SEARCH FOR SUPPERRADIANT EMISSION FROM "COMPLEX" ORGANIC MOLECULES IN THE VAPOR PHASE *

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ABSTRACT

Vapors of perylene, coronene, 9-10 diphenyl-anthracene, dimethylpopop, rubrene and Rhodamine β have been optically pumped with picosecond pulses from a mode-locked, frequency-doubled ruby laser, in an attempt to produce single-pass superradiant emission in the respective broad-band emission. The results were negative or inconclusive. The feasibility of achieving population inversion in vapors of "complex" organic molecules is qualitatively discussed.

It was recently proposed that some of the efficient organic fluorescers (or luminophors) used in solution dye-lasers could be used as active media in a gaseous analog of the solution dye-laser.[1] In effect, some of the compounds used in solution dye-lasers will fluoresce in the vapor phase both under optical and discharge excitation.[2]

In an initial attempt to obtain population inversion in such vapors, we have pumped them with the picosecond-short, intense pulses from a mode-locked, frequency-doubled ruby-laser in a configuration similar to that used by Mack.[3,4] Under these conditions of single-pass excitation, solutions of Rhodamine 6G will easily lase, while so far we have found no clear evidence of super-radiant emission from the vapors we studied.

The output from a mode-locked ruby-laser (20 to 30 mJ) was frequency-doubled in a KDP crystal (3 to 4 mJ energy after doubling) and focused by means of a quartz lens (6 cm or 8 cm focal length) inside a quartz cylindrical cell, typically 2 inches long and 1/2-inch inner diameter, which contained the vaporized substance (Figure 1). The pumping geometry was of the longitudinal kind. The crystalline solids were loaded in the cell as follows. After the empty cell had been torched and degassed in a vacuum line, it was returned to ambient pressure in argon atmosphere and loaded with ~ 50 mg of the crystalline organic luminophor. The cell was returned to the vacuum line, exhausted, filled with a buffer gas and sealed off. Once the cell was in the laser-beam path, it was heated until a blue fluorescence was emitted under 365-nm excitation from a fluorescent lamp. The density of the vapor was then adjusted so that the laser beam produced fluorescence over the entire length of the cell. At ~ 1 torr (~ 250°C) the number density for perylene, $\sim 2 \cdot 10^{16}$ molecules/cm^3, is comparable to that of a 10^{-4} M/liter dye solution.

The emission from the vapor cell was monitored in the pump-beam direction using a fast photodiode (TRG photodetector Model 105C, with S-20 spectral sensitivity) and a Tektronix 519 oscilloscope, and/or by collecting the emission on the slit of a 1/2-meter grating spectrograph provided with a camera attachment. Corning Glass filters 3-76, 3-56, and 5-61 were used to eliminate the pump radiation at the ruby
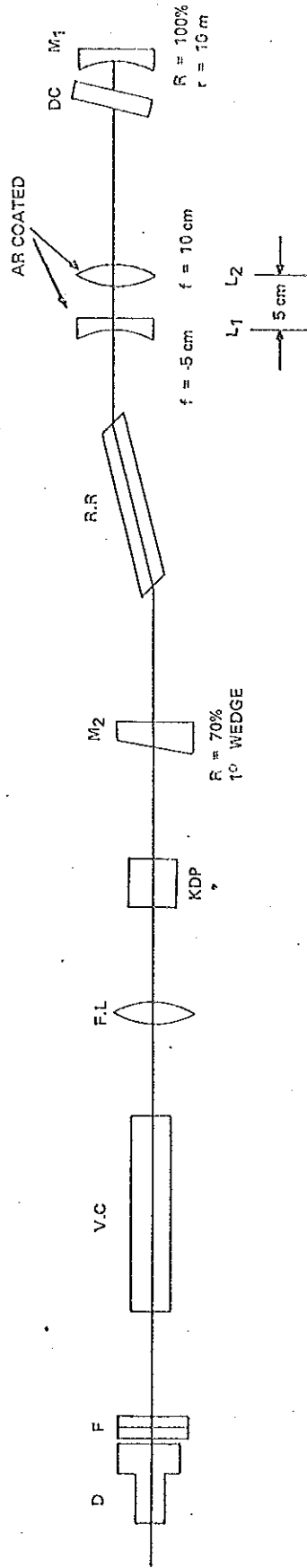
Figure 1. Block Diagram of the Experimental Arrangement. M_1 and M_2 define the ruby-laser cavity. M_2 is a wedged plane mirror and M_1 has a 10 m radius of curvature. The reflectivities (70% and 100%) refer to 6943Å. The lens doublet L_1 and L_2 with antireflection coating is used to reduce the beam size. DC is a dye cell for mode-locking and contains cryptocyanine in acetone. RR is the ruby-rod. The KDP crystal was phase-matched for second-harmonic generation. FL is a quartz converging lens. VC is the quartz cell with the vapor. D is the photodetector with the filters F eliminating the pump radiation at the ruby frequency and at its second harmonic.

frequency and at its second harmonic. No signal was observed when the laser passed through the cell at room temperature, so that the spurious detection of pump light by the photodiode is to be excluded. Examples of the fluorescence pulses from the vapors are give in Figure 2.

The following substances were tested: perylene, coronene, 9, 10-diphenyl-anthracene, dimethylpopop, rubrene, and Rhodamine B. Incidently, the first four substances also emit blue molecular fluorescence under electronic excitation in buffered discharges.[2] The test substances were chosen mainly on the basis of: a) compatibility of their absorption bands with the pump light; b) high quantum yield for fluorescence in solution; and c) laser action in solution under fast (less than 1 μs) optical excitation.

The study aimed at producing single-pass super-radiance; no mirrors were used to provide optical feedback. Up to the present time we found no unequivocal indications that single-pass super-radiance was achieved in any of the substances investigated. Only in the case of perylene did we find an indication of possible intensity-dependent radiative-lifetime shortening. In a train of strong emission pulses, the fluorescence decay-rate (Figure 2) is appreciably faster $(3.0 \pm 0.3$ ns) for the more intense signals than for the weaker pulses of the train $(4.0 \pm 0.3$ ns). The evidence for spectral narrowing in the emission is as yet inconclusive. Some of the emission bands are indicated in Figures 3 and 4. In the case of coronene, the band for cw excitation at 366 nm ranges from 366 to 546 nm, with a very weak anti-Stokes tail. The laser-excited emission appears to be somewhat narrower in the spectrogram, but the effect is not pronounced. Definite maxima in the emission bands could be noticed at low levels of detected light, but they were not followed in detail. The fluorescence band from laser-excited perylene seems to have a different spectral position depending on the buffer gas (Figure 4). Here again, only qualitative conclusions can be drawn from the Polaroid pictures.

The radiative lifetimes for the vapor fluorescence under laser excitation are listed in Table 1, and compared with the corresponding known values for vapors and solutions,[5] whenever available. Some comments concerning the measurements listed in the Table are now appropriate. In a sample of perylene containing 20-torr argon buffer, the leading edge of the emission pulse leveled off near the peak and had a fast initial decay. These features and the unusually short decay time observed (2.3 ns) suggest quenching of fluorescence, possibly by traces of oxygen. The decay time for the nitrogen-buffered perylene sample was longer (3.7 ns) and in good agreement with values reported by Ware and co-workers.[6] A different argon-buffered sample showed lifetimes
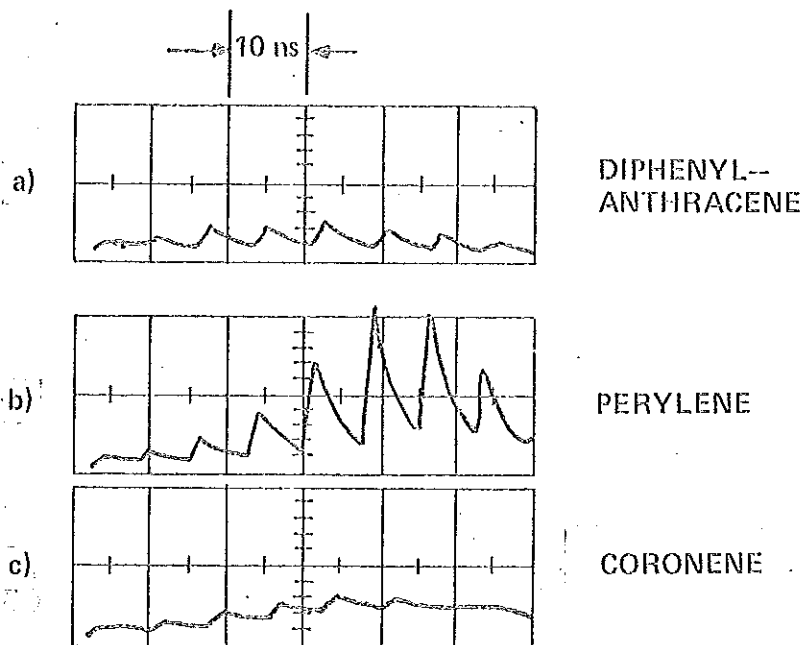
Figure 2. Examples of Fluorescence Pulses from Some of the Vapors Studied, As Detected by the Photodiode and Displayed on a Textronix Oscilloscope Model 519. The pump pulses have a ~9 ns periodicity and the fluorescence pulses reflect this pattern. a) Emission from 9,10 diphenyl-anthracene; b) from perylene; and c) from coronene. The perylene emission was the strongest among the substances studied. The fluorescence lifetime of coronene is longer than that of the other vapors considered, and the fluorescence emission from one pump pulse overlaps that from the following pulse.

a) $\lambda_{exc} = 347$ nm

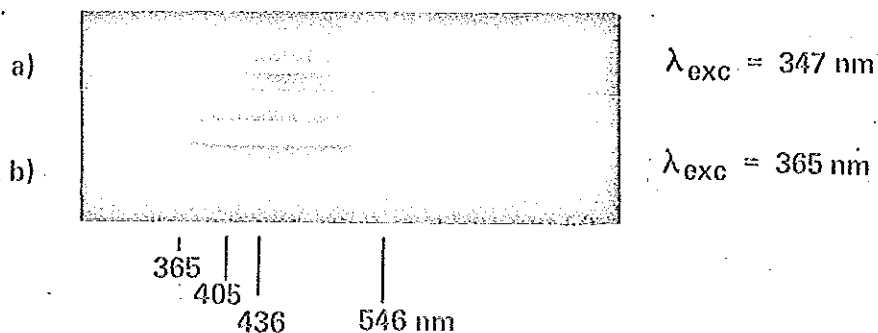b) $\lambda_{exc} = 365$ nm

365
405
436   546 nm

Figure 3.   Fluorescence of Coronene Vapor.   a) Under laser excitation at 347 nm; b) under cw-excitation at 365 nm. The spectral position of the exciting line in b) is shown by some scattered source light. There is also in b) a weak anti-Stokes component of the emission. The laser-excited fluorescence seems to cover a narrower spectral range

4047 Å   4358 Å   4900 Å

a)   20 TORR Ar
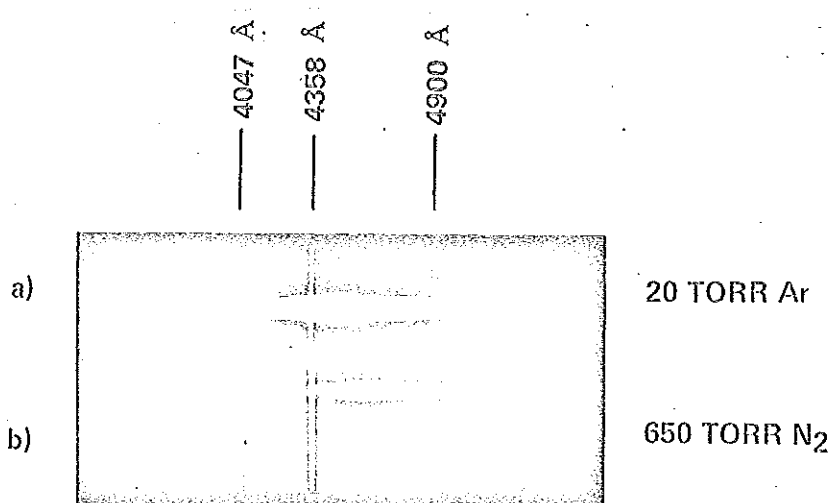
b)   650 TORR N_2

Figure 4.   Fluorescence from Perylene Vapor Under Laser Excitation at 347 nm, and for Different Buffer-Gas Pressures. The presence of nitrogen at fairly high pressures seems to produce a narrower emission band.

TABLE 1

FLUORESCENCE LIFETIME τ_f AND QUANTUM YIELD FOR FLUORESCENCE γ_f IN LIQUIDS AND VAPORS

Compound	Liquid		Vapor		Buffer Gas	Remarks
	τ_f (ns)	γ_f	τ_f	γ_f		
Perylene	6.4[a]	0.94[a]				a
Perylene			~4.1	0.39	CO_2 (1 Atm)	b
Perylene			3.7 ± 0.3		650 torr N_2	c
Perylene			4.0 ± 0.3 to 3.0 ± 0.3		20 torr Ar	c, d
Perylene			2.3 ± 0.3		20 torr Ar	c, e
9, 10 Diphenyl-anthracene	9.35	1.00				a
				0.04		f
				0.8		g
			2.8 ± 0.3		100 torr Ar	c, h, i
Coronene	~300	≥ 0.9				m
Coronene			≳ 7		200 torr Ar	c
Rhodamine B	3.2					a
			3.0 ± 0.3		200 torr He	c, j
Rubrene	16.5		2.6 ± 0.3		200 torr He	c, j
Dimethyl-popop	1.5	0.93	1.5		100 torr Ar	c, k
			0.6		100 torr Ar	c, l

a) Ref. 5
b) Ref. 6
c) This work
d) The shorter lifetime refers to the stronger emission pulses
e) Probable fluorescence quenching due to gas impurities (oxygen?)
f) Ref. 15
g) Ref. 16
h) Thermal decomposition
i) Indication of spiking at pulse peak
j) Blue emission
k) At 315°C
l) At 391°C
m) At 100°K, from Ref. 8

ranging, as already mentioned, from 3 to 4 ns, depending on the emission intensity. Another luminophor tested, namely 9,10-diphenylanthracene, quickly decomposed on heating the cell; before extensive decomposition occurred, the emission pulses showed indication of spiking at the pulse peak. Both Rhodamine B and Rubrene weakly emitted blue fluorescence under uv excitation. The same vapors, when excited with blue and green argon-laser lines, gave a yellow emission. The reasons for different emission behavior from these vapors as a function of excitation wavelengths are presently unknown. Galanin and Chizhikova have recently reported a blue fluorescence in solutions of Rhodamine 6G originating from an upper excited electronic level.[7]

The decay time for coronene was unusually long (< 7 ns) and could not be reliably measured with the pump pulse-train used, which was characterized by an interpulse separation of 9 ns. Coronene has been lased under flashlamp excitation in an organic glass at low temperatures.[8]

The failure to observe stimulated emission in the organic luminophor vapors, when the same effect is easily achieved in solutions or Rhodamine 6G, prompts an examination of the feasibility of the proposed process itself, and of the actual procedure followed to reveal it. We shall indicate how we see no basic physical reasons against obtaining population inversion in vapors of complex organic molecules. Hence, our lack of success was due either to inappropriate choice of pumping conditions, or to a poor choice of test substances. Although these two aspects of the problem are closely inter-related, we are inclined to ascribe our negative results to the limitations in our particular choice of pumping, with its inherent lack of optical feedback. The basic question of feasibility will be considered first, with emphasis on emission, Stokes-shift, and quantum yield for fluorescence in the vapors.

The different behavior of solutions and vapors with respect to obtaining population inversion under laser pumping must be sought in the features that are typical to the vapor state of the compounds considered, namely a temperature at least 100°C above room temperature and the absence of solvent collisions. The vapor state is attractive from the point of view of exciting the active species in an electrical discharge,[2] but a price has to be paid for the absence of the solvent molecule.

In the liquid phase, collisions with the solvent molecules quite generally insure fast thermalization of the excited electronic state, resulting in the all-important Stokes shift between absorption and emission bands. In the vapor phase, the dense distribution

of vibrational-rotational levels in "complex" molecules is effective in redistributing excess vibrational energy prior to radiative decay, even in the absence of intermolecular collisions. The Stokes shift of absorption and emission bands is thus realized, and the gross features of the vapor emission parallel those of the corresponding solutions. As for the details of the vibrational relaxation in the vapor phase and, ultimately, the value of the quantum yield for fluorescence, the situation is more complicated than in solutions. Even from the very scant information that is presently available on relaxation processes in the excited electronic states of complex molecules, it appears that the molecular geometry of each individual compound plays an important role[9] in the relaxation, in sharp contrast to the case of solutions. In the case of vapors, it is safe to assume, even if exceptions do exist, that nonradiative deactivation plays a proportionally greater role than in solutions, and that this role is steeply enhanced by the increase of the vibrational energy content in the excited electronic state. This topic has been thoroughly considered using a statistical approach in a recent monograph by Borisevich.[10] In the case of vapors, all processes that reduce the vibrational energy content of the excited state (namely, reduced system temperature, longer wavelength of excitation, and collision with a buffer gas) will in general increase (Neporent's stabilization effect)[11] both the fluorescence quantum yield and the fluorescence lifetime. The latter quantities are connected to the transition probabilities of radiative and nonradiative deactivation by the simple expressions:

$$\gamma_f = \frac{\overline{A(E^*)}}{\overline{A(E^*)} + \overline{d(E^*)}} \qquad \text{and} \qquad \tau_f = \frac{1}{\overline{A(E^*)} + \overline{d(E^*)}}$$

where γ_f is the quantum yield for fluorescence, τ_f is the radiative lifetime, $A(E^*)$ and $d(E^*)$ are the radiative and nonradiative transition probabilities, respectively, dependent on the vibrational energy E^* in the excited state, the dependence being quite strong for $d(E^*)$. The statistical averages over A and d are carried out over the manifold of levels of the excited electronic state, the averaging procedure depending on the exact details of the excitation.[10]

On the basis of the above equation, and the vapor-phase fluorescence lifetime, the quantum yield for fluorescence for vapors of the substances considered here should be typically

lower than the corresponding solution values by at most a factor of 2 to 3 (except for the case of Rubrene), since the ratio $\gamma_f/\tau_f = \overline{A(E^*)}$ should remain fairly unchanged from the liquid to the gaseous phase. The two combined effects of reduced γ_f and τ_f in the vapors (in conjuction with spectrally broader absorption and emission bands by comparison with solutions) will undoubtedly raise the threshold requirements for stimulated emission. The dyes commonly used in lasers have quantum yield for fluorescence $\gamma_f \sim 0.8$ to 0.9; but lower values of γ_f like those of the vapors considered here should not preclude laser action under fast, intense excitation. As a limiting case we may point out that solutions with γ_f as low as 10^{-3} have been lased in solutions,[12] using transverse excitation from a Q-switched ruby-laser and with the active solution in a resonator. On the one hand, these considerations confirm the feasibility of the effect, and conversely suggest a better experimental approach to the problem. An experiment in which the chances of success are maximized would involve the use of a Q-switched laser, without frequency-doubling, and pumping transversely a dye vapor in a resonator structure. As test substances, to be pumped at the ruby frequency, we suggest dyes of the cyanine class, since the phthalocyanines, for example, are known to be sublimable.

The question of the proper choice of the test substances in our studies will now be considered. Of all the samples studied, perylene had the strongest fluorescence and was chemically stable at the vaporization temperatures. In addition, some spectroscopic parameters for vapor-phase perylene are known, so that perylene should be an excellent candidate for population inversion.

The absorption and emission spectra of perylene vapor have been reported by Borisevich and Gruzhinsky.[13] Their data make it possible to estimate the efficiency of pumping at 347 nm, the wavelength used in our experiments. At this wavelength, excitation takes place on the high-energy side of the main absorption peak, in a region where the normalized absorption coefficient ϵ/ϵ_{max} is $\sim 10^{-1}$. As for the rate of internal relaxation within the excited electronic state, Borisevich and Gruzhinsky[13] conclude from the study of the absorption and emission spectra of perylene that Stepanov's universal relation is satisfied; namely, that the equilibrium distribution of vibrational energy in the excited electronic state is established prior to the radiative decay. In the excited electronic state, the effective temperature characterizing this equilibrium is roughly 40°C above the gas temperature for excitation near the main absorption peak. For excitation at 347 nm (our pumping wavelength), the situation is less favorable because the effective excited-state temperature is roughly 180°C above the system temperature (see Borisevich,[10] page 152). This would suggest that at 347 nm

we may run into difficulties due to an increased role of radiationless vs. radiative deactivation. But Gruzhinsky[14] also reported that the fluorescence efficiency in perylene is independent of ν_{exc} (excitation frequency), and, as a further evidence of the insensitivity of the molecule toward nonradiative decay, that γ_f is fairly independent of changes in temperature, ν_{exc}, and the average collision time with a buffer gas. If this is the case, the fairly high value ($\gamma_f \sim 0.39$ in Table 1) of the quantum yield for fluorescence should apply to a wide range of experimental conditions, including those employed in our experiments.

We still maintain that perylene is an excellent candidate to test the feasibility of lasing in vapors of complex inorganic molecules. The experiments should be repeated by transversely pumping perylene vapor in a resonator structure using a frequency-doubled, Q-switched ruby-laser, or simply a nitrogen-laser. An even better experimental approach to test the effect in general would be the use of a Q-switched ruby-laser, without frequency-doubling, to transversely pump one of the cyanine dyes, again contained in a resonator.

We may also add that, for a better insight into the mechanisms involved in the optical pumping, there is a definite need for more complete spectroscopic parameters of the vapors involved; namely, absorption and emission spectra, excited-state absorption, and the determination of the number density in the vapors at the various operating temperatures. This is because, contrary to the case of solutions, the optical properties of the vapors are generally quite sensitive to temperature and excitation wavelength. Thus, Bakhshiev, et al.[15] have reported, for instance, that τ_f of 9,10-diphenyl-anthracene decreases with increased temperature and excitation frequency, ν_{exc}. They report a fluorescence quantum yield of 0.04 in the vapor, a precipitous drop from the solution value[5] of 1.00 in cyclohexane and 0.74 in ethanol. Stevens,[16] on the contrary, reports $\tau_f = 0.80$ for the vapor. These discrepancies are a further indication of the need for additional detailed data on the emission properties of complex organic molecules in the vapor phase.

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