

# Spin-lattice relaxation in triplet states of isolated molecules and pure crystals in zero field

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(Received 27 June 1978)

This Note presents an experimental study of the temperature-dependent spin-lattice relaxation (SLR) rates of the triplet spin sublevels of 1, 2, 4, 5-tetrachlorobenzene (TCB) in a durene host and as a pure crystal. Pure TCB crystals exhibit well-defined exciton emission,<sup>1</sup> which above 4.2°K is not affected by exciton trapping.<sup>2</sup> This permits exploration of the differences between isolated molecule and pure crystal SLR.

Single crystals were grown by the Bridgeman method using recrystallized, vacuum-sublimed and zone-re-

finned materials. Below 4.2°K crystals were immersed in liquid He and the temperature determined from the He vapor pressure. Above 4.2°K the samples were bathed in cold He gas and the temperature measured with an Au-0.07% Fe, chromel thermocouple, contacted thermally to the sample. The samples were excited by an arc lamp, establishing steady state. Excitation was then cut off and decay of the phosphorescence recorded using a high resolution monochromator, PM tube, and a 2048 channel analog-to-digital transient recorder interfaced to an on-line computer. After many repeti-

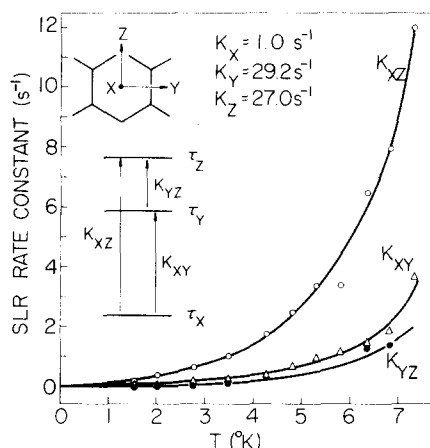


FIG. 1. Temperature dependent SLR rate constants of TCB in durene. Insets show axis system, relative energies and intrinsic rate constants of the triplet sublevels.

tions the computer-averaged signal was recorded on magnetic tape for later analysis.

El-Sayed has given a detailed discussion of the three coupled rate equations, including SLR, describing decay from the triplet spin sublevels.<sup>3</sup> Given the three intrinsic decay rate constants,  $K_i$ , the SLR rate constants can be determined either from observed decay constants,  $K_i^{\text{ob}}$ , or from the three initial intensities,  $I_i^{\text{ob}}$ . TCB in durene was studied in detail in this manner. The spin sublevel ratios of radiative rate constants and of inter-system crossing rate constants were employed in the analysis.<sup>4</sup> Emission to the origin occurs from the  $\tau_x$  and  $\tau_y$  sublevels while emission to the  $B_{2g}$  vibration effectively occurs from  $\tau_x$  and  $\tau_z$ . Since  $K_x \ll K_y \approx K_z$ , it is possible to obtain the  $K_i^{\text{ob}}$  by recording decay curves from both the origin and  $B_{2g}$  vibration. The temperature dependence of the  $K_i^{\text{ob}}$  becomes quite flat below 4.2°K, and extrapolation to 0°K yields the intrinsic decay constants,  $K_i$ . Using these, the  $K_i^{\text{ob}}$ , and the  $I_i^{\text{ob}}$ , the SLR rate constants were obtained (see Fig. 1). Note that SLR has not vanished at 4.2°K. This results in temperature-dependent lifetimes even at pumped He temperatures. At 1.4°K  $1/K_x^{\text{ob}} = 810 \text{ ms}$  while at 4.2°K this has decreased to 340 ms. By 20°K, SLR has become so fast that emission occurs as a single exponential with  $K^{\text{ob}} = (K_x + K_y + K_z)/3 = 19 \text{ s}^{-1}$ .

The exciton lifetimes were obtained at 4.2°K and above. Emission to the origin and  $B_{2g}$  vibration were

TABLE I. Exciton sublevel decay constants ( $\text{s}^{-1}$ ).

$T$ (°K)	$K_1^{\text{ob}}$	$K_2^{\text{ob}}$	$K_3^{\text{ob}}$
4.2	32 <sup>a</sup>	91 <sup>a</sup>	370 <sup>a</sup>
10.0	55	160	670
20.0	120	460	b
40.0	100	560	b

<sup>a</sup>Intrinsic exciton decay constants.

<sup>b</sup>Not resolvable.

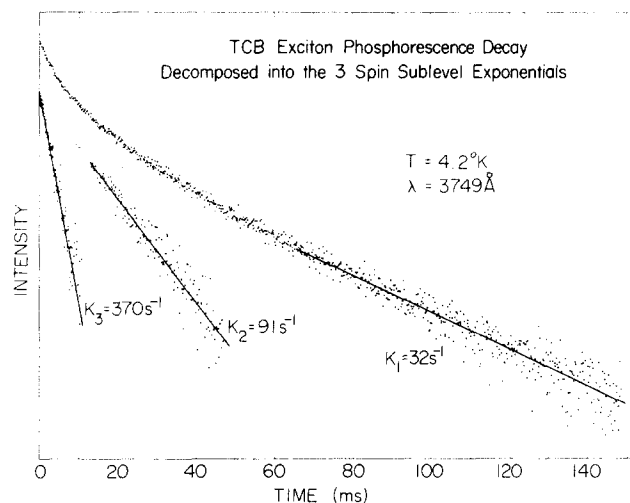


FIG. 2. Time-resolved TCB exciton phosphorescence decay curve at 4.2°K. The slow, medium, and fast exponentials are well resolved over 3, 3, and 4 lifetimes, respectively, and their sum reproduces the entire curve at all times.

found to be identical, reflecting the symmetry reduction due to the extended nature of the exciton state. Figure 2 shows the exciton decay at 4.2°K and its decomposition into three exponentials. The significant differences in the decay constants permit them to be accurately determined. Table I lists the exciton decay constants at four temperatures. The observed decay constants change more slowly than in the TCB in durene cases. Therefore the 4.2°K values are reasonable approximations to the intrinsic decay constants. By 40°K the exciton decay has not yet coalesced into a single exponential, indicating that SLR is significantly slower in the exciton system.

In ionic solids the SLR mechanism involves phonon modulation of the crystal field, which perturbs the electron orbital motion and in turn affects the spin via spin-orbit coupling.<sup>5</sup> In molecular triplet states, the spin-orbit interaction makes only a small contribution to the zero-field splitting tensor. Comparing the SLR rates of TCB in durene and of other molecules in zero field<sup>3,6</sup> shows that SLR is not directly dependent on the extent of spin-orbit coupling. This suggests that a mechanism not involving the spin-orbit interaction may be appropriate. A possible mechanism may involve phonon-induced local potential fluctuations which produce anisotropic perturbations of the molecular orbital wave function. This can directly modulate the principal axes of the zero-field splitting tensor and therefore induce SLR. The proposed mechanism is consistent with the TCB exciton results since the extended nature of the exciton state<sup>7</sup> tends to average the effect of local potential fluctuations,<sup>8</sup> reducing the SLR rates.

We would like to thank Professor H. C. Andersen for many interesting conversations on this subject.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

<sup>2</sup>Alfred P. Sloan Fellow.

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