GAS, LIQUID AND SOLID STATE STUDIES OF MUON SPIN RELAXATION IN ORGANIC RADICALS

S.F.J. COX¹, R.M. MACRAE,¹* W.G. WILLIAMS¹ and D.G. FLEMING²

¹ ISIS Pulsed Muon Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK
² Chemistry Department, University of British Columbia, Vancouver, BC V6T 2A3, Canada

A distinctive field dependence of longitudinal muon spin relaxation in acetone liquid and vapour suggests that modulation of the isotropic hyperfine coupling of the (CH₃)₂COMu radical is the dominant relaxation mechanism. The temperature dependent correlation time extracted from the data then corresponds to the lifetime of the states of internal libration of the molecule. The variation of relaxation rate may also be followed into the solid phase, peaking at the freezing transition.

Longitudinal muon spin relaxation has been studied for the muonic radical (CH₃)₂COMu formed in acetone in the saturated vapour, in the liquid and in the solid phase. The relaxation rates fall well within the μSR dynamic range in all three phases; the present measurements were made at the ISIS Pulsed Muon Facility. The aim of this work is, initially, to understand the mechanism of the spin relaxation which is operative in each phase. Once this is established, we expect that information on the molecular dynamics can be extracted from the data.

The gas phase data show a remarkable increase in relaxation rate with magnetic field at low field values [1]. This is illustrated in Figure 1 together with liquid phase data which show a similar behaviour, somewhat attenuated. The rate reaches a maximum at a field which is a small multiple of the hyperfine field before showing the more familiar decrease at higher fields. The same behaviour is observed for the C₆H₆Mu radical in benzene vapour [1] and the CH₂CH₂Mu radical in ethylene gas. Such a field dependence is consistent with relaxation via modulation of the isotropic

*Now at the School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK
Fig. 1. Field dependence of the longitudinal muon spin relaxation rate in acetone (a) in the saturated vapour at 400 K and (b) in the liquid at 200 K. The curves represent fits to expression (2), as described in the text.

The static or average muon–electron hyperfine interaction between the muon spin $I$ and the electron spin $S$ has the usual form $A I.S$ (with anisotropic terms averaged to zero in the fluid phases) and we suppose that the dominant motional perturbation may be written $\delta A(t)I.S$. Having a scalar product spin operator, the perturbation induces transitions only between coupled states of the muon and electron spin having $m_I + m_S = 0$, and then only in non-zero magnetic field. The square matrix element responsible is $(2\pi \delta A)^2 x^2/(1 + x^2)$, where $\delta A$ is the average change in hyperfine interaction between accessible states. In this expression, $x$ is the reduced field, in units of hyperfine field, $2\pi A/\gamma_e$. At room temperature, the hyperfine constant is $A \simeq 25$ MHz (as measured in the transverse-field $\mu$SR experiments which served to identify the $(\text{CH}_3)_2\text{COMu}$ radical formed in hyperfine interaction, a mechanism which should be particularly potent for radicals with appropriate internal degrees of freedom. The requirement is that the hyperfine interaction depends strongly on conformation, e.g. on some internal librational state of the molecule, and that various different states are thermally accessible so that the molecular dynamics provide a means of jumping from one state to another.