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Shemood, R. D.; Tindall, P. J.; Cox, D. M.; Smith 111, A. Mueller: Monitoring the Dynamics of Fullerenes from Inside the Cage


School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK, and Physikalisch-Chemisches Institut, Universitat Zürich, CH-8057 Zurich, Switzerland

(Rceived: September 29, 1992)

Positive muons (μ+) may bind an electron to form a muonium atom (Mu = μ+e−), the light isotope of hydrogen (m_Mu = (1/9)m_H). Mu encapsulated inside fullerene cages has been recently observed by transverse-field muon spin rotation (TF-μSR) techniques. Here we present the results of a muon spin relaxation study of the endohedral Mu@Cm complex in zero field (ZF-μSR) between 10 and 310 K. A single-frequency oscillation at ν = 0.70 (2) MHz appears on cooling near 270 K and signals the presence of an axially symmetric hyperfine interaction that lifts the Mu triplet degeneracy. The rapid tumbling of the fullerene molecules drastically slows upon orientational ordering, and the Mu@Cm rotational correlation time is estimated to be ~30 (5) ns at 200 K. Below 150 K, there is evidence for a completely asymmetric hyperfine matrix, indicating a further change in molecular motion. The results show that muonium, trapped in the cavity of a fullerene, can be used as a highly sensitive microscopic probe of both the molecule's rotational dynamics and the anisotropy in its electronic distribution.

The Cm sample (~98.5% average purity, ~500 mg) was prepared as described previously. Sublimation at 650 °C fol- lowed by extended annealing at 250 °C (2-2 days) leads to highly crystalline material with no traces of trapped solvent and a face-centered-cubic structure at room temperature. The sample was characterized by powder X-ray and high-resolution neutron diffraction, 13C NMR spectroscopy, and prompt γ-ray neutron activation analysis. ZF-μSR experiments (≤2 μT) were performed in longitudinal geometry between 10 and 310 K using the pulsed muon facility at the Rutherford Appleton Laboratory, UK. Extended runs were recorded at 10, 100, and 200 K in order to improve the statistics. Relaxation of the μ+ polarization was monitored by detecting the decay positrons emitted preferentially along the muon spin direction. Data are shown as the asymmetry A(t) = [(N(u) - aN(μ))/aN(μ)], where N(u) and N(μ) refer to the number of positrons detected behind and in front of the sample, and a is a normalization constant obtained from preliminary calibration using a weak (20 G) transverse field.

Solid fullerene are very effective media for the formation of muonium centers. Some Mu can add exohedrally across C-C bonds to form muonated fullerene radicals. Other Mu atoms can also enter (probably as muons) and become trapped inside the cage, forming an endohedral fullerene complex. In contrast, no muonium signal has been observed in graphite, whereas both "normal" Mu and "anomalous" Mu are encountered in diamond. "Normal" or "vacuum" Mu is a simple two-spin-1/2 system, characterized by the Hamiltonian (in units of h):

\[ H_{\text{iso}} = -\mu_S H - \mu_I H + A_S I \]  

where \( \mu_S = \gamma_S H = H \times 13.55 \text{kHz/G} \) and \( \mu_I = \gamma_I H = H \times 2.8025 \text{MHz/G} \) are the muon and the electron Larmor frequencies,
respectively, $\gamma_\mu$ and $\gamma_e$ are the muon and the electron gyromagnetic ratios, respectively, and $A_i = \langle \gamma_\mu | \mathbf{J}_i \mathbf{J}_f | \gamma_e \rangle$ is the isotropic (Fermi-Hargreaves contact) hyperfine interaction coupling the muon spin $\mathbf{I}$ and the electron spin $\mathbf{S}$ with $A_i = 4463$ MHz. In the absence of a magnetic field the four states combine to form a triplet $| F=0, m_F=0, \pm 1 \rangle$ and a singlet $| F=0, m_F=0 \rangle$ system. The triplet degeneracy is lifted in a magnetic field (Figure 1c), and $A_i$ is commonly identified through its triplet precession frequency $\nu_{A,i} = H \times 1.394$ MHz/G in fields $\leq 20$ G, where the two low-frequency transitions are degenerate.\(^1\)

The presence of anisotropy in the hyperfine interaction through dipolar interactions necessitates modification of the Hamiltonian (1); e.g., for a traceless anisotropic dipolar part $B$ of the hyperfine tensor which is axially symmetric, (1) becomes

$$H = H_0 + 6 B_S: \mathbf{I}$$

where $3B$ is the hyperfine anisotropy and $z$ is the unique symmetry axis. Figure 1a,b shows modified Breit-Rabi diagrams for the muonium eigenstates in low applied fields for a grossly exaggerated value of the dipolar interaction, $3B = 1000$ G for clarity; the energies depend sensitively on the direction of the applied field with respect to the hyperfine tensor orientation, and one expects a slowly-relaxing background. The relaxation rate $\Gamma = \exp(-\Delta t)$ together with $A_i$, $A_i \pm 3B$, and $A_i$, independent of the orientation of the crystallites.

Figure 1 shows the ZF-$\mu$SR spectra of C$_{60}$ at various temperatures. At 310 K, we observe relaxation of the Mu component at zero frequency, and the polarization can be described by an exponential relaxation function $A(t) = A_0 \exp(-\lambda t)$ together with a slowly-relaxing background. The relaxation rate $\lambda$ increases as the temperature is lowered until, in the vicinity of 270 K, oscillations in the asymmetry become apparent. The modulation in the polarization is present down to 10 K and can be modeled by an exponentially-damped precession signal together with a constant slowly-relaxing background:

$$A(t) = A_0 \exp(-\lambda t) \cos(2\nu t + \phi) + A_{\text{back}} \exp(-\lambda_{\text{back}} t)$$

Excellent fits using a single precession frequency $\nu$ are obtained down to 170 K. At lower temperatures, the data suggest that more than one frequency may be contributing to the polarization. However, fits to the data with more than one oscillating component were not obviously superior.

Mu@C$_{60}$ has been identified\(^1\) through its large isotropic hyperfine parameter $A_i = 4346$ (36) MHz, close to the value for Mu in vacuum (4463 MHz). Its presence in our sample was confirmed by applying a field of $\sim 2.2$ G and observing the triplet precession. If the hyperfine Hamiltonian were isotropic, the triplet degeneracy would not be removed at zero field and no precession would be observed (Figure 1c). This is the case for temperatures $>270$ K, as the Mu@C$_{60}$ molecules should be in a plastic phase, tumbling fast enough on the time scale of the inverse dipolar interaction to average out the anisotropy present (Figure 2a). However, below 270 K the characteristic precession is present at zero applied field (Figure 2b), signaling the slowing down of the molecular reorientations and the appearance of an axial anisotropy. Fitting the time evolution of the asymmetry at 200 K (Figure 2c) using eq 3 leads to a hyperfine anisotropy $3B = 0.772 (15)$ MHz, a relaxation rate $\lambda = 0.70 (13) \mu$s$^{-1}$, and an initial value for the asymmetry $A_0 = 1.41 (21)\%$. Using the results from a silver foil calibration run, we estimate the yield for Mu@C$_{60}$ formation to be 27 (4)%. We can also obtain, through the relationship $\lambda = ((2\pi \times 3B^2)\tau_\text{r})$ an order of magnitude for the endothelial complex reorientational time: $\tau_\text{r}$ is equal to $\sim 30$ (5) ns at this temperature.

This is comparable with the correlation times found for both pristine C$_{60}$\(^13\) and its exohedral muonated radicis\(^14\) in the same temperature range. The presence of an oscillating signal persists to the lowest temperature studied (Figure 2d). However, the possible presence of more than one frequency below $\sim 150$ K could be the outcome of freezing of the fullerene motion and formation of an orientational glass, in an analogous fashion to C$_{60}$\(^15\).

The ZF-$\mu$SR data of Mu@C$_{60}$ in the orientationally ordered phase (2270 K) provide an accurate measure of the anisotropic dipolar interactions. Since no anisotropic contribution is expected from the 1s state of the muonium atom, the value of the measured triplet precession reflects the $2p_z$ character of the Mu wave function. Comparison of the observed zero-field frequency, $3B = 0.772$ MHz, with the dipolar interaction ($<r^2>^1/2$) for a pure $2p_z$ state of a Mu atom, $3B_0 = 27.89$ MHz, leads to a 8.92 (2)% $2p_z$ admixture in the ground-state wave function of Mu@C$_{60}$:

$$\psi_{\text{Mu@C}_{60}} = 0.9954\psi_{1s} + 0.0959\psi_{2p_z}$$

Noting that only the 1s state contributes to the isotropic hyperfine coupling arising via the Fermi-Hargreaves contact interaction at the nucleus, we can also derive an independent estimate of $A_i$ in Mu@C$_{60}$ using eq 4. The fullerene cage acts as a small perturbation of the Mu wave function both through the static overlap with C orbitals and the dynamic pinching of the Mu atom as it oscillates in the cage. Thus, $A_i$ is expected to be slightly reduced from the vacuum value and, as a result, in Mu@C$_{60}$ it is $1^2$ 4341 MHz. Any additional deviation from this value should be a consequence of the small $2p_z$ admixture and $A_{\text{back}}$ for Mu@C$_{60}$ is estimated to be 4301 MHz, in excellent agreement with the value of 4346 (36) MHz derived from TF-$\mu$SR measurements.\(^5\) In Figure 3, we show the electron density calculated for Mu@C$_{60}$ using the wave function of eq 4. As a result of the finite $2p_z$
In conclusion, we have shown that Mu encapsulated inside a fullerene cage provides a highly sensitive probe of both the electronic structure and the orientational dynamics of the fullerene. Furthermore, Mu @ C70 are a readily accessible class of endohedral fullerene complexes, and ZF-μSR studies of the kind described here on fullerene analogues and derivatives promise to provide unique electronic, structural, and dynamic information on the changes which occur when fullerenes react.

Note Added in Proof. The Mu yield derived from this experiment agrees with an independent determination in transverse field.5 The three Mu adduct radicals are not expected to contribute to the observed oscillation since their anisotropy is higher (for the most prominent of them we expect16 based on experiments using the ALC technique, a frequency of 2–9 MHz with a strong temperature dependence) and since 50% of these radicals contain at least one 13C nucleus which in zero field has the effect of distributing the signal over further frequencies.

Acknowledgment. We thank C. A. Scott, J. P. Hare, and S. D. Johnston for invaluable help with the experiments and the Science and Engineering Research Council (UK) for financial support and access to ISIS. K.P. and E.R. also acknowledge financial support through a collaborative research grant from the British Council and the Swiss National Science Foundation.

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