crossing spectroscopy

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The hyperfine (hf) couplings of all the ^{19}F nuclei in the muonated free radical $\cdot C_6F_6$-Mu have been measured using a level-crossing-resonance technique. Slow damped oscillations of the muon-spin polarization in a large longitudinal magnetic field or frequency splittings in transverse field occur at particular field values at which there is a near degeneracy in the muon fluorine hf levels. Thus a resonantlike effect is observed in the muon-spin-rotation spectrum as a function of magnetic field. The positions of such level-crossing resonances allow an accurate determination of the magnitude and sign of the fluorine hf parameters relative to the muon hf parameter.

One of the interesting aspects of muoniumlike systems, such as muonated free radicals and muonium defect centers in solids, arises from the fact that the μ^+ mass is only $\frac{1}{9}$th that of a proton. The μ^+ exhibits an enhanced zero-point motion compared to a proton in a similar environment, and this may alter the electronic structure of the radical or muonium center. The resulting hyperfine (hf) isotope shifts are useful in elucidating the relationship between internal dynamics and electronic structure. In high transverse magnetic fields (TF) where the spin system is almost decoupled, the muon-spin-rotation (μSR) technique can be used to measure the hf interaction between the muon and the unpaired electron.[1-4] Often the spin Hamiltonian contains terms describing the hf interaction between the unpaired electron and the surrounding nuclear spins. The muon frequency spectrum is insensitive to the nuclear hf interaction in high TF and is too complicated to resolve in low TF fields (except in a few ideal situations.[2,5]) Resolution of the nuclear hf structure would provide new information on the electron spin density at the neighboring nuclei, which could be used to test theoretical models of the electronic structure and to determine the site of the muon.

The possibility of using level-crossing-resonance (LCR) spectroscopy in μSR was first pointed out by Abragam.[6] The first successful μLCR experiment was performed in copper.[7] In this Rapid Communication we report on a new type of μLCR which allows precise measurements of nuclear hf parameters in muoniumlike systems. The effect is demonstrated in the case of a muonated free radical, $\cdot C_6F_6$-Mu, but may also be applied to muonium defect centers in semiconductors.

During the experiment a 4-cm-diam beam of 28.6-MeV/c polarized positive muons from the M20B beam line[8] at TRIUMF was detected by a thin scintillation counter and stopped in liquid hexafluorobenzene (C_6F_6). The C_6F_6 had been purified by fractional crystallization and degassed with a series of three freeze-pump-thaw cycles prior to being sealed in a welded 321 stainless-steel cell. A superconducting coil[9] was used to apply a magnetic field parallel to the muon momentum direction. The field was calibrated with the diamagnetic muon precession signal in C_6F_6. Positrons from muon decay were detected with four scintillation detectors which served either as forward-backward or up-down telescopes depending on whether the muon-spin polarizations was parallel or spin rotated[8] perpendicular to the magnetic field direction.

An integral technique was used to search for level crossings, which for radicals may occur over a wide range of magnetic fields, 0–3 T. The integral technqiue permits a large increase in the data rate compared to the more standard time-differential μSR technique. In this part of the experiment the positron detection rate was typically 5×10^5 s^{-1}. Figure 1 shows the μLCR spectrum in C_6F_6. The signal $\mathcal{A}^+ - \mathcal{A}^-$ is defined in terms of integrated muon-decay asymmetry

$$\mathcal{A}^+ = (F^{\pm} - B^{\pm})/(F^{\pm} + B^{\pm}) \ , \qquad (1)$$

where $F^{\pm}$ and $B^{\pm}$ are the total number of positron events in the forward and backward telescopes, respectively, normalized to the number of incoming muons. The $\pm$ refer to the direction of a small square-wave modulation field (5.2 mT) which was alternated at a frequency of about 1 Hz. This modulation was necessary to average out the systematic fluctuations observed in the raw integrated asymmetry. When the LCR's are broad, as in C_6F_6, the signal is approximately equal to the derivative of the muon-decay asymmetry with respect to the applied magnetic field.

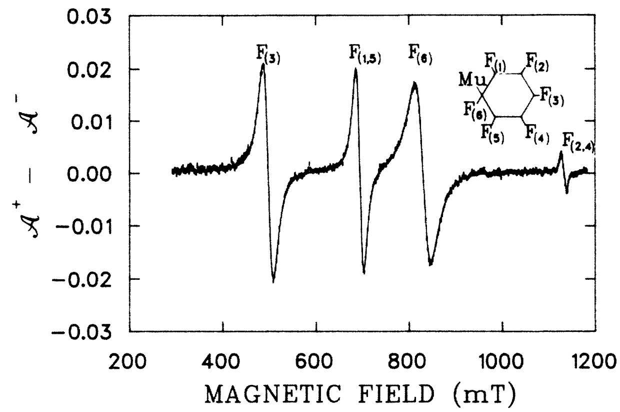

FIG. 1. Muon level-crossing spectrum for the $\cdot C_6F_6$-Mu radical. The magnetic field was applied along the muon-spin direction.

The four resonances in Fig. 1 are attributed to the level crossings in the muonated free radical $\cdot C_6F_6$-Mu, whose muon hf parameter has been reported previously at room temperature.[10] The resonances occur at magnetic fields where a muon spin-flip transition frequency ($\nu_\mu^\pm$) matches a corresponding ^{19}F transition frequency ($\nu_F^\pm$). Here, $\pm$ refer to the z component of electron spin. Such resonances will always be observable, provided the muon and nuclear hf parameters are sufficiently different so that the level crossings occur in high magnetic fields. On resonance there is a near degeneracy between two muon-fluorine hf levels, which mixes the levels and results in flip-flop oscillations between the muon and the fluorine spins. The oscillations, which are suppressed away from the level crossing, result in a change in the integrated muon-decay asymmetry. In the high field limit $\nu_\mu^\pm$ and $\nu_F^\pm$ are approximately given by[2]

$$\nu_\mu^\pm = \gamma_\mu B + \frac{A_\mu^2}{4\gamma_e B} \mp \tfrac{1}{2}A_\mu \ , \quad (2a)$$

$$\nu_F^\pm = \gamma_F B + \frac{A_F^2}{4\gamma_e B} \mp \tfrac{1}{2}A_F \ , \quad (2b)$$

where A_μ and A_F are the isotropic muon and fluorine hf parameters, respectively, and B is the magnetic field. The gyromagnetic ratios for the electron, muon, and ^{19}F nuclei are all positive in our notation. An approximate condition for the LCR is obtained by equating the right-hand sides of Eq. (2), yielding

$$A_F^2 + 2|A_\mu - A_F|\gamma_e B_R + 4\gamma_e(\gamma_F - \gamma_\mu)B_R^2 - A_\mu^2 = 0 \ , \quad (3)$$

where B_R is the magnetic field where the LCR occurs. For the $\cdot C_6F_6$-Mu radical the solution of Eq. (3) gives A_F in terms of B_R and A_μ to within about 0.01%. There are four possible solutions of Eq. (3) for each value of B_R. Two result from the fact that from a measurement of B_R alone one does not know whether $\nu_\mu^+ = \nu_F^+$ or $\nu_\mu^- = \nu_F^-$. This ambiguity can be resolved in transverse fields (see below). In most cases one of the two remaining solutions is unphysically large.

The time evolution of the muon polarization near a level crossing involving a single spin-$\frac{1}{2}$ nucleus may be estimated using degenerate perturbation theory, treating the off-diagonal parts of the muon and fluorine hf interactions as the perturbation. Approximate eigenstates and eigenvalues for the two mixed levels are then obtained by diagonalizing a 2×2 matrix. Substituting these into a general formula for the time evolution of the muon polarization in a longitudinal magnetic field,[2] leads to the following result:

$$P_z^\mu(t) = \tfrac{3}{4} + \tfrac{1}{4}[\cos^2\theta + \sin^2\theta\cos 2\pi\nu t] \ , \quad (4a)$$

where ν and θ are approximately given by

$$\nu = [\nu_{res}^2 + (\nu_\mu^\pm - \nu_F^\pm)^2]^{1/2} \ , \quad (4b)$$

$$\nu_{res} = A_\mu A_F / 2\gamma_e B_R \ , \quad (4c)$$

$$\sin\theta = \nu_{res}/\nu \ . \quad (4d)$$

On resonance, $\frac{1}{4}$ of the muon polarization is expected to oscillate at a frequency ν_{res}, where $h\nu_{res}$ is the energy splitting between the two mixed levels. In TF the level crossing manifests itself as a small splitting in either ν_μ^- or ν_μ^+, equal to ν_{res}. A more complete theory of level crossing in radicals, allowing for equivalency of nuclei, is given elsewhere.[11] The most remarkable feature of the LCR's in high field is that the position and magnitude of each resonance are insensitive to the number of nuclei off resonance. Consequently, this type of μLCR can be used to measure nuclear hf parameters in complicated spin systems. In conventional TF-μSR the amplitudes of the precession frequencies decrease rapidly as the number of neighboring nuclei with spin increases. This prohibits the use of conventional TF-μSR to measure nuclear hf parameters in all but the simplest cases.

The observed time dependence of the muon-decay asymmetry, which is proportional to the muon polarization, is shown in Fig. 2, on and off the LCR for the F(6) nucleus. A time-independent component, which depends on the probability for muons to thermalize in a diamagnetic environment and a small offset in the position of zero asymmetry, has been removed. On resonance a single fast re-

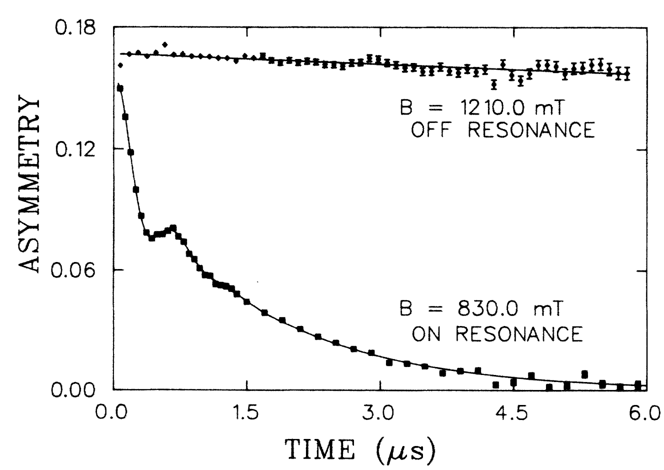

FIG. 2. Time evolution of the muon-decay asymmetry in a longitudinal magnetic field on and off the F(6) level-crossing resonance.

TABLE I. Comparison of the isotropic hyperfine parameters A_i of the $\cdot C_6F_6$-Mu and $\cdot C_6F_6H$ radicals at 321 and 265 K, respectively. The ^{19}F hyperfine parameters for the C_6F_6-Mu radical are determined from level-crossing resonances which occur at the magnetic fields B_R. The ^{19}F nuclei are labeled as in Fig. 1.

Nucleus i	B_R [a] (mT)	A_i in $\cdot C_6F_6Mu$ (MHz)	A_i in $\cdot C_6F_6H$ [b] (MHz)
μ^+/p	...	63.04(1) [c]	54.1
F(6)	830.0(2)	357.27(4)	353.7
F(1,5)	694.4(2)	67.20(4)	67.5
F(2,4)	1133.1(2)	−16.27(4)	−16.2
F(3)	497.7(2)	104.62(4)	105.4

[a]The error estimate is primarily due to a systematic uncertainty in the magnetic field calibration.
[b]From Ref. 14.
[c]The muon hyperfine parameter has been multiplied by 0.31413—the ratio between the proton and muon magnetic moments. The value given here is for a slightly higher temperature than in Ref. 10.

laxing oscillation is observed, which is described by the following functional form:

$$\mathcal{A}(t)=\mathcal{A}(0)[\alpha/4\exp(-\lambda t)+(1-\alpha/4)\exp(-\beta\lambda t)\cos(2\pi\nu_{res}t)] \;, \quad (5)$$

where $\mathcal{A}(0)$ is the maximum experimental asymmetry times the radical formation probability and where α and β are very close to 3. The fitted value for ν_{res} [1.46(3) MHz] is within the expected accuracy of Eq. (4c), using the experimentally determined values for A_μ and A_F (see Table I). This confirms that the resonance involves a single spin-$\frac{1}{2}$ nucleus. The fact that the entire radical polarization relaxes in a few μs indicates that there is both fluorine and electron relaxation and that the relaxation rates are of similar magnitude. This is in contrast to the situation where there is just electron relaxation from spin-orbit coupling, in which case only $\frac{1}{2}$ the muon polarization is relaxed on resonance. We attribute the fluorine relaxation, and at least part of the electron spin relaxation, to fluctuations in the effective local fields on the fluorine and electron due to the anisotropic part of the fluorine hf interaction.[12] The form of Eq. (5) has been verified by an numerical treatment of the relaxation using a master equation approach.[13] The on-resonance curve in Fig. 3 is a fit neglecting electron spin relaxation due to spin-orbit coupling. A single-fit parameter, $\Lambda=3.0(2)\ \mu s^{-1}$, determines α, β, and λ. The quantities α and β have a very weak dependence on Λ whereas λ is approximately equal to $\Lambda/4$. The parameter Λ equals $(2\pi\Delta)^2\tau_c$, where Δ is a measure of the fluorine hyperfine anisotropy, and τ_c is the correlation time for reorientation of the radical in the liquid. Assuming τ_c is of order 5×10^{-12} (Ref. 13), then the fitted value for Λ requires that Δ be of order 50–100 MHz. The Einstein-Podolsky-Rosen results on the $\cdot C_6F_6H$ radical near 300 K also indicate there is incomplete averaging of the fluorine hf anisotropy.[14,15] The small muon T_1 relaxation rate [0.0104(9) μs^{-1}], determined from the off-resonance spectrum (see Fig. 2) implies that the muon hf anisotropy is considerably smaller than for the fluorine. The presence of fluorine and electron relaxation tends to broaden and enhance the size of the LCR's.

The muon frequency spectra taken in transverse fields on and off resonance are shown in Fig. 3. The $\pm$ assignment of the lines is based on the assumption that A_μ is positive. On-resonance ν^- is split by 1.52(21) MHz, whereas no change in the line shape associated with ν^+ was observed. This implies that $A_\mu - A_F < 0$ in Eq. (3). The splitting in ν_μ^- is in agreement with the longitudinal field measurement of ν_{res}. In general, transverse field measurements are necessary to unambiguously determine which muon hf level and which radical is involved in the resonance. The other LCR's in the $\cdot C_6F_6$-Mu radical occur when $\nu_\mu^+ = \nu_F^+$. The measured T_2 relaxation rate [3.0(1)

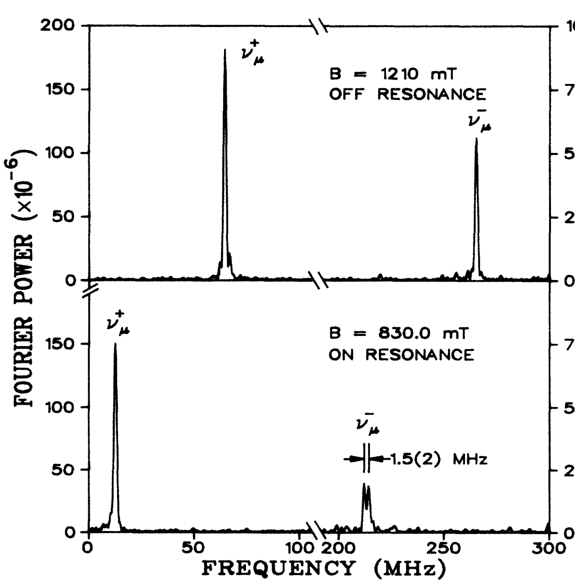

FIG. 3. Transverse field frequency spectra for the $\cdot C_6F_6$-Mu radical on and off the F(6) level-crossing resonance.

μs^{-1}] is about twice that expected from the simple model described above, indicating there may be some additional electron spin relaxation. Incorporating this into the model leads to a value for Λ about a factor of 2 smaller.

The positions of the LCR's allow an accurate determination of the fluorine hf parameters. The curve in Fig. 1 is a fit to a theoretical difference signal, assuming that the integrated muon-decay asymmetry is composed of four Lorentzian shaped lines. Table I contains the positions of the LCR's and the resulting fluorine hf parameters determined from Eq. (3). For comparison, we include the corresponding parameters for the $\cdot C_6F_6H$ radical. The shifts in hf parameters after substituting a muon for the proton are on the order of 1% or less. The largest of these hf isotope shifts are for the muon and the adjacent F(6) nucleus, both of which are positive. This is consistent with earlier, although much less accurate TF-μSR measurements on the $\cdot C_6H_6$-Mu and Ph—C=CH-Mu radicals (where Ph is an abbreviation for phenyl), which indicate that the hf isotope shift on the adjacent protons is positive.[2,5] The origin of these hf isotope shifts is under current debate.[16,17] It has been suggested recently that the muonium substitution promotes delocalization of the unpaired electron over the entire C-Mu-H group, leading to positive hf isotope shifts for both the proton and muon.[17] Our present results are consistent with this view for the C-Mu-F group in the $\cdot C_6F_6$-Mu radical.

In conclusion, we have demonstrated a new type of μLCR which can be used to obtain detailed information on previously unresolved hyperfine structure of muoniumlike systems. There are numerous applications which include testing calculations on electronic structure and making site assignments for the muon in muonated radicals and muonium defect centers in solids.

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