# THE PHOTOCHEMICAL CHARACTERISTICS OF RHODAMINE 6G–ETHANOL SOLUTIONS


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SUMMARY

Absorption spectra and extinction coefficients for triplet–triplet and photo-decomposition product absorption in Rhodamine 6G–ethanol solutions are reported. The rate constants for quenching of the Rhodamine 6G triplet by oxygen and 1, 3, 5, 7-cyclo-octatetraene were observed to be $1.64 \pm 0.2 \times 10^9 \, M^{-1} \, s^{-1}$ and $7.0 \pm 1.0 \times 10^8 \, M^{-1} \, s^{-1}$ respectively. The quantum efficiency for intersystem crossing was observed to be $2.1 \pm 0.2 \times 10^{-3}$. The quantum efficiency for photo-decomposition of Rhodamine 6G in ethanol was observed to be dependent on the excitation conditions.


INTRODUCTION

Rhodamine 6G (R6G), a member of the xanthene class of dyes, is widely used in dye laser media and is the most efficient lasing dye at present known[1,2]. Under fast pump flash conditions output energies >100 J and efficiencies (*i.e.* energy output/electrical input energy) >1% have been reported[3,4] for R6G–ethanol solutions. The performance of a dye laser is strongly influenced by the presence of transient and permanent light absorbing species produced during photoexcitation of the lasing medium. Such species include excited state dye molecules, radicals and photodecomposition products. The absorption spectrum and lifetime of triplet state dye molecules strongly influence the behaviour of continuous wave (c.w.) and long pulse dye lasers[5-7].

In the present work the photochemical characteristics of the dye, including triplet state parameters and photodecomposition, were investigated using conventional and laser flash photolysis techniques. Since the intersystem crossing

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ratio $\Phi_T$ for R6G in ethanol is small (*i.e.* $<10^{-2}$) triplet energy transfer from naphthalene to R6G was used to generate high concentrations of R6G triplet. The triplet–triplet absorption spectrum of R6G in polymethyl methacrylate has been reported by Buettner[8]. Detailed direct measurements of quantum efficiencies for intersystem crossing and photodecomposition have not previously been reported. The chemical structure of R6G is shown for reference in Fig. 1.
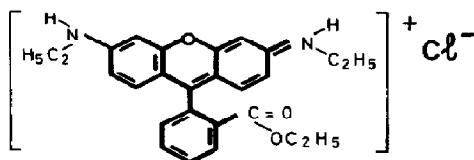


Fig. 1. The chemical structure of the R6G molecule.

EXPERIMENTAL

*Chemicals*

Eastman Kodak dye laser grade R6G was used as supplied after extensive purity checks using chromatographic and spectroscopic techniques. The naphthalene, ferric alum, potassium oxalate, ammonium acetate, ammonium fluoride, *o*-phenanthroline and ethanol used were identical to those described previously[9]. The 1, 3, 5, 7-cyclo-octatetrane (COT) was supplied by R. E. Emanuel. The latter material containing 0.1% hydroquinone as inhibitor was in general used as supplied since removal of the inhibitor was observed to have no influence on the results obtained.

*Apparatus and procedure*

The conventional flash photolysis system and procedure is described in detail elsewhere[9]. Photolyzing flash energies in the range 2–250 J were used and for most experiments a Pyrex glass filter jacket (2 mm thickness) was placed around the reaction cell in order to limit the exciting radiation to wavelengths $>300$ nm. Unless otherwise stated all solutions were de-aerated by bubbling with argon for at least 1 h.

Laser flash photolysis experiments were carried out using the second harmonic of a giant pulse ruby laser and a flash pumped dye laser as excitation sources. The giant pulse ruby laser system consisted of a 3 in. $\times$ $^3/_8$ in. ruby rod pumped by a helical flash tube with a three plate resonant reflector and a roof top prism as cavity resonators. The laser was Q-switched using a solution of cryptocyanine in methanol and the Q-switched mode was capable of giving output pulses of half-width 15 ns and containing up to 1 J of 694.3 nm radiation. The second harmonic at 347 nm was generated at an efficiency of $\sim$ 5% by passing the pulse through a frequency doubling crystal of KDP (1¼ in. $\times$ 1¼ in. $\times$ 1 in.). The energies of

the fundamental and second harmonic pulses were monitored by using glass beam splitters to deflect a small part of each pulse onto a vacuum photodiode with an S20 spectral response (Instrument Technology Ltd. Type HCB1 in HCB2 mount). The response of the diodes was calibrated using a calorimeter (Quantronix Type 504) to measure pulse energies. The dye laser used is described in detail elsewhere[9]. Using a $2 \times 10^{-4}$ $M$ solution of 7-diethylamino-4-methylcoumarin in ethanol as the lasing medium an output pulse of $\sim 150$ mJ at 460 nm was obtained. Chemical actinometry, using potassium ferrioxalate[9,10] was carried out on the exciting pulses obtained from both the dye and ruby lasers.

Fluorescence spectra were measured on an American Instrument Co. Aminco–Bowman spectrophotofluorimeter using the procedures reported previously[9]. Absorption spectra were recorded on a Perkin-Elmer Hitachi spectrophotometer (type EPS-3T).

RESULTS

*Flash photolysis of R6G/naphthalene/ethanol solutions*

The changes in optical densities, given as $\underline{\varrho}_\lambda$ and $\gamma_\lambda$ values*, observed in the wavelength region 360–650 nm at 200 $\mu$s and 2 ms after flash photolysing a solution containing $2 \times 10^{-6}$ $M$ R6G and $10^{-3}$ $M$ naphthalene using an electrical input flash energy of 50 J are shown in Fig. 2. As can be seen from Fig. 2 transient absorption signals were observed in the wavelength regions 360–470 nm and 560–660 nm. In the wavelength region 470–500 nm and 550–565 nm corresponding to regions of intense R6G ground state absorption, transient increases in transmission were observed following photolysis. The transient absorption signal observed at 415 nm, the peak of the naphthalene triplet–triplet absorption, showed the presence of a fast initial decay during the period 0–200 $\mu$s after the photolyzing flash. This fast decay due to naphthalene triplet–triplet absorption, was superimposed on a large longer lived absorption. Since the naphthalene triplet–triplet absorption had completely decayed after 200 $\mu$s, it may be concluded that the absorptions observed at 200 $\mu$s and 2 ms (Fig. 2) after the flash were due to absorbing species originating from R6G excited states. This conclusion was verified, as described later by photolyzing R6G solutions in the absence of naphthalene.

The transient absorption due to the R6G triplet in the region 560–650 nm was observed to decay *via* mixed first and second order kinetics with a first order rate constant $k_1^{R6G} = 7.0 \pm 2.0 \times 10^2$ s$^{-1}$ and a second order rate constant $k_2^{R6G}/\varepsilon_{600}^{R6G} = 2.3 \pm 0.4 \times 10^5$ cms$^{-1}$. In the wavelength range 360 to 460 nm, the transient absorption exhibited an initial decay (lifetime $<2$ ms) similar to the

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* The symbols $\varrho_\lambda$ and $\gamma_\lambda$ which refer to changes in optical density due to absorption (i.e. decrease in transmission on photolysis) and depletion (i.e. increase in transmission on photolysis) signals respectively are discussed in detail elsewhere[9].
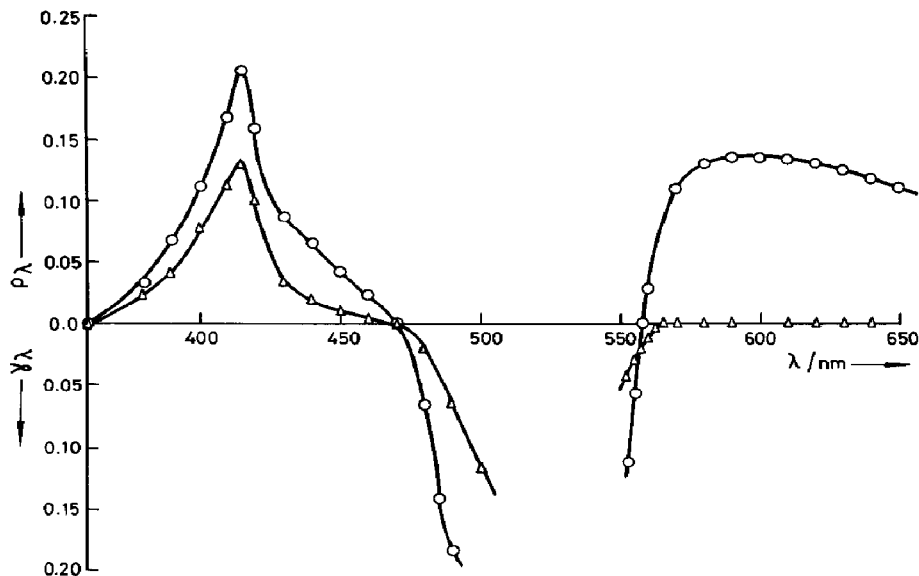
Fig. 2. Changes in optical density observed at 200 $\mu$s (O) and 2 ms ($\triangle$) after flash photolyzing a $2 \times 10^{-6}$ $M$ R6G/$10^{-3}$ $M$ naphthalene/ethanol solution using a 50 J flash.

R6G triplet absorption in the region 560–650 nm. In carefully de-aerated solution this relatively fast decay due to the R6G triplet was superimposed on a permanent absorption which was attributed to some photodecomposition product of R6G (hereafter referred to as product P).

The changes in the optical density function $\gamma(t)$ during the period 200 $\mu$s to 2 ms after the flash correspond to depletion of the ground state by an amount equal to the sum of the R6G triplet state and product P concentrations. Since the R6G triplet state absorption had decayed to zero after 2 ms the optical density function $\gamma_\lambda(t)$ ($t > 2$ ms), due to product P alone at any wavelength within the R6G ground state absorption spectrum (Fig. 3) is given by:

$$\gamma_\lambda(t) = (\varepsilon^s{}_\lambda - \varepsilon^P{}_\lambda)\ C^P(t)\ l \tag{I}$$

where $C^P(t)$ is the concentration of product P at a time $t$ after the flash, $\varepsilon^s_\lambda$ and $\varepsilon^P_\lambda$ are the extinction coefficients for ground state and product P absorptions at wavelength $\lambda$ respectively and $l$ is the absorption path length. Since $\gamma$ was observed experimentally to be zero for $\lambda = 460$ nm and 470 nm it may be assumed that for these wavelengths $\varepsilon^s = \varepsilon^P$. Therefore $\varepsilon^P_{460} = 5000 \pm 1500$ $M^{-1}$ cm$^{-1}$ and $\varepsilon^P_{470} = 7000 \pm 1500$ $M^{-1}$ cm$^{-1}$. The uncertainty in the latter values arises from the detection limits of the transient analysing system.

It can be seen from Figs. 2 and 3 that the value of $\varrho_\lambda$ at 2 ms after the exciting flash is decreasing rapidly with increase in wavelength within the region 415–450 nm whilst $\varepsilon^s_\lambda$ is relatively constant and small (*i.e.* <3000 $M^{-1}$ cm$^{-1}$). It may therefore be assumed that in the region 480–565 nm $\varepsilon^P_\lambda$ is small in com-
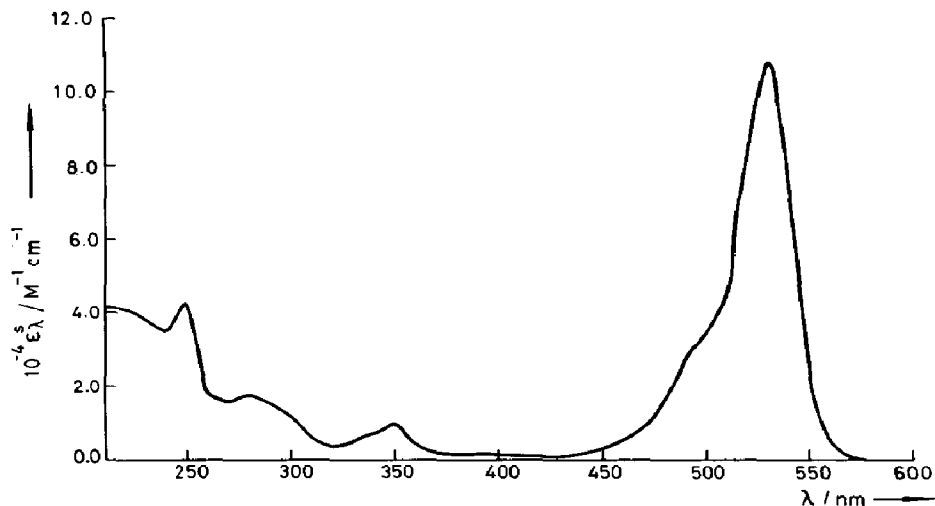
Fig. 3. Absorption spectrum of the R6G ground state.

parison to $\varepsilon_\lambda^s$. Using this approximation and assuming that the depletion in R6G ground state absorption at 2 ms after the exciting flash is due solely to the decomposition product yielding the 360–460 nm absorber, the concentration of this decomposition product may be calculated using the data from Figs. 2 and 3 in eqn. (I). For wavelengths 555 nm, 500 nm, 490 nm and 480 nm, the value of $C^P$ obtained for 2 ms after the flash was $2.05 \pm 0.15 \times 10^{-7}$ $M$. The extinction coefficients shown in Fig. 4 for absorption by product P were calculated from $\varepsilon_\lambda^s$ (Fig. 3) and the values $\varrho_\lambda$ and $\gamma_\lambda$ at 2 ms after the flash (Fig. 2) assuming that the concentration of
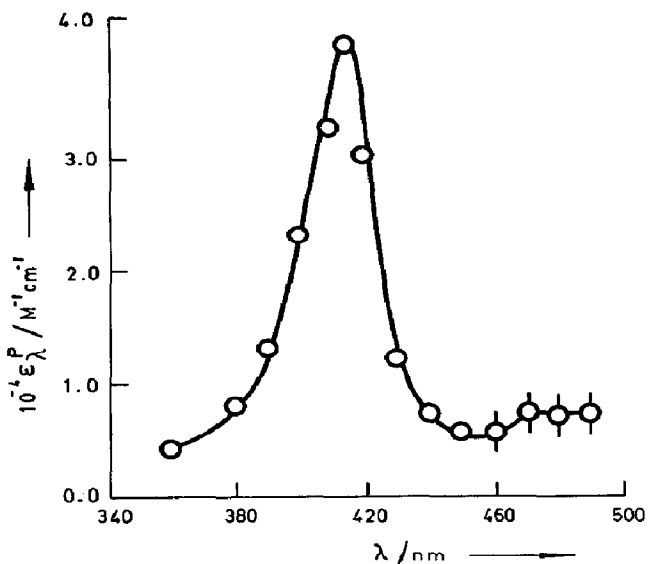


Fig. 4. Absorption spectrum of product P.

product P was $2.0 \pm 0.15 \times 10^{-7}$ $M$. It should be noted that in the derivation of the extinction coefficients in Fig. 4, it was assumed that the disappearance of 1 molecule of R6G leads to 1 molecule of the decomposition product P.

*Flash photolysis of R6G–ethanol solutions*

R6G–ethanol solutions of concentration $10^{-6}$–$10^{-5}$ $M$ were flash photolyzed in the presence and absence of a Pyrex glass filter jacket around the reaction cell. The transient absorption spectra observed in the wavelength region 560–660 nm were identical in shape to the R6G triplet–triplet absorption spectrum reported above (Fig. 2). The absorptions in the wavelength region 380–490 nm at 2 ms after the exciting flash were consistent with those reported above for the photo-decomposition product P. At times <2 ms the absorption signals in the region 440–490 nm were due predominantly to the R6G triplet whilst in the region 400–420 nm the absorption signals were observed to build up slowly after the flash in some cases from almost zero. This gradual build up of optical densities was more pronounced in the experiments in which the Pyrex glass filter jacket was absent. This build up from almost zero is due to the production of a large concentration of P but relatively smaller concentration of R6G triplet. In the energy transfer systems discussed above the build up in concentration of P was masked by the absorption due to the high concentration of R6G triplet.

Owing to severe overlap of R6G triplet and product P absorptions in the region 360–460 nm when R6G/naphthalene/ethanol and R6G–ethanol solutions were flash photolyzed, it was not possible to determine the component optical densities of the R6G triplet and product P absorptions in this region. Further information was obtained as reported below, by addition of the triplet state quencher 1,3,5,7-cyclo-octatetraene (COT).

*Flash photolysis of R6G/1,3,5,7-cyclo-octatetraene/ethanol solutions*

Flash photolysis of $10^{-6}$–$10^{-5}$ $M$ COT–ethanol solutions failed to yield any detectable absorptions in the wavelength region 340–660 nm.

Solutions containing $10^{-5}$ $M$ R6G and various concentrations of COT were flash photolyzed using a 50 J flash. The rate constant for quenching of the R6G triplet state by COT was estimated from the first order decays at 600 nm in the presence of various COT concentrations to be $7.0 \pm 0.1 \times 10^{8}$ $M^{-1}$ $s^{-1}$. In the wavelength region 340–470 nm the absorption signals obtained in the presence of COT showed a fast initial decay superimposed on the slow build up of a permanent absorption. The absorption spectrum of the permanent component at 5 ms after the flash was identical to that of the product P reported above (see Fig. 4).

In Fig. 5 the total optical densities measured at 415, 430 and 600 nm are shown for a $10^{-5}$ $M$ R6G/$7.5 \times 10^{-6}$ $M$ COT/ethanol solution. The absorption signals at 415 and 430 nm can be resolved into two components, *i.e.* the permanent product P which builds up from zero after the flash (broken line in Fig. 5) and
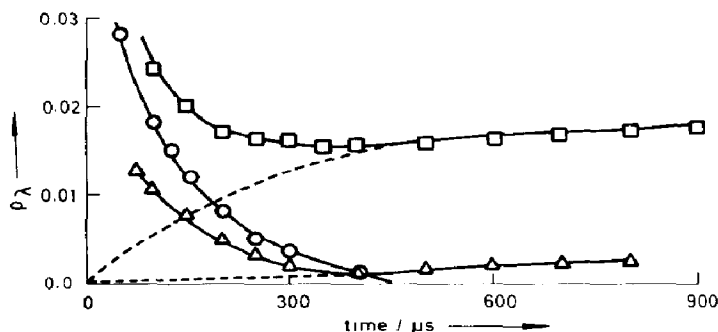
Fig. 5. The transient absorption signals observed at 415 nm ($\square$), 430 nm ($\triangle$) and 600 nm (o) after flash photolyzing a $10^{-5}$ $M$/R6G 7.5 $\times$ $10^{-6}$ $M$ COT/ethanol solution using a 50 J flash.

the fast decaying species. Since the first order rate constants for decay of the short lived absorptions at 415 and 430 nm were identical to that of the R6G triplet absorption at 600 nm the former were assumed to be also due to the R6G triplet. The optical densities due solely to the R6G triplet at 100 $\mu$s after flash exciting $10^{-5}$ $M$ R6G 7.5 $\times$ $10^{-6}$ $M$ COT ethanol in the wavelength region 360–470 nm and at 600 nm are given in Table 1.

TABLE 1

OPTICAL DENSITIES DUE TO R6G TRIPLET

| Walvelength $\lambda$/nm | Optical density $\varrho_\lambda{}^{R6G}$due to the R6G triplet as calculated for 100 $\mu$s after flash photolyzing a $10^{-5}$ $M$ R6G/7.5 $\times$ $10^{-6}$ $M$ COT/ethanol solution |
|---|---|
| 360 | 0.00364 |
| 380 | 0.00545 |
| 390 | 0.01380 |
| 400 | 0.0145 |
| 415 | 0.0182 |
| 420 | 0.016 |
| 430 | 0.010 |
| 440 | 0.007 |
| 460 | 0.00628 |
| 470 | 0.00517 |
| 600 | 0.0183 |

*Determination of the extinction coefficients for R6G triplet–triplet absorption*

The extinction coefficients for the R6G triplet–triplet absorption in the wavelength region 560–660 nm were determined by investigation of the triplet energy transfer from naphthalene to R6G[9] following flash photolysis of a $10^{-3}$ $M$ naphthalene/$10^{-6}$ $M$ R6G/ethanol solution using a 2 J flash.

The optical density at 600 nm due to the R6G triplet was observed to build up to a maximum after 250 $\mu$s (see curve A, Fig. 6) and then decay by predominantly first order kinetics with a rate constant of $k_1{}^{R6G} = 2.9 \pm 0.1 \times 10^2$ s$^{-1}$.
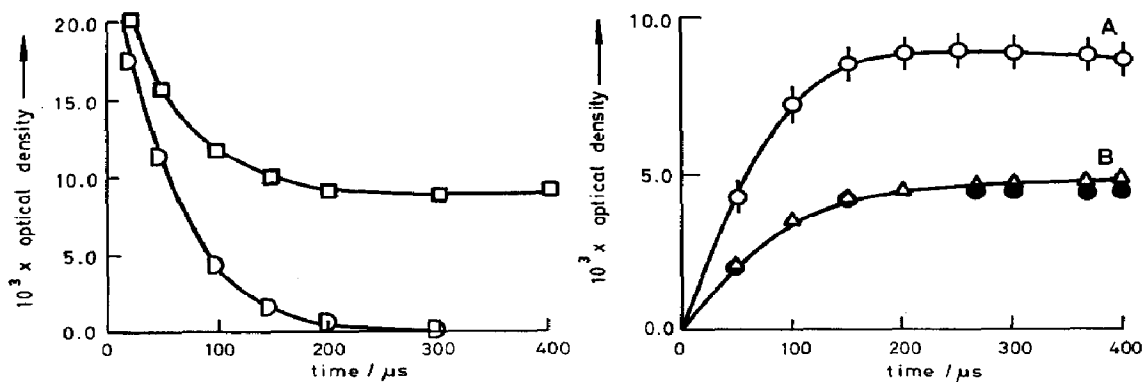
Fig. 6. Right: Transient absorption signals observed at 600 nm (o) and 430 nm (△) after flash photolyzing a $10^{-3}$ $M$ naphthalene/$10^{-6}$ $M$ R6G/ethanol solution using a 2 J flash. The calculated transient absorption due to the R6G triplet at 430 nm (●) is shown for comparison. Left: Total transient absorption at 415 nm (□) and the transient absorption at 415 nm due to the naphthalene triplet (D).

The transient absorption observed in the wavelength region 390–440 nm may arise from three absorbing species, *i.e.* the naphthalene triplet, the R6G triplet and the product P. The total optical density at 430 nm (curve B, triangular points) and the calculated optical densities due to the R6G triplet at 430 nm (curve B, circular points) are also shown in Fig. 6. The calculated points were obtained by assuming that $(\varepsilon^{R6G})_{430}/(\varepsilon^{R6G})_{600} = 1.00/1.85$ as given in Table 1. It can be seen from Fig. 6 that the absorption at 430 nm is due solely to the R6G triplet and hence the concentration of photodecomposition product is negligible over the period 0–300 $\mu$s after the flash. To find the optical density due to the naphthalene triplet at 415 nm, it was therefore necessary only to subtract the optical density due to R6G triplet from the total optical density at 415 nm. In Fig. 6 the total optical density as measured at 415 nm, and the optical density due to naphthalene alone (calculated by assuming $(\varepsilon^{R6G})_{600} = (\varepsilon^{R6G})_{415}$, see Table 1) are plotted as a function of time after the excitation flash.

Under the excitation conditions used the first and second order processes which lead to deactivation of the naphthalene triplet and the R6G triplet, were observed to be negligibly slow in comparison to the triplet energy transfer process during the period 10–150 $\mu$s after the exciting flash. Since the 2J exciting flash used in the energy transfer experiment was of short duration (halfwidth $<$1 $\mu$s) all of the R6G triplet state molecules formed at times $>$10 $\mu$s after the photolyzing flash are formed *via* triplet energy transfer from naphthalene. It may be assumed, therefore, that for short time intervals (*i.e.* 50 $\mu$s) within the period 10 $\mu$s–150 $\mu$s after the flash, the number of naphthalene triplet molecules deactivated is equal to the number of R6G triplet state molecules formed during that interval. The value of $(\varepsilon^{R6G})_{600}$ was calculated to be 18,000 $\pm$ 3000 $M^{-1}$ s$^{-1}$ assuming $(\varepsilon^{Naph})_{415}$

$= 40,000 \ M^{-1} \ cm^{-1}$ [9]. The complete R6G triplet–triplet absorption spectrum in the wavelength region 360 nm to 650 nm, shown in Fig. 7 was determined from Fig. 2, Table 1 and $(\varepsilon^{R6G})_{600} = 18,000 \pm 3000 \ M^{-1} \ s^{-1}$.
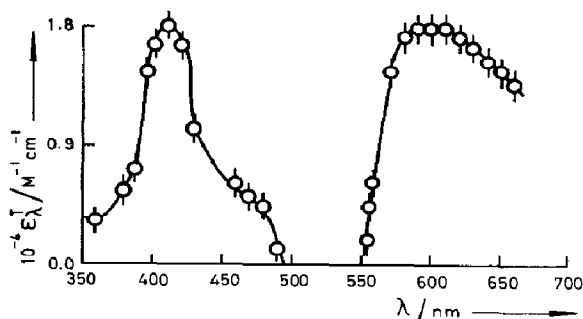
Fig. 7. The triplet–triplet absorption spectrum of R6G in ethanol.

## Quenching of the R6G triplet state and the product P by oxygen

When $10^{-5} \ M$ R6G–ethanol solutions containing known concentrations of oxygen, calculated using the Bunsen absorption coefficient[11], were flash photolyzed using a 50 J flash the triplet–triplet absorption in the wavelength regions 550–660 nm and 360–490 nm was observed to decay with good first order kinetics. The rate constant for quenching of the R6G triplet state by molecular oxygen was determined from these first order plots to be $1.64 \pm 0.20 \times 10^9 \ M^{-1} \ s^{-1}$. The absorption due to product P was also observed to decay via good first order kinetics in the presence of oxygen and the rate constant for quenching of the product P by molecular oxygen was determined to be $7.0 \pm 0.1 \times 10^8 \ M^{-1} \ s^{-1}$.

When a carefully de-aerated solution of $10^{-5} \ M$ R6G in ethanol was flash photolyzed, the absorption in the wavelength region 390 nm to 450 nm due to the photodecomposition product P, was observed to build up to a maximum at relatively long times after the flash ($>1$ ms) and then remain constant. The absorption spectrum observed in the region 390–450 nm at 5 s after the flash was identical to that observed at 2 ms after the flash. Upon subjecting the solution to successive photolyzing flashes the concentration of product P, as measured by monitoring the optical density of the solution at 415 nm, was observed to reach an equilibrium value. When this procedure was repeated and the optical density at 480 nm investigated, the concentration of R6G in the ground state was observed to continue to decrease even after the concentration of product P had reached its equilibrium value. It can only be concluded from these results that subsequent subjection of the product P to photolyzing flashes led to photolysis of P with the eventual attainment of an equilibrium concentration.

When traces of oxygen were introduced into the solution before photolysis, the absorption due to product P was observed to decay. The rate and amount of

decay observed was dependent on the concentration of oxygen added. Figure 8 shows the changes in absorption observed following excitation of a $10^{-5}$ $M$ R6G solution which initially contained a trace of oxygen, by three consecutive 50 J flashes. As can be seen from Fig. 8 the first flash resulted in strong absorption at 415 nm which decayed with a half-life of $\sim$ 3.5 ms. The concentration of oxygen present ($1.7 \times 10^{-7}$ $M$) was calculated from the decay kinetics, using the quenching constant of $7.0 \times 10^8$ $M^{-1}$ $s^{-1}$ measured above. The second flash again resulted in the production of product P, but the decay was much slower (*i.e.* half-life $\sim$ 23.0 ms). The concentration of oxygen, present in solution before the second photolyzing flash was therefore reduced to about one-tenth of its initial concentration (*i.e.* $<2.0 \times 10^8$ $M$). The third flash resulted in the production of less of the product P than either the first or second flash and the 415 nm absorption was permanent in nature. Further flashing resulted in the production of an equilibrium concentration of the product P.
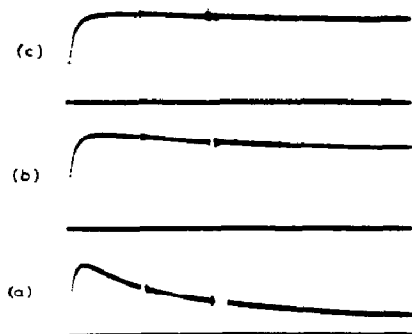


Fig. 8. Transient absorption signals, due to product P, observed at 415 nm following excitation, by three consecutive 50 J photolyzing flashes, of a $10^{-5}$ $M$ R6G–ethanol solution which intitially contained a trace of oxygen. (a) First flash, $\tau_{1/2} \approx$ 3.5 ms; (b) second flash, $\tau_{1/2} \approx$ 23 ms; (c) third flash, $\tau_{1/2} \approx \infty$.

In the presence of oxygen, the absorption at 415 nm due to product P was observed to decay and the R6G ground state, monitored *via* the ground state depletion at 485 nm, recovered at a corresponding rate. Furthermore in the presence of a large concentration of oxygen, the R6G ground state concentration remained unchanged even after successive flashings. It can only be concluded that deactivation of the product P by oxygen leads to the regeneration of the R6G ground state, and that during or after the photolytic flash, oxygen is removed from solution.

When a de-aerated $10^{-5}$ $M$ R6G–ethanol solution was exposed to 200 flashes, each of 250 J, and the conventional ground state absorption spectrum of the solution subsequently investigated almost complete (*i.e.* $>95\%$) photo-decomposition of the dye was observed. The conventional absorption spectrum after 200 flashes did not, however, show the presence of any detectable 340–460 nm

absorption due to product P indicating that product P formed by early flashes is decomposed by subsequent flashes. In the presence of oxygen (*i.e.* aerated solution) no appreciable permanent decomposition of R6G was observed after 200 flashes.

*Fluorescence characteristics of R6G–ethanol solutions*

The possible direct photodecomposition of R6G on absorption of u.v. light (*i.e.* $\lambda$ <400 nm) was investigated by measuring, using conventional fluorescence techniques[9], the fluorescence quantum efficiency, $\Phi_F$, as a function of excitation wavelength over the range 250–520 nm. The value of $\Phi_F$ was constant within experimental accuracy (*i.e.* $\pm$ 10%) for excitation wavelengths over the range 250–520 nm and R6G concentrations <$10^{-4}$ $M$.

*Dependence of product P yields on solution and excitation conditions*

As already pointed out, the ratio of the R6G triplet yield to the yield of the decomposition P is highly dependent on solution and excitation conditions such as flash energy, presence or absence of a Pyrex filter jacket around the reaction cell, the presence or absence of energy donor molecules, and the R6G ground state concentration. The effects of the above parameters on the yield of product P are summarized in Table 2.

When R6G/naphthalene/ethanol solutions were flash photolyzed, the ratio of the yield of decomposition product P to the yield of R6G triplet was observed to be reasonably constant (*i.e.* $\sim$ 0.23) for a 2 J to 50 J variation in exciting flash energy indicating that the product P may arise from a reaction involving the R6G triplet state. When concentrated R6G–ethanol solutions (*i.e.* >$10^{-5}$ $M$) were flash photolyzed in the presence and absence of a Pyrex filter jacket, the ratio of the yield of P to the yield of R6G triplet, increased from a value of 0.44 (with the Pyrex jacket) to a much higher ratio of 1.88 (without the Pyrex jacket). In the latter experiment the yield of R6G triplet increased by only 36% when the Pyrex filter jacket was removed whilst the yield of P increased by 580%. With less concentrated R6G–ethanol solutions ($10^{-7}$ to 2 $\times$ $10^{-6}$ $M$) the ratios of the yields of P to R6G triplet increased still further (*i.e.* $\sim$ 2.6).

Ground state depletion signals at 480, 485, 490 and 557.5 nm and absorption signals at 415 nm were monitored following the flash photolysis of $10^{-6}$–2 $\times$ $10^{-6}$ $M$ R6G–ethanol solutions in the absence of the Pyrex filter jacket. The ground state depletion signals were observed to build up to a maximum in a time corresponding to the build up of the absorption signals at 415 nm due to P. The build up in the latter absorption and in the ground state depletion occurred during the first 3 ms after the flash whist the R6G triplet state lifetime was <1 ms under these conditions. Increase in R6G ground state concentration resulted in an increase both in the rate of build up of P and in the ratio of the yield of P to the yield of R6G triplet when R6G–ethanol solutions were flash photolyzed using a 250 J flash in the absence of a Pyrex filter jacket.

TABLE 2
YIELDS OF R6G TRIPLET AND PRODUCT P

| Excitation system | Solution | Yield of R6G triplet*/$M$ | Yield of product P*/$M$ | Yield of P/ yield of R6G triplet |
|---|---|---|---|---|
| 2J flash with Pyrex jacket | $10^{-6}$ $M$ R6G – $10^{-3}$ $M$ Naphtalene | $3.47 \times 10^{-8}$ | $0.75 \times 10^{-8}$ | 0.22 |
| 20J flash with Pyrex filter | $10^{-6}$ $M$ R6G – $10^{-3}$ $M$ Naphtalene | $2.84 \times 10^{-7}$ | $0.7 \times 10^{-7}$ | 0.245 |
| 50J flash with Pyrex filter | $2 \times 10^{-6}$ $M$ R6G – $10^{-3}$ $M$ Naphtalene | $9.0 \times 10^{-7}$ | $1.9 \times 10^{-7}$ | 0.21 |
| 50J flash with Pyrex filter | $1.5 \times 10^{-5}$ $M$ R6G | $1.25 \times 10^{-7}$ | $5.5 \times 10^{-8}$ | 0.44 |
| 50J flash without Pyrex filter | $1.0 \times 10^{-5}$ $M$ R6G | $1.70 \times 10^{-7}$ | $3.2 \times 10^{-7}$ | 1.88 |
| 50J flash without Pyrex filter | $10^{-6}$ $M$ R6G | $5.0 \times 10^{-8}$ | $1.27 \times 10^{-7}$ | 2.55 |
| 50J flash without Pyrex filter | $2 \times 10^{-6}$ $M$ R6G | $6.65 \times 10^{-8}$ | $1.74 \times 10^{-7}$ | 2.60 |

* The yields of R6G triplet and product P are reported as molarities in the reaction cell volume of 100 cm³. Yields were calculated assuming $(\varepsilon^{R6G})_{600} = 18,000$ $M^{-1}$ cm⁻¹ and $(\varepsilon^P)_{415} = 37,500$ $M^{-1}$ cm⁻¹.

The infleunce of excitation flash conditions (*i.e.* wavelength, energy) on the quantum efficiency $\Phi_P$ for formation of product P was investigated for a $10^{-7}$ $M$ R6G–ethanol solution. Since the fluorescence quantum efficiency of R6G was observed to be independent of excitation wavelength (see previous section) the fluorescence from the reaction cell at 590 nm was taken as a measure of the number of photons absorbed from the excitation flash. The ratio of the maximum yield of product P formed after the flash to the yield of fluorescence during the flash therefore gives a measure of the relative quantum efficiency for formation of product P. The relative $\Phi_P$ values obtained for a 7.5–50 J variation in flash energy (obtained using a 0.25 $\mu$F capacitor at various voltages) in the absence and presence of the Pyrex jacket are shown as curves A and B respectively in Fig. 9. As can be seen from Fig. 9 the presence of the Pyrex filter limiting the excitation wavelengths to >300 nm results in a decrease in $\Phi_P$ by a factor of ~ 7. The Pyrex jacket led to a 45% decrease in the number of photons absorbed from the flash (as measured by the R6G fluorescence at 590 nm during the flash). Increase in flash energy led to a decrease in $\Phi_P$. The latter decrease was particularly pronounced for flash energies of 100–300 J in the absence of the Pyrex filter jacket (see curve C, Fig. 9).

*Quantum efficiencies for intersystem crossing and product P formation*

The quantum efficiencies for intersystem crossing ($\Phi_T$) and product P formation ($\Phi_P$) were investigated using a 7-diethylamino-4-methylcoumarin dye laser (output wavelength 460 nm) and the second harmonic of a ruby laser (wave-



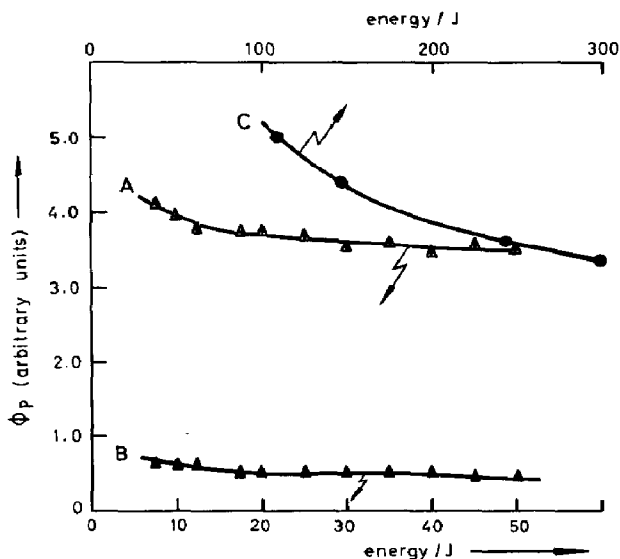Fig. 9. Effect of photolyzing flash energy on the quantum efficiency for formation of product P for a $10^{-7}$ $M$ R6G–ethanol solution in the absence (curve A) and presence (curve B) of a Pyrex filter. Curve C, for a 100–300 J variation in flash energy was obtained using a different flash tube to curves A and B but has been normalized to similar scales for convenience.

length 347 nm) as excitation sources. The photon output of both lasers was measured using potassium ferrioxalate actinometry[9,10].

When a $10^{-4}$ $M$ R6G ethanol solution in a 1 cm cube cell was subjected to pulses from the ruby laser system ($\sim$ 1.6 $\times$ $10^{16}$ photons/pulse) no detectable absorption signals due to R6G triplet or product P were observed. The values of $\Phi_T$ and $\Phi_P$, were calculated from the maximum sensitivity of the detection system to be $<9.0$ $\times$ $10^{-3}$ and $<6.0$ $\times$ $10^{-3}$ respectively.

When the coumarin dye laser was used as excitation source easily detectable concentrations of R6G triplet and product P were obtained. The maximum yields of R6G triplet and product P formed were measured for ten consecutive laser pulses. The results obtained yielded values of 2.1 $\pm$ 0.2 $\times$ $10^{-3}$ and 0.75 $\pm$ 0.05 $\times$ $10^{-4}$ for $\Phi_T$ and $\Phi_P$ respectively. It should be noted, however, that $\Phi_P$ is strongly dependent on the excitation conditions (see previous section).

DISCUSSION AND CONCLUSIONS

The results reported above show that the photolysis of R6G–ethanol solutions can result in formation of at least two species *i.e.* the R6G triplet, and a product P. Product P is permanent in nature provided no oxygen is present in solution whilst in the presence of oxygen P decays to form the normal R6G ground state molecule. It would therefore seem likely that P is a metastable reduced form of R6G. Absorption spectra, extinction coefficients and quantum efficiencies for formation of R6G triplet and product P are reported in the present work.

The results reported here indicate that P is formed *via* at least two mechanisms, the relative importance of these depending markedly on the excitation wavelength. The formation of P is particularly marked for excitation wavelengths $<300$ nm. Under the latter conditions build up of P occurs at relatively long times after the flash when the R6G triplet concentration has fallen to zero and the rate for formation of P increases with increase in R6G ground state concentration. The results indicate that for excitation wavelengths $<300$ nm the predominant mechanism for formation of P involves the reaction of a species X (which is not the R6G triplet) with R6G ground state molecules, i.e.:
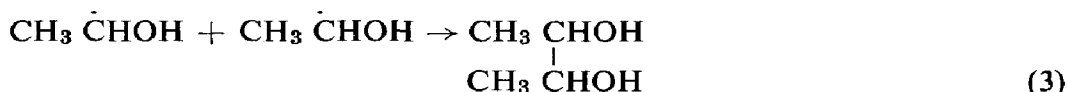
$$X + R6G \rightarrow P \tag{1}$$

Since $\Phi_P$ and the ratio of the yield of P to the yield of R6G triplet both increase markedly on removal of the Pyrex filter it must be concluded that X is found by photolysis of either the solute or solvent by wavelengths $<300$ nm. Since $\Phi_F$ for R6G is independent of excitation wavelength and the triplet–triplet absorption of R6G is weak in the wavelength region 200–300 nm direct photolysis of R6G (either ground or triplet state) to yield species X is unlikely. The solvent ethanol, however, absorbs appreciably in the wavelength region 200–250 nm[12] where both the photon output of the flashtube and the transmission of the

Spectrosil reaction cell are high. Radicals, R· formed on direct photolysis of the solvent (or solutes) will rapidly undergo the hydrogen atom abstraction reaction (2) to yield $CH_3 \dot{C}HOH$ radicals[13].

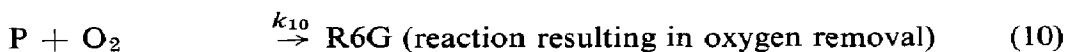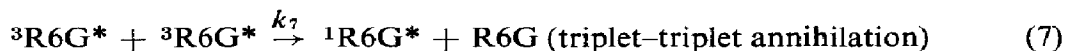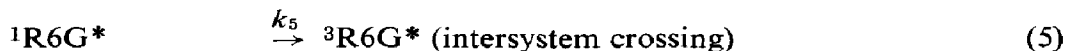$$R· + CH_3CH_2OH \rightarrow RH + CH_3 \dot{C}HOH \tag{2}$$

In the absence of reactive solutes the $CH_3 \dot{C}HOH$ radical will decay *via* the bimolecular reaction (3) with a rate constant of $\sim 10^{-9} \ M^{-1} \ s^{-1}$ [13]. For initial $CH_3 \dot{C}HOH$ concentrations $<10^{-6} \ M$ the half-life of the $CH_3 \dot{C}HOH$ radical will be $>1$ ms. The slow build-up of product P absorption and the corresponding removal of R6G ground state molecules after the flash may therefore be attributed to reaction (4).

$$CH_3 \dot{C}HOH + CH_3 \dot{C}HOH \rightarrow \begin{array}{c} CH_3 \ CHOH \\ | \\ CH_3 \ CHOH \end{array} \tag{3}$$

$$CH_3 \dot{C}HOH + R6G \rightarrow CH_3 \ CHO + R6G\text{–}H \ (\textit{i.e.} \ P) \tag{4}$$

The low yields of P formed in the presence of the Pyrex filter jacket (*i.e.* excitation wavelengths $>300$ nm) result from excitation of the solute only. In this case P may arise *via* hydrogen atom abstraction from the solvent by excited singlet and/or triplet R6G molecules followed by reaction (4). Hydrogen abstraction reactions of the triplet state have been discussed in detail by Howard[14].

The rate constants for reactions (5) to (10) measured in the present work are summarized below:

$$^1R6G^* \quad \xrightarrow{k_5} \quad {}^3R6G^* \text{ (intersystem crossing)} \tag{5}$$

$$^3R6G^* \quad \xrightarrow{k_6} \quad R6G \text{ (first order decay)} \tag{6}$$

$$^3R6G^* + {}^3R6G^* \quad \xrightarrow{k_7} \quad {}^1R6G^* + R6G \text{ (triplet–triplet annihilation)} \tag{7}$$

$$^3R6G^* + O_2 \quad \xrightarrow{k_8} \quad R6G \text{ (triplet quenching)} \tag{8}$$

$$^3R6G^* + COT \quad \xrightarrow{k_9} \quad R6G \text{ (triplet quenching)} \tag{9}$$

$$P + O_2 \quad \xrightarrow{k_{10}} \quad R6G \text{ (reaction resulting in oxygen removal)} \tag{10}$$

$k_5 = 4.2 \pm 0.4 \times 10^5 \ s^{-1}$
$k_6 = 10^3$ to $10^4 \ s^{-1}$ (dependent on excitation conditions)
$k_7 = 4.1 \pm 1.0 \times 10^9 \ M^{-1} \ s^{-1}$
$k_8 = 1.64 \pm 0.2 \times 10^9 \ M^{-1} \ s^{-1}$
$k_9 = 7.0 \pm 1.0 \times 10^8 \ M^{-1} \ s^{-1}$
$k_{10} = 7.0 \pm 1.0 \times 10^8 \ M^{-1} \ s^{-1}$

The value of $k_7$ was calculated using $18{,}000 \pm 3000$ $M^{-1}$ cm$^{-1}$ for the R6G triplet extinction coefficient at 600 nm. The value of $k_5$ was calculated from the expression $\Phi_T = k_5 \tau_F$ with $\Phi_T = 2.1 \pm 0.2 \times 10^{-3}$ and $\tau_F = 5.0 \times 10^{-9}$ s[15,16]. The value of $k_5$ is considerably smaller than the values of $2.8 \times 10^7$ s$^{-1}$ and $3.4 \times 10^6$ s$^{-1}$ reported previously[2,16]. The value of $k_8$ reported above indicates that in aerated ethanol solutions (oxygen concentration $= 1.34 \times 10^{-3}$ $M$) the lifetime of the R6G triplet, $\tau_T$, is 450 ns. Previous reports of $\tau_T$ lie in the range 50–250 ns[2,16].

The value of $k_9$ is of particular interest in view of the widespread use of COT as a triplet-state quenching additive in dye laser media[6,17]. Bunkenburg[3] reports that addition of $2 \times 10^{-4}$ $M$ COT to aerated R6G–ethanol solutions resulted in an increase in laser efficiency (i.e. output energy/electrical input energy) from 0.725% to 1.14%. The present work indicates that the addition of $2 \times 10^{-4}$ $M$ COT results in a reduction of $\tau_T$ from 450 ns (in aerated ethanol) to 430 ns and the triplet state quenching effect of COT is therefore of negligible importance in aerated R6G–ethanol solutions. The latter conclusion is supported by the fact that the authors have recently obtained conversion efficiencies of 1% from a co-axial dye laser system[3] using aerated R6G–ethanol solutions in the absence of COT. The ethanol used was extensively purified before use and addition of $2 \times 10^{-4}$ COT resulted in a slight decrease in output rather than an increase as reported by Bunkenburg[3]. The authors observe that u.v. photolysis (wavelengths <250 nm) of ethanol, particularly reagent grades, results in formation of high concentrations of transient species (i.e. radicals) which absorb strongly in the wavelength region 200–400 nm. "Indirect" quenching by additives under u.v. excitation[17] may therefore be due to scavenging of high concentrations of absorbing radicals formed on u.v. photolysis of the solvent (and/or impurity solutes).

The quantum efficiency $\Phi_P$ for formation of the photodecomposition product P was observed to be in the range $4 \times 10^{-4}$ to $10^{-3}$ dependent on excitation conditions particularly excitation wavelength. In the presence of oxygen, however, the quantum efficiency for formation of P and hence the quantum efficiency for R6G photodecomposition are considerably reduced. It should be noted that reaction (10) results in permanent removal of oxygen from solution. The excitation wavelength dependence of $\Phi_P$ is in agreement with previous observations[18] on R6G photodecomposition.

REFERENCES

1 M. Bass, T. F. Deutsch and M. J. Weber, *Technical Report R-69*, Research Division, Raytheon Company.
2 B. B. Snavely, *Proc. IEEE*, 57 (1969) 1374.
3 J. Bunkenburg, *Rev. Sci. Instrum.*, 43 (1972) 1611.
4 F. N. Baltakov, B. A. Barikhin, V. G. Kornilov, S. A. Mikhnov, A. N. Rubinov and L. V. Sukhanov, *Soviet Phys. (Technical)*, 17 (1973) 1161.
5 B. B. Snavely and F. P. Schafer, *Phys. Lett.*, 28A (1969) 728.
6 R. Pappalardo, H. Samelson and A. Lempicki, *Appl. Phys. Lett.*, 16 (1970) 267.
7 O. G. Peterson, S. A. Tuccio and B. B. Snavely, *Appl. Phys. Lett.*, 17 (1970) 245.
8 A. V. Buettner, B. B. Snavely and O. G. Peterson, *Proc. Int. Conf. Molecular Luminescence, New York*, 1969, p. 403.
9 D. N. Dempster, T. Morrow, R. Rankin and G. F. Thompson, *J. Chem. Soc., Faraday Trans. II*, 68 (1972) 1479.
10 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
11 *International Critical Tables*, Vol. 3, McGraw-Hill, New York, 1968, p. 254.
12 *U.V. Atlas of Organic Compounds*, Vol. 1, Butterworths, London, 1966.
13 I. A. Taub and L. M. Dorfman, *J. Am. Chem. Soc.*, 85 (1963) 2370; 84 (1962) 4053.
14 J. A. Howard, *Adv. Free Radical Chem.*, 4 (1972) 49.
15 M. E. Mack, *J. Appl. Phys.*, 39 (1968) 2483.
16 J. P. Webb, W. C. McColgin and O. C. Peterson, *J. Chem. Phys.*, 53 (1970) 4227.
17 J. B. Marling, D. W. Gregg and L. Woods, *Appl. Phys. Lett.*, 17 (1970) 527.
18 A. N. Rubinov, T. I. Smol'skaya and S. A. Mikhnov, *Zh. Prikl. Spektros.*, 13 (1970) 368.