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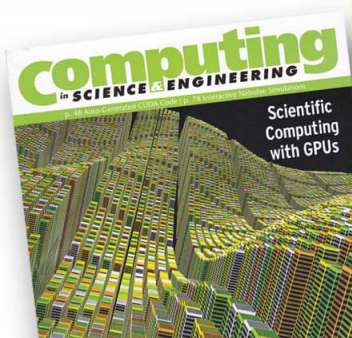
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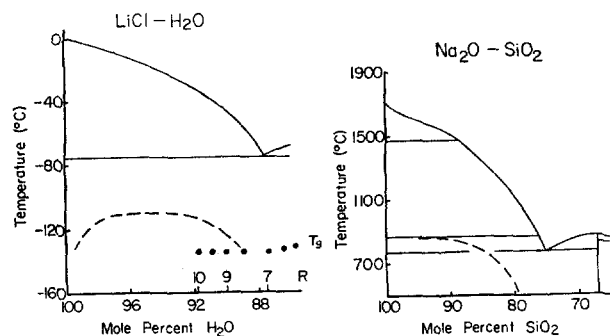


FIG. 2. Comparison of proposed metastable immiscibility region in $\text{LiCl-H}_2\text{O}$ system with known region in $\text{Na}_2\text{O-SiO}_2$ system. ---, miscibility temperature ($\text{Na}_2\text{O-SiO}_2$, Ref. 6); ... glass transition temperature ($\text{LiCl-H}_2\text{O}$, Ref. 9).

by the presence of one component (H_2O , SiO_2 , B_2O_3) which in the pure state exists in an open network-type structure with bond character quite distinct from the ionic liquids formed in the presence of large concentrations of the second (ionic) component. The two-liquid region in these systems also occupies the composition region between the pure network component and the first eutectic. A comparison of the suggested $\text{LiCl-H}_2\text{O}$ phase diagram with the known $\text{Na}_2\text{O-SiO}_2$ phase diagram is given in Fig. 2. In the silicate and borate cases, both separated phases are stable in the amorphous state, thus the whole two-liquid dome can be mapped and a metastable critical solution temperature can be observed.

The phase separation postulate is also supported by the observation of unusually large and temperature-dependent Raleigh peaks in laser studies of concentrated salt solutions,⁸ an indication of large spontaneous composition fluctuations even at room temperature.

The homogeneous-solution phase boundaries are obviously of interest in connection with the hydration number problem. Data to be reported in more detail in a subsequent publication⁹ will suggest that where for LiCl this number is 6-7, for divalent metal chlorides it is 17-20, and for trivalent metal chlorides, it is 24-27. These numbers also correspond roughly with the R values of the respective eutectic compositions.

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† N.D.E.A. fellow.

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Optical Detection of Magnetic Resonance in Phosphorescent Triplet States: Naphthalene and Quinoxaline in Durene and Biphenyl*

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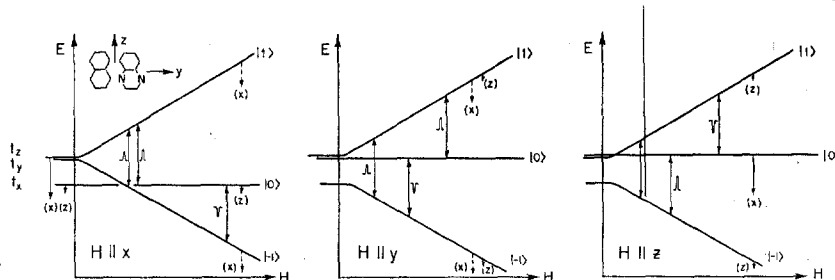
The microwave-induced ESR transitions between the Zeeman levels of phosphorescent triplet states have been detected by monitoring the optical emission from the Zeeman levels.¹⁻³ Naphthalene in durene and quinoxaline in durene were among the first systems that we studied with this method.² Our preliminary results for both cases were consistent with what would be predicted assuming that the phosphorescence was from the top zero-field state corresponding to a predominant out-of-plane polarization.

However, our results were in conflict with the results obtained by other methods.⁴⁻⁶ Based on conventional, or "static," optical polarization studies Chaudhuri and El-Sayed^{4,5} concluded that the phosphorescence of naphthalene in durene (N/D) and of quinoxaline in durene (Q/D) was apparently anomalous, in that it was predominantly in-plane (long-axis) polarized (corresponding by our usual assumptions² to emission from the bottom Zeeman level). The emission from N and Q in biphenyl or EPA was normal. Suspecting the validity of our own results, obtained by the optical detection of magnetic resonance (ODMR),⁷ we began an extensive study of the emission properties of naphthalene and quinoxaline in various hosts.

Naphthalene, naphthalene-*d*-8 (*d*N), and quinoxaline were separately incorporated ($\sim 0.1\%$) into durene and biphenyl (Φ_2). Crystals were grown from the melt. The emission spectra of the mixed crystals at 4.2°K were recorded on a Cary 14 spectrophotometer (operated in reverse for this purpose) in order to determine the purity of the samples and the wavelengths of the phosphorescence bands. The normal ESR spectrum was subsequently recorded in order to confirm the sample orientation. Finally, the magnetic resonance transitions were detected optically as described previously² using a polarizer and an interference filter to study the 0-0 band emission.

In Fig. 1 we show schematically the Zeeman levels as a function of a magnetic field directed in turn along each of the principal axes of the fine-structure tensor. The choice of a molecular axis system is made on the basis of the conventions discussed in Ref. 2. The x axis and the z axis are chosen perpendicular to the molecular plane and along the twofold axis, respectively. In the case of naphthalene, where there is an ambiguity in the choice of the axes, we have chosen them to corre-

FIG. 1. A schematic representation of the Zeeman levels for the lowest triplet state of either N or Q as a function of H . The zero-field states appear on the far left; the high-field states on the right. The expected changes in the optical signals for the various ESR transitions are indicated.



spond with the quinoxaline system so that both molecules can be discussed on an equal footing. The $\Delta m=1$ and $\Delta m=2$ transitions are shown together with the expected changes in the optical signal assuming the top level to be the major source of emission intensity. Measurements were made on N/D, dN/D , Q/D, N/ Φ_2 , and dN/Φ_2 for each ESR transition, along each of the three principal axes, and for various polarizer orientations. For Q/ Φ_2 we measured only the $\Delta m=2$ transition. In every instance, our ODMR results agreed with the predicted changes shown in Fig. 1 regardless of whether the host was durene or biphenyl. As a further check of the emissive properties of N and Q we used the ODMR method to determine the character of the emission from randomly oriented molecules dissolved in rigid glasses.⁸ Again, these results are in agreement with our single-crystal results and imply that emission is mainly from the top zero-field level.

Recently Schmidt *et al.*³ reported their new results, for quinoxaline in durene, obtained by the ODMR method as well as by flash-excitation studies.⁶ They also concluded that the emission was mainly from the top zero-field level.

It is important to note at this point that the results of measurements using the "static" optical polarization technique and those using "dynamic" techniques do not depend on the same combination of parameters. The static measurements are a function primarily of the *radiative* rate constants (or their ratios) whereas ODMR measurements depend upon the *nonradiative* rate constants as well. Although the nonradiative rate constants are not known, it does not appear possible to choose values for them such that the ODMR results and the static results can be made compatible.

We would like to suggest, therefore, that the emission from the lowest triplet state of naphthalene and quinoxaline originates primarily from the top zero-field level not only in EPA and biphenyl but in durene as well. This would imply that the *interpretation* of the results obtained by the static method will require re-evaluation, although it is not clear at this point how that should be done.

The foregoing discussion has of necessity been qualitative since the nonradiative rate constants for the individual zero-field states are unknown. However, it should be possible, in principle, to determine both the

radiative and the nonradiative rate constants for each of these states using the ODMR technique. Work toward this end is currently in progress.

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[†] Alfred P. Sloan Fellow.

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T_1/T_2 and Spin Relaxation in the Benzene Anion*

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The anomalously broad linewidths of the radical anion of benzene^{1,2} (B^-) and associated radicals of high symmetry have been the subject of considerable interest. A number of possible explanations have been proposed which are all based on time-dependent interactions between polar solvent (or cation) and B^- that affect the otherwise vibronic ground-state degeneracy of the molecule.³⁻⁶ There is the crucial question as to which spin-dependent interaction would then be affected, and this can be at least partially answered in terms of comparison with detailed spectral observables. For example, solvent-induced hyperfine fluctuations³ have been ruled out⁷ because of the absence of any significant variation in widths among the hyperfine components. Also, field-dependent contributions were shown not to be important.⁸ Spin-orbit (and associated)