

# Luminescence and emission of free radicals in gaseous and condensed phases

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A study has been made of the dynamics of the formation of aminophenylthiyl radicals during picosecond laser photolysis of bis(para-aminophenyl)-disulfide,  $\text{H}_2\text{N}-\square-\text{S}-\text{S}-\square-\text{NH}_2 \rightarrow 2\text{S}-\square-\text{NH}_2$ . A luminescence and an emission by free radicals of aromatic compounds in the gas phase have been observed for the first time.

The luminescence of the free radicals formed in the photolysis of complex organic compounds in solutions is an extremely rare effect because of the effective recombination of radicals in the vicinity of solvent molecules. Only a few of the aromatic radicals luminesce in solutions.<sup>1-5</sup> The appearance of aminophenylthiyl radicals as a result of a selective dissociation of the S-S bond during the photolysis of bis(para-aminophenyl)-disulfide has been demonstrated by ESR methods.<sup>6</sup>

As the sources of exciting radiation we use the second- and third-harmonic pulses from a neodymium laser ( $\lambda_e = 353$  nm and  $\lambda_e = 530$  nm; pulse length  $\tau_p = 6$  ps; energy  $E = 10$  mJ) and an excimer laser ( $\lambda_e = 308$  nm;  $\tau_p = 20$  ns;  $E = 100$  mJ). The luminescence and the emission are detected with a polychromator, a vidicon, and a multichannel analyzer. The absorption spectra of the radicals are measured with a picosecond laser spectrometer<sup>7</sup> in which pulses of a picosecond continuum are used as probing light. An optical multichannel analyzer is used for an automatic processing of the results of the kinetic measurements.

Figure 1 shows the absorption spectrum of a solution of bis(para-aminophenyl)-disulfide in diethyl ether (1), which lies in the UV region. When this substance is excited by laser light with  $\lambda_e = 353$  nm, the absorption spectrum of a radical appears in a longer-wave region (2). The intensity of the radical absorption is a linear function of the intensity of the exciting light, and the position and shape of the spectrum remain constant at delay times up to 200 ps of the probing pulse.

The kinetics of the buildup of the absorption of this radical is illustrated by Fig. 2. The experimental results on the dependence of the optical density ( $D$ ) of the radical on the time  $\theta$  agree with theoretical curve 1, found from a solution of the balance equations for the populations of the initial and final states and the radiation transport equations in the medium under the assumption of a Gaussian profile for the laser pulse, for a pulse length  $\tau_p = 6$  ps, and for a scale time  $< 1$  ps for the formation of the radical. This result confirms that the observed absorption is in fact due to radicals, rather than to products of some structural regrouping or secondary bimolecular reactions, which would require a longer time.

During the laser excitation of the solution of bis(para-aminophenyl)-disulfide in

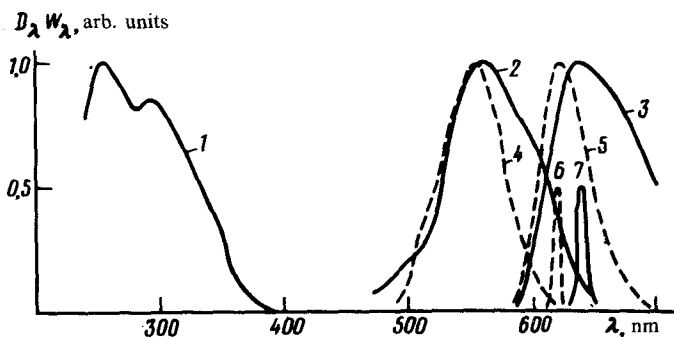


FIG. 1. 1—Absorption spectra of bis(para-aminophenyl)-disulfide in diethyl ether; 2,4—absorption spectra; 3,5—luminescence spectra; 6,7—emission spectra of the aminophenylthiyl radical in a diethyl ether solution (2,3,7) and in vapor (4,5,6) at a diethyl ether pressure of 300 atm ( $T = 510$  K).

diethyl ether at  $\lambda_e = 353$  nm, with a flux density on the order of  $\Phi = 10^{26}$  cm $^{-2}$ ·s $^{-1}$ , we observe a luminescence of the free radical, whose spectrum is the mirror image of the absorption spectrum (curve 3 in Fig. 1). The intensity of this luminescence is a quadratic function of the flux density of exciting light, telling us that some of the photons of the exciting light are expended on the photolysis of the bis(para-aminophenyl)-disulfide molecules, while some are absorbed by rapidly forming radicals, whose luminescence is observed. The two-photon mechanism for the occurrence of the luminescence is confirmed by the sequential application to the system of ultrashort pulses at  $\lambda_e = 353$  nm and  $\lambda_e = 530$  nm. In this case the second exciting pulse is delayed 20–200 ps with respect to the first. When only the light at  $\lambda_e = 530$  nm bombards the bis(para-aminophenyl)-disulfide (this light is not absorbed by this substance), and radicals correspondingly do not form, no luminescence is detected. The application to this system of light at  $\lambda_e = 353$  nm and then of light at  $\lambda_e = 530$  nm, which is at the peak of the absorption spectrum of the radical, gives rise to an observable luminescence whose intensity is an order of magnitude greater than that found when only light with  $\lambda_e = 353$  nm is applied to the system.

A specific feature of the electronic structure of free radicals, which distinguishes them from ordinary polyatomic molecules, is the presence of one unpaired electron.

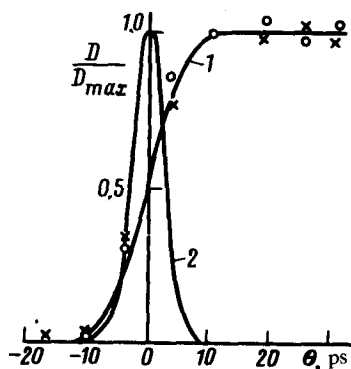


FIG. 2. Theoretical (1) and experimental results on the optical density  $D/D_m$  of the aminophenylthiyl radical in hexane (×) and diethyl ether (○) versus the delay time ( $\theta$ ) between the pulse of exciting light and the pulse of probing light; 2—time profile of the exciting pulse ( $\tau_p = 6$  ps).

Consequently, the unexcited electronic state and the first excited electronic state are doublets. Free radicals have no triplet excited states, while "metastable" quartet states lie above the first excited doublet on the energy scale. This circumstance means that free radicals should be regarded as potentially efficient laser media, because in them there is no loss of the emitted light or of the pump light in the system of triplet levels, as occurs for ordinary complex molecules. The first observation of emission by free radicals in solutions was recently reported by Hiroka and Kotani.<sup>5</sup>

We have observed that during excitation of bis(para-aminophenyl)-disulfide by light at  $\lambda_e = 353$  nm in vapor in the presence of a second gas, diethyl ether (or hexane), at a pressure on the order of 300 atm, we observe an intense luminescence. As in the solutions, this is a two-photon luminescence, but its spectra are shifted in the short-wave direction (curves 4 and 5 in Fig. 1). In low-density vapor, the luminescence spectrum of the radical lies at even shorter wavelengths, with a maximum at  $\lambda_m = 540$  nm.

The fact that an intense luminescence of aminophenylthiyl radicals occurs in the gas phase means that an emission in a vapor can be achieved. We know that the addition of other gases to the vapor of organic compounds substantially lowers the threshold and increases the intensity of emission.<sup>8,9</sup> In an effort to evaluate a possible specific effect of a second gas, we carried out a preliminary study of the emission by free radicals in the condensed phase, in various solvents, with pumping by the beam from an excimer laser, with  $\lambda_e = 308$  nm. We found that, despite the intense luminescence of the radical in hexane, this solution yields no emission. When diethyl ether is added to the hexane solution, an emission occurs. Varying the ratio of hexane to diethyl ether in the mixture from 3:1 to 1:3 causes the maxima ( $\lambda_m$ ) of the luminescence and emission spectra to shift from 623 and 626 nm to 632 and 648 nm, respectively. The observed shifts of the spectra for these radicals in solutions differing in nature are evidence that intermolecular interactions are playing an important role. The lowest threshold for the emission of a radical is achieved in a diethyl ether solution ( $\lambda_m = 637$  nm, curves 3 and 7 in Fig. 1). In view of this circumstance, we sought emission of the aminophenylthiyl radical in the gas phase in the presence of diethyl ether as a second gas. Curve *b* in Fig. 1 shows the emission spectrum recorded by us. The emission by free radicals in the gas phase which we have achieved here currently holds the record for the longest wavelength among known vapor lasers.<sup>9</sup>

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