Bull. Chem. Soc. Jpn., 53, 2466—2467 (1980) [Vol. 53, No. 9

Study of Triplet-Triplet Energy Transfer between Like Molecules in a Rigid Glass Solution by Means of Optical Detection of Magnetic Resonance

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(Received January 22, 1980)

The triplet-triplet energy transfer between like molecules was investigated for the system of quinoxaline in ethanol by using the method of optical detection of zero-field magnetic resonance at 1.4 K. The concentration dependence of the spin state population indicates that the energy transfer between quinoxaline molecules takes place at concentrations higher than about 2×10^{-2} mol/dm^3.

The triplet-triplet energy transfer between like molecules has so far been studied by the method of the concentration depolarization of phosphorescence[1,2] or by magnetophotoselection.[3] However, these methods are subject to the masking effect due to the singlet-singlet energy transfer, since molecules are initially excited into singlet states in most cases. Two of the present authors (AI and NE) have also developed a method which eliminates the effect of the S-S energy transfer by making use of isotopic mixtures.[4,5]

A more sophisticated approach would be to apply the method of optical detection of zero-field magnetic resonance (ZF ODMR), in which the use of an isotopic mixture is not necessary. As the perturbation causing the T-T energy transfer does not depend on the spin variables, the direction of the spin angular momentum is conserved during the energy transfer. Hence, the relative populations initially prepared in the spin states by optical pumping, followed by intersystem crossing, are modified as a result of the energy transfer according to the relative orientations of the solute molecules. Therefore, the modified relative populations may be used as an indication of the presence of the energy transfer, if the populations are compared with those obtained in the absence of energy transfer (*i.e.*, those in a sufficiently dilute solution).

In the present communication, we will describe an application of this method to a study of the T-T energy transfer among quinoxaline molecules dissolved in ethanol.

Experimental

Quinoxaline was distilled under reduced pressure. Ethanol was distilled after passing it through silica gel columns. The equipment for the ZF ODMR experiments has been described elsewhere.[6] Samples were excited with light from a high-pressure mercury lamp through an appropriate filter, and the phosphorescence was monitored at 474 nm.

Results and Discussion

The phosphorescent triplet state of quinoxaline has been thoroughly studied by ZF ODMR.[7] It is well established that the ordering of the spin sublevels is $T_x < T_y < T_z$ and that the phosphorescence emission occurs predominantly from T_z, where the x axis is defined as the normal to the molecular plane; the y axis, as the short axis, and the z axis, as the long axis. Most studies so far reported have been made in mixed crystals, such as quinoxaline in durene and in naphthalene-d_8.[7]

In the ethanol rigid glass solution (3×10^{-3} mol/dm^3) at 1.4 K, we observed MIDP (microwave-induced delayed phosphorescence) signals at 3.49 and 1.12 GHz; these signals indicate that the zero-field splitting parameters are not much different from those in the mixed crystals. On the other hand, the decay-rate constants were obtained as 1.2, 1.3, and 6.5 s^{-1} for the T_x, T_y, and T_z states respectively. Apparently, these values are affected by the spin-lattice relaxation. Therefore, the kinetic parameters given in Table 1 should be considered to represent just apparent properties. It is reasonable to assume that the spin-lattice relaxation does not depend on the concentration of quinoxaline. As a matter of fact, it will turn out that the spin-lattice relaxation does not significantly affect our main conclusion, since we focus our attention only on the concentration dependence of the parameters.

The steady-state population ratio, r_{ij}, of the sublevel, i, with large radiative and total decay rates, to another sublevel, j, is given by:

Table 1. The phosphorescence decay rates, k_i, relative radiative decay rates, k_i^r, and relative steady-state populations, N_i^0, of quinoxaline

	k_x/s^{-1}	k_y/s^{-1}	k_z/s^{-1}	k_x^r/k_z^r	k_y^r/k_z^r	N_x^0/N_z^0
In ethanol[a)]	1.2	1.3	6.5	0.040	0.035	0.30
In naphthalene-d_8[b)]	0.42	0.80	12.0	0.013	0.013	0.36
In durene[b)]	0.40	0.59	11.1	0.015	0.020	0.68

a) 3×10^{-3} mol/dm^3 and at 1.4 K. b) From Ref. 7.

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$$r_{ij} = N_j^0/N_i^0 \simeq h_{ij}(t_1) \exp (k_j t_1)/fI_0 + \exp (k_j - k_i)t$$

where $h_{ij}(t_1)$ is the magnitude of the MIDP signal at time t_1 ($t_1 \simeq 1$ s), where I_0 is the steady-state phosphorescence intensity tacitly approximated to be proportional to $k_i^r N_i^0$, and where f is the transfer efficiency of the population from T_j to T_i by means of a microwave pulse. In the present case, the concentration dependence of this quantity was measured for the T_x-T_z transition. The value thus obtained, r_{zx}, is also the apparent ratio of the steady-state population of T_x to that of T_z, because the above equation is valid only under the isolation conditions.

The observed r_{zx} values are plotted against the concentration in Fig. 1. The values remain almost constant ($\simeq 0.3$) in the range of 10^{-3} mol/dm^3. This indicates that the population in the T_z state is larger than that in the T_x state in the absence of any energy transfer. When the concentration is increased, the T-T energy transfer gradually becomes effective and results in *population randomization* among the spin states. As a result, the value of r_{zx} may be expected to increase, as we observed.

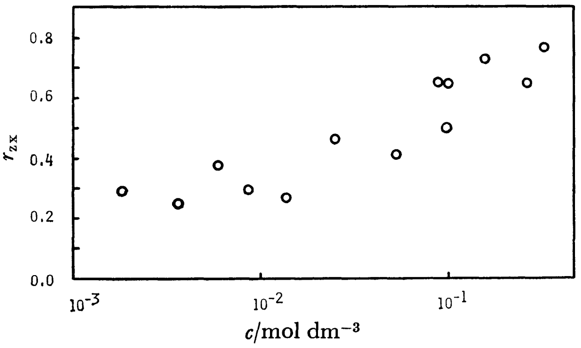

Fig. 1. Variation of the population ratio, r_{zx}, with concentration at 1.4 K.

However, before drawing any conclusion, we should discuss various possibilities which might influence the value of r_{zx} at high concentrations. As the values of f and I_0 changed from sample to sample, we used the values obtained in each measurement to estimate the value of r_{zx} from the equation. Therefore, the results in Fig. 1 cannot be due to the change in these quantities. Changes of the decay rates, k_x and/or k_z, might also affect the value of r_{zx}. However, it was found that the value of k_x does not show a significant variation in the concentration range studied. This is shown in Fig. 2. The values in Fig. 2 were obtained by plotting ln $h_{zx}(t)$ *vs.* t in the region comparable to t_1 (*i.e.*, $\simeq 1$ s); the plots gave good straight lines. This means that, at both low and high concentrations, the effect of k_z on the magnitude of $h_{zx}(t)$ is not important and that, therefore, the second term of the equation can be neglected in this time region.

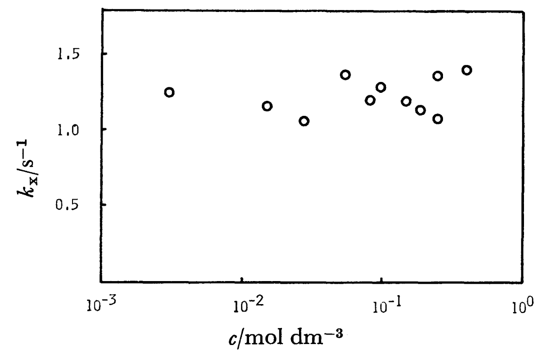

Fig. 2. Concentration dependence of the phosphorescence decay rate, k_x.

The rigid glass solutions were transparent, although cracked, at the highest concentration of 0.4 mol/dm^3, and the formation of microcrystals was not observed visually. Furthermore, the T_x-T_z transition was observed at nearly the same microwave frequency (3.48 GHz) in the 0.1 mol/dm^3 solution as in the solutions of lower concentrations. The phosphorescence spectrum of the same solution showed little difference compared with that of the samples of lower concentrations. These results suggest that the observed variation of r_{zx} is not due to a dimer or aggregate formation at high concentrations.

Triplet-triplet annihilation is an alternative possibility which might be responsible for the observed variation in r_{zx} with the concentration, because the population in T_z would be most effectively diminished by the annihilation. To check whether or not this possibility is operative, we measured the population ratios at different excitation light intensities and the phosphorescence decay curves at different concentrations. The intensity of the incident light was reduced to about a half by the use of an appropriate filter. The values of r_{zx} were found to be 0.55 and 0.50 for the 0.1 mol/dm^3 solution with and without the attenuation of light intensities respectively. These values are essentially in agreement with each other within the range of experimental error. The possibility of T-T annihilation is thus eliminated.

From these considerations, it may be concluded that the observed increase of r_{zx} at high concentrations is caused by the randomization of the relative populations in the spin states as a result of the triplet-triplet energy transfer among the randomly oriented quinoxaline molecules in the ethanol rigid glass. The energy transfer was found to become efficient at concentrations higher than 2×10^{-2} mol/dm^3; this finding essentially coincides with the corresponding concentration for the T-T energy transfer between dissimilar molecules.[18)]

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