Magnetic resonance of excited complexes with charge transfer revealed by fluorescence at room temperature

E. L. Frankevich and A. I. Pristupa

Institute of Chemical Physics, USSR Academy of Sciences
(Submitted July 16, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 7, 397–400 (5 October 1976)

PACS numbers: 78.60.Dg, 81.50.Qx

Excited complexes with charge transfer are produced in molecular crystals and solutions when an exciton or an electron-excited molecule collides with an impurity that has donor or acceptor properties. The fluorescence of singlet-excited complexes is one of the ways of deactivating them, and the competing processes are dissociation into free ion radicals or intercombination transitions to a triplet state of the complex. It was shown earlier[1–2] that the singlet S and triplet T states of a complex can be mixed by an external magnetic field. This mixing of the spin states, due to the presence of g-factors of the ion radicals

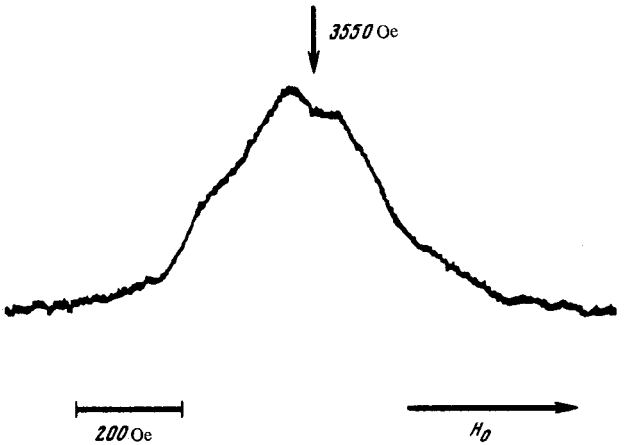

FIG. 1. Magnetic resonance spectrum of excited complexes of rubrene. Ordinates—amplitude of signal from the output of the photomultiplier at the microwave-power modulation frequency.

of the pair, manifests itself in the quenching of the fluorescence of molecular crystals containing impurities,[3] and in a change in the photoconductivity.[4] The effect exerted on these parameters by weak magnetic fields (10—100 Oe) has shown that the singlet and triplet excited states of the complexes coincide in energy and that during the lifetime of the complex the spin-lattice relaxation does not manage to establish an equilibrium distribution over the Zeeman sublevels of the ion-radical pair: in a magnetic field $H \gg 10$ Oe, only the mixed sublevel $(S - T_0)$ turns out to be activated. Under these conditions one can expect that realization of resonant transitions between the levels $(S - T_0)$ and T_+ or T_- will lead to a decrease of the population of the $(S - T_0)$ level and will manifest itself in an additional resonant quenching of the fluorescence of the excited complexes. The possibility of realizing such transitions was indicated earlier in[1-5]. In contrast to the know method of optical detection of magnetic resonance (ODMR) on triplet particles,[6] where the difference between the populations of the Zeeman sublevels is the result of the low temperature of the sample, in the present case this difference is due to dynamic polarization of the spins.

We investigated the fluorescence of thin (3—5 μ) polycrystalline layer of rubrene (tetraphenyltetracene) of area 0.3 cm^2, deposited by vacuum sublimation of a quartz substrate and placed in the resonator of the ODMR spectrometer. The impurity in the rubrene was molecular rubrene perioxide produced by photo-oxidation.[3,4] The magnetic components of the microwave field in the resonator was perpendicular to the direction of the constant magnetic field of the spectrometer. The microwave oscillations were generated with a 10-W klystron at 9500 MHz and modulated 50% in amplitude at a frequency 10^3 Hz.

The fluorescence was excited with a 100-watt incandescent lamp in the spectral range $360 < \lambda < 520$ nm. The excitation intensity was 4×10^{15} quanta/cm^2 sec. The fluorescence quantum yield of the excited rubrene complexes was 0.1. The fluorescence was registered in the wavelength range $\lambda > 540$ nm with an FÉU-55

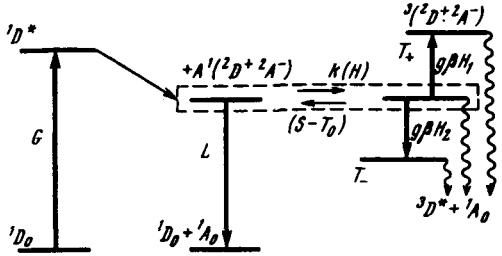

FIG. 2. Scheme of transitions in photoexcitation of rubrene. Explanations in the text.

photomultiplier screened against the influence of the stray magnetic fields. The signal at the modulation frequency was fed from the photomultiplier output to a tuned amplifier with a synchronized detector and automatically plotted as a function of the spectrometer magnetic field intensity. The noise signal at the recorder, at a registration time constant 10 sec, was 10^{-6} of the total fluorescence intensity. Since the sample was not force-cooled, turning on the microwave power heated the sample to a temperature 50 °C, determined by measuring the temperature quenching of the fluorescence. Figure 1 shows the ODMR spectrum registered under these conditions. It consisted of two broad lines spaced $\delta H = 150$ Oe apart. The change in the intensity of the excited light or of the microwave power caused a proportional change only in the ODMR signal amplitude. The measurements have shown that the phases of the signal from the microwave receiver differed by 180°, i.e., an increase of the microwave power in the resonant magnetic field causes a decrease in the fluorescence intensity. The resonant character of the observed influence of the microwave radiation on the fluorescence intensity excludes the possibility of explaining the observed effect as being due to the thermal action of the microwave power. The observed signal is apparently connected with the resonant transitions $(S-T_0) \rightarrow T_+$ and $(S-T_0) \rightarrow T_-$ due to the microwave power. The waveform of the signal in Fig. 1 corresponds to the waveform of the ESR signal observed from radical pairs isotropically distributed in the matrix.[7] This waveform is natural also for short-lived pairs of ion radicals that determine the fluorescence of the complexes in the rubrene. The observed splitting of the signal is apparently connected with the magnetic-dipole interaction in the complexes and makes it possible to estimate the distance between the ion radicals of the complex at $r = (\frac{3}{2} g\beta/\delta H)^{1/3} = 5.8$ Å.

Figure 2 shows the transition scheme in the investigated system and explains the observed effect. Here D is the rubrene donor molecule, A is the rubrene-peroxide acceptor molecule; the labels on the left identify the multiplet character of the state; G is the excitation intensity, L is the registered fluorescence intensity and $k(H)$ is the rate constant of the intercombination transitions and increases with the increasing intensity of the external magnetic field. The decay of the triplet state of the complexes $^3(D^+A^-)^*$ leads to the formation of triplet excitons of rubrene $^3D^*$.[4] The observed resonant quenching of the fluorescence L is determined by the transitions $g\beta H_1$ and $g\beta H_2$.

It should be noted that when the magnetic resonance is registed by means of

the fluorescence at room temperature, an exceedingly high sensitivity to the number of spins in the sample is obtained. Thus, the signal of Fig. 1 corresponds to 10^7 particles in a sample with a lifetime 5×10^{-9} sec at a signal to noise ratio 20. This ratio can be increased by approximately one order of magnitude by using a cooled photomultiplier. The use of single-crystal samples increases the sensitivity by one or two more orders of magnitude as a result of narrowing of the ODMR lines.

The described results suggest the feasibility of experimentally investigating other short-lived ion-radical or radical pairs in the condensed phase, which play an important role in photochemical and radiation-chemical processes. It becomes possible in principle to register magnetic resonance not only with the aid of fluorescence, as described by us, but also with the aid of the resonant influence on other macroscopic characteristics of the investigated system, such as photoconductivity, the yield of triplet excited states, or the rate of the chemical reaction.

The authors thank B. M. Rumyantsev and V. I. Lesin for help in the preparations for the experiment and Ya. S. Lebedev for taking a part in a discussion of the results.

[1]E. L. Frankevich, Zh. Eksp. Teor. Fiz. **50**, 1226 (1966) [Sov. Phys. JETP **23**, 814 (1966)].
[2]P. W. Atkins, Chem. Phys. Lett. **18**, 355 (1973).
[3]E. L. Frankevich, B. M. Rumyantsev, and V. I. Lesin, Opt. Spektrosk. **37**, 376 (1974) [Opt. Spectrosc. **37**, 215 (1974)].
[4]E. L. Frankevich, M. M. Tribel, and I. A. Sokolik, Phys. Status Solidi [b] **77**, No. 1 (1976).
[5]B. Broclehurst, Nature **221**, 921 (1969).
[6]M. Sharnoff, J. Chem. Phys. **46**, 3263 (1967).
[7]Ya. S. Lebedev, Dokl. Akad. Nauk SSSR **171**, 378 (1966)