

Biophoton Emission

New Evidence for Coherence and DNA as Source

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ABSTRACT

The phenomenon of ultraweak photon emission from living systems was further investigated in order to elucidate the physical properties of this radiation and its possible source. We obtained evidence that the light has a high degree of coherence because of (1) its photon count statistics, (2) its spectral distribution, (3) its decay behavior after exposure to light illumination, and (4) its transparency through optically thick materials. Moreover, DNA is apparently at least an important source, since conformational changes induced with ethidium bromide *in vivo* are clearly reflected by changes of the photon emission of cells. The physical properties of the radiation are described, taking DNA as an exciplex laser system, where a stable state can be reached far from thermal equilibrium at threshold.

Index Entries: Biological photon emission; coherent photon emission, from DNA; DNA-exciplex laser model; emission, of photons from DNA; photons, emission from DNA; laser, DNA photons as possible.

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INTRODUCTION

The widespread, if not general, phenomenon of "ultraweak" photon emission from living cells and organisms, which is different from bioluminescence (1), has been extensively reviewed (2-4). Recently, there appeared an overview concerning the most modern aspects of chemiluminescence of this phenomenon and its applications (5).

The following characteristics of biological photon emission are now generally accepted (5):

- (1) The intensity of the continual luminescence turns out to be usually of the order of a few up to some thousand photons per square centimeter per second.
- (2) The spectral range, in which the ultraweak cell radiation has been detected, spreads at least from infrared to ultraviolet.
- (3) Proliferating cell cultures radiate more intensely than do those in which growth has ceased. The cells mainly emit in the G₁ phase.
- (4) Dying cells exhibit a relatively intense photon emission, regardless of the cause of death, whether it be by heat, refrigeration, centrifugation, or treatment with toxic agents.
- (5) No agent is known that cannot influence the photon emission.

However, nothing is known about the biological significance of this phenomenon. The interpretations reach from "imperfections" (chaotic spontaneous chemiluminescence from various source) (7) to messages of genetic information (8).

Regarding to Fröhlich's fundamental paper on energy storage and long-range coherence in biological systems (9) and the basic work of Prigogine (10) and Haken (11), we feel that the aspect of coherence plays an important, if not the essential role in describing and understanding biological phenomena, and that DNA is an important source of photon emission. This stimulated us to investigate some characteristics of biological photon emission with respect to these aspects. We will show that (1) there are in fact some distinct indications of at least partial coherence of this ultraweak radiation in biological systems, (2) there is evidence for DNA as an actual source, (3) we can describe these features in terms of coherent DNA-exciplex formation, and (4) a variety of biological phenomena can be understood within the framework of this model.

MATERIAL AND METHODS

As biological material we used suspension cultures of *Glycine max* cv. Harosy 63 (soy-bean) and seedlings of *Cucumis sativus* (cucumber). The soy bean material was obtained from callus cultures grown in the Department of Biology on Murashige and Skoog medium (40). The cells were

suspended in 150 mL B5 medium (40) at a concentration of 25,000 cells/mL. The cultures were used on the third day, when a concentration of 100,000–120,000 cells/mL was reached. The cuvetts used had a total volume of 5 mL.

The measurements were carried out with a photomultiplier of high sensitivity in the range from 200 to 800 nm. The living material was kept within cuvetts in a dark chamber in front of the photomultiplier (for a more detailed description, see refs. 4,6). Figure 1 displays the principal parts of the equipment. With our apparatus a photon current density of 2 photons/s/cm² can be detected at a significance level of 99.9% within 6 h. The uptake of count numbers within given time intervals and calculations are carried out with an interfaced computer. The measurement errors are of the order of a few cps (counts per second). As far as they are not specified in this paper, they may be disregarded compared to the quoted values.

For examining besides an entire biological system (e.g., cucumber seedlings, a simpler system), we extended our measurements to soybean cell cultures. They are subject of current investigations also of other groups (5). The transparency of cells for biophotons thus tested by determining the extinction coefficient E/d (mm⁻¹) of spectrophotometer light of 550 nm wavelength was determined with a Gilford 250 instrument, and compared with the extinction coefficient of biophotons of cucumber seedlings radiating respectively through a layer of sea as an inorganic substrate, sand, and soy bean cells as a bioassay, of various thickness.

To find out whether DNA is a source of photon emission from living cells, each of six cuvetts was filled with the suspension culture of soy bean cells (150 mg cells). While one was taken as control, the others were incu-

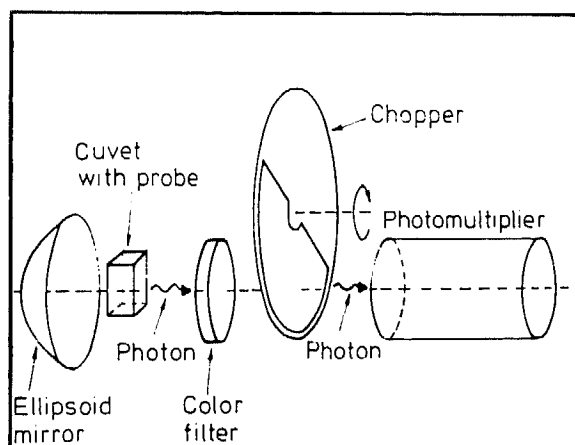


Fig. 1. Diagram to illustrate the photomultiplier system used for the measurements of ultraweak photon emission from biological systems.

bated with ethidium bromide (EB) in concentrations between 0.3 and 3000 $\mu\text{g/L}$, corresponding to 2.5×10^{-5} – 2.5×10^{-1} M EB/M DNA.

RESULTS AND DISCUSSION

Some Physical Properties of the Radiation

The analysis of the radiation intensity i of a radiating system at a position R at a time t yields the following differential equation (12,13):

$$di/d\tau = i - s \quad [1]$$

where $i(R, t)$ represents the differential spectral intensity (energy per units of time, wavelength, cross-sectional area, and solid angle), and τ is a dimensionless quantity known as "optical thickness." It can (in principle) be calculated from molecular data and the structure of the medium. For a homogeneous medium we have

$$\tau = Bd\lambda/4\pi c (t_g/t_a \cdot m_a - m_g) \quad [2]$$

The following notations have there been used:

B	Einstein's coefficient of induced transitions
d	Geometrical distance between source and detector (with respect to the surface of the medium)
λ	Wavelength
c	Velocity of light
m_a, m_g	Density of excited and non-excited molecules, respectively, that take part in the absorption (and emission) of the radiation under investigation
t_g/t_a	Relation of degeneracy factors of the corresponding states

$s(R, t)$ is the "source" term, responsible for spontaneous emission of excited states. By definition we have

$$s(R, t) \equiv hc^2/4\pi\lambda \cdot A/B \cdot m_a[m_g - (t_g/t_a)m_a] \quad [3]$$

where h is the Planck's constant, and A represents the Einstein's coefficient for spontaneous transitions.

Equation [1] accounts for an increase (decrease) of radiation intensity within the medium in case that the intensity exceeds (keeps below) the contribution s of spontaneous emission, which is, by definition, not dependent on i . Let us confine ourselves to a stationary state, which means that all variables become independent on t . In addition, we consider a homogeneous medium, thus reflecting the case that s does not depend on τ and R ($ds/d\tau = 0$). Then we get the following solution of Eq. [1]:

$$i(R_o) = s + [i(R) - s] \cdot e^\tau \quad [4]$$

R_o, R are fixed positions within the medium under consideration, where one of them may represent a point at the medium's surface. In case of d

$\neq 0$ we get, for $\tau = 0$, $s \rightarrow \infty$. This accounts for the optical behavior at the laser threshold. Providing $\tau \rightarrow 0$ and at the same time $\tau \ll i/s$, the medium becomes transparent for i , since the source term s of Eq. [4] cancels [$\exp(\tau) \approx 1$] and consequently we obtain $i(R_0) \approx i(R)$.

Experimental data on radiating biological systems point to just this case. Figure 2 shows the result of measurements of the transparency of cells: One set of experiments was made with a Gilford spectrophotometer. Cuvets of various diameters were either filled with wet sea sand, or with soy bean cells in suspension. According to the Beer-Lambert law,

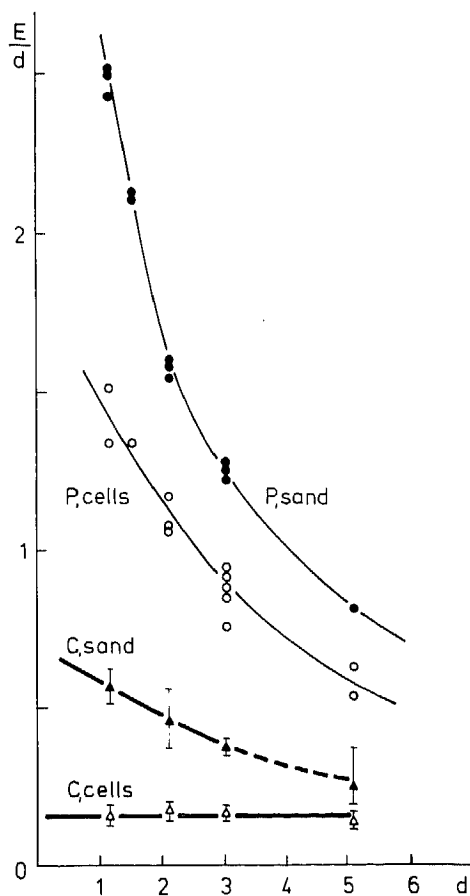


Fig. 2. Experimental data indicating the transparency of living (soya bean) cells (in suspension culture). The extinction coefficient, E/d (mm^{-1}) of sea sand (P, sand) and soya cells (P, cells) of various thickness, d (mm), was first measured at $\lambda = 550$ nm in a Gilford 250 spectrophotometer, and then the E/d of photons emitted by cucumber seedlings, and passing through the layers of sand (C, sand) and cells (C, cells), respectively, was determined. It can be seen that there is no decrease in E/d , if the emitted photons pass through soya-bean cell layers of increasing thickness, d (mm), and an unexpected low decrease, if the photons from the cucumber seedlings pass through layers of sea sand.

the extinction of a substance in solution increases with the thickness of the layer, i.e., the diameter of the absorber. A second set of experiments was made with the photomultiplier system, using double-cuvets: the photomultiplier-faced chamber was filled with sand and soy bean cells, respectively, in varying thickness, whereas the rear chamber was filled with cucumber seedlings. So the photons emitted by the cucumber seedling had to pass through the front chamber to reach the photomultiplier.

The extinction coefficient E/d (mm^{-1}) of 550 nm photons is represented by the two upper curves in Fig. 4 (P, sand; P, cells), and the ultraweak cell radiation (PE) of cucumber seedlings radiating through the layer of sand and soya bean cells, respectively (C, sand, C, cells) in the two lower curves. Since, in the registered wavelength range of PE (from 200 to 800 nm), the extinction coefficient of photometer light decreases with the thickness of the layer for wavelengths longer than 550 nm by about 10% only, while it can only increase for shorter wavelengths, the very low value of E/d of ultraweak photon emission from cucumber seedlings compared to that of photometer light can never be explained by the wavelength dependence of optical absorption. Obviously, this extremely strong alteration (about two orders of magnitude) does also not depend on the optical medium, since the same wet sand layers (P, sand; C, sand) and the same soya bean cultures (P, cells and C, cells) have been used for both photometer light and PE determinations. Rather, the very low extinction coefficient of PE has probably to be explained in terms of its high degree of coherence. This interpretation is supported by further characteristics of Fig. 2. There is shown that the extinction coefficient decreases with increasing thickness of the layer (with the exception of C, cells). As has been pointed out by E. Wolf (14), multiple propagation and diffraction can improve the degree of coherence of light. This means that, with the exception of PE-transmitting soya bean cells, the degree of coherence increases with increasing thickness of penetrated layers; and at the same time, the extinction coefficient E/d decreases. Control experiments have shown that this violation of Beer's law is actually not an error depending on a technical defect. These findings coincide with findings on "light piping" in plant tissues (15,16). Photons can be transferred there without much loss over distances of at least some centimeters. When one violates a plant seedling at a certain position, one observes a considerable increase of photon emission, not only at the position of attack, but also at regions which are far away from this position (17) at the same time. Hence, we have to conclude that τ for biological radiation is actually lower than one expects from the common absorbance measurements. However, the very low extinction coefficient of biological radiation cannot be only assigned to the structure and occupation of biological material itself, as it shown by the high transparency of sea sand. Rather, it also corresponds to the order and/or low intensity of the biological pho-

tons. On the other hand, the absorption by nonscattering neutral density filters exhibits the expected ordinary reduction.

$\tau \approx 0$ provides population inversion of molecular states at threshold [$m_a \approx m_g$ for $t_a = t_g$ from ref. (2)]. The blueprint of emitted radiation from this matter may not be identified as thermal radiation, since in this case we would have the Boltzman distribution:

$$f = m_a/m_g = \exp -hc/kT\lambda$$

where λ corresponds to the energy difference of these states.

In fact, spectral measurements of ultraweak photon emission of biological systems show that f_λ does not depend on λ , indicating that any two levels taking part in the optical transitions are occupied with the same probability (Fig. 3). This shows that biological systems are not governed by thermal equilibrium, but may be the subject of phase transitions between chaotic ($m_a < m_g$) and ordered ($m_a > m_g$) states far away from thermal equilibrium.

Consequently, the radiation from biological systems has to exhibit at least partial coherence.

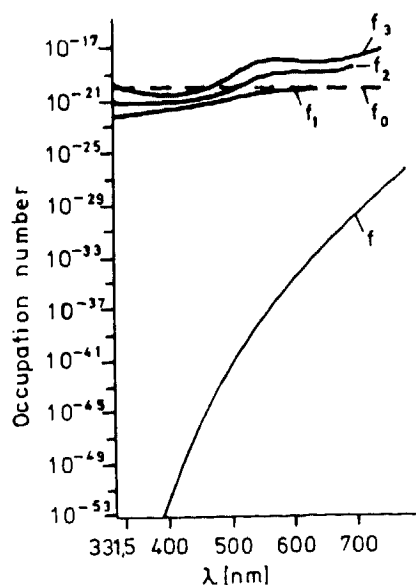


Fig. 3. Probabilities of occupying excited states with energies hc/λ [spectral occupation numbers $f(\lambda)$] for thermal equilibrium (f), for constant spectral energy density (f_0), for untreated cucumber seedlings (f_1), for Cialith®-(f_2) and acetone-treated cucumber seedlings (f_3). Since f_1 , f_2 , and f_3 represent measured values, we can conclude that the cell population in its stationary states is probably governed by the laser threshold: $f(\lambda_1) \cong f(\lambda_j)$ for $\lambda_j > \lambda_i$. This implies possible laser activity for nonstationary observations.

However, the intensity is too low for the usual interferometry. We used, therefore, photocount statistics [PCS experiments (18)] and the analysis of decay curves of photon emission after exposure to light illumination.

As a rule, for stationary states the emitted light is the more coherent, the less the intensity fluctuates around its mean value. The probability p of registering n photons (with $n = 0, 1, 2, \dots$) within a suitably given time interval Δt follows for coherent light modes a Poisson distribution (5) and for a totally chaotic (thermal) mode the geometrical distribution (6) (18, 19).

$$p(n)_{\text{coherent}} = m^n \cdot \exp(-m)/n! \quad [5]$$

$$p(n)_{\text{chaotic}} = m^n / (1 + m)^{n+1} \quad [6]$$

m represents the mean value of the photon number within Δt .

Our analysis of a multimode field (18) (with different wavelenths, see Fig. 2) shows that the hypothesis of a purely chaotic biological photon field must be refused on a sufficiently high significance level even for the highest possible number of independent modes. The statement of agreement with the Poisson distribution, on the other hand, cannot be rejected (20,21).

Figure 4 displays an example in which the photocount statistics of cucumber seedlings have been compared to those of scattered sunlight of the same intensity admitted through a diminutive slit of the dark chamber of our apparatus. As is well-known, the sunlight becomes coherent at sufficiently small areas of about 10^{-6} cm^2 (22). Hence we provide with this measurement a comparison of radiation from biological materials with relatively coherent light. Most experiments that we have carried out so far yield similar results, as shown in Fig. 3, namely a smaller distribution $p(n)$ of biological radiation than that of sunlight of just the same intensity focused into the apparatus. This again indicates a possibly high degree of coherence of ultraweak photon emission from biological systems.

As has been shown already (20), the photon intensity $P_e(t)$ after exposure of some biological samples of light illumination (which is switched off at a time t_0) drops down according to a hyperbolic function (7), even for spectral observation.

$$P_e(t) = P_e(t_0)[1 + a(t - t_0)^\beta] \quad [7]$$

where a (β) and β are constants and β depends on the system under consideration. In most cases we find $1 < \beta < 3$. This decay behavior indicates in addition a strong mode coupling (19).

In Appendix I it is shown that the decay function (7) corresponds to an oscillator system with coherent (in this case, frequency stabilizing) feedback scattering of radiation to its damped source. A more detailed discussion of the quantum theoretical aspects has been given in ref. (23).

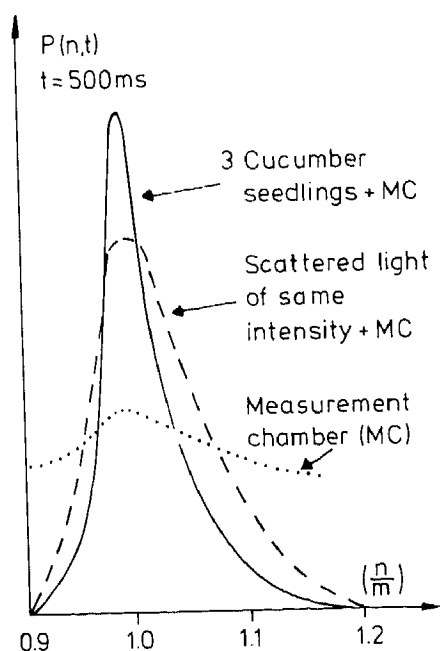


Fig. 4. The probability distributions $[P(n, t)]$ that indicate the probability of n photons being registered within time t . It can be seen that biological objects exhibit less stray radiation than normal scattered light. The greatest variance is contributed by the measurement chamber itself, which emits a rather chaotic light because of the dark current of the photomultiplier.

The Question of the Source

Provided that the very weak biological photon field takes on some degree of coherence, the source cannot any longer be seen as a single molecule exhibiting spontaneous chemiluminescence. However, it admits correlations between photon intensity and biochemical reactions, which in fact have been established within a wide range of possible chemiluminescence activities (5). Of course, we have to conclude that a manifold of biochemical and biophysical processes may be related to this phenomenon of ultraweak photon emission, suggesting some regulatory functions. This point of view is supported by investigations on the so called "photochemistry without light" [for review, see ref. (24)], where excitation energy can be transferred to photochromic molecules and/or may trigger an amplification mechanism, and promote photochemical processes in the dark (24,25).

The experimental results so far justify the search for a common mechanism serving the role of a central regulation circuit. And interest focuses on a macromolecule that can store and emit photons over a wide spectral range. This macromolecule should also be structured in such a way that it can generate some degree of coherence.

Our investigations show that DNA may play this role. This has been indicated by using ethidium bromide (EB) as a tracer molecule. EB intercalates into the DNA without significant reactions with other biomolecules. The intercalation of EB induces, depending on the concentration, the unwinding of DNA-superhelical structures. After complete unwinding, a rewinding with an opposite direction of rotation takes place. The intensity of photon emission of resting seedlings exhibits an increase and decrease parallel to the structural changes of DNA (26). We now repeated this experiment using suspension cultures of soy bean cells. Figure 5 shows again this characteristic behavior, indicating that DNA is the essential source of ultraweak photon emission from biological systems.

A Physical Model

All oligo- and polynucleotides have absorption spectra very similar to those of the equivalent monomer mixtures (27), except for hypochromism. This indicates that there are no interactions between nucleotides, in particular with respect to their similar electron affinities in the ground state. Therefore, they are unable to form complexes as, for instance, chromophores. The properties of excited states of nucleic acid bases, on the other hand, do not only determine the photophysical and photochemical processes of the whole DNA, but also its conformational stability. From this point of view, the most essential feature of DNA compared to its monomeric units is caused by its pairing and stacking of bases, which implies interbase electronic excitation and exciplex

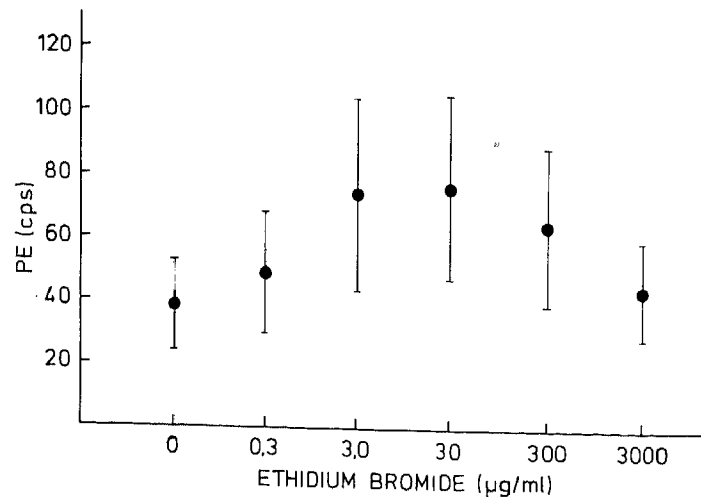


Fig. 5. Photon emission (PE) from soya cells (*Glycine max* cv. Harosoy 63) after a 75 min incubation with ethidium bromide at various concentrations. Bars: standard deviation of six experiments. The biophoton emission is highest at the concentration known to decondense tertiary structures in isolated DNA solutions.

(excimer) formation. The strong geometric influence on electronic transitions is demonstrated by the structureless red-shifted fluorescence of DNA bases in comparison to its monomer spectrum. It is now generally accepted that this band refers to exciplex (excimer) formation (28, 30). Exciplexes (excimers) exist only in the excited state, whereas the ground states are repulsive (dissociative states). Such materials form a medium with an equivalent negative absorption coefficient. The extension from simple units to macromolecules leads to an increase in size, complexity, and diversity. Thus, the range of exciplex phenomena is extended without changing its physical nature. Exciplexes remain a physical entity.

Although the theory of excimer (exciplex) states has been developed for aromatic hydrocarbons, its basic elements can be applied also to the DNA bases (28). Hauswirth and Daniels (28) have described the potential energy diagram of base excimers as follows: The configuration interaction is based on (1) a "charge resonance state" [$\alpha\Psi(A^+)\Psi(B^-) + \beta\Psi(A^-)\Psi(B^+)$] involving ionization potentials and electron affinities of monomers A and B, and Coulomb interaction between the complementary molecular ions, and (2) an "exciton resonance state" [$\gamma\Psi(A^*)\Psi(B) + \delta\Psi(A)\Psi(B^*)$] involving transition dipole-dipole interactions. Hence, the relative stacking of bases and their ability of acting as charge donors and acceptors is expected to play a dominant role in determining the extent of exciplex formation in a given dinucleotide phosphate. With decreasing distance r between the base pairs, a repulsive term caused by van der Waals forces [$R(r)$] has to be considered in both the ground and exciplex states. Since the ground state is dissociative at close distances, the discrete transition between vibrations becomes continuous. The resultant energy $D(r)$ of the excited state is then (see Fig. 5):

$$D(r) = V(r) + R(r)$$

where $V(r)$ is an attractive excimer interaction potential, $R(r)$ represents a short-range repulsion energy (27).

Figure 6 displays the energy diagram corresponding to a four-niveau system; k_4 represents the radiationless transition rate from level 4 to level 3, and k_2 is that from 2 to 1. A and B are the Einstein's coefficients for spontaneous and induced transitions, respectively; n_i is the occupation number of level i ; ρ represents the radiation energy density corresponding to transitions between levels 3 and 2; N is the total number of base pairs; and \bar{n} is the total number of excimers.

Because of repulsion in the excimer ground states, the monomers are normally separated, flying apart with a mean kinetic energy of kT . This is not the case for DNA bases, which are bound at definite positions of the DNA chain. The repulsions give rise there to the vibration of bases against one other around their equilibrium positions, which may themselves be slightly changed. Hence, level 2, which might be occupied within the vibration lifetime becomes a sensitive state in the interaction of the DNA with photons.

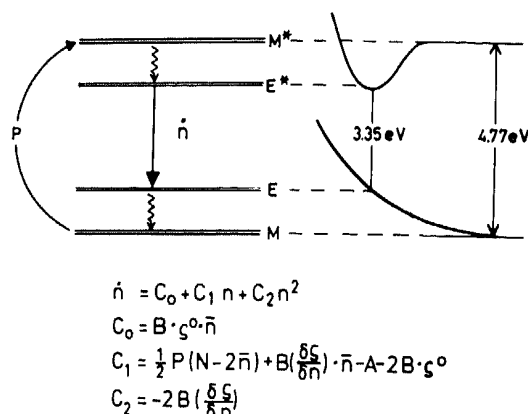


Fig. 6. Model of DNA emitting coherent light, in the form of an energy diagram corresponding to a four-level system: k_4 represents the radiationless transition rate from level 4 to level 3, and k_2 is that from level 2 to 1; A and B are the Einstein's coefficients for spontaneous and induced transitions, respectively; n_i is the occupation number of energy level i ; p represents the energy density of the radiation field caused by transitions between level 3 and 2.

The absorption of photons or supply of corresponding "chemical" energy exciting monomers represent a pumping P of the four-niveau laser of DNA (31), which was already discussed by one of us some years ago (32). The calculation (33) (see Appendix II) yields then the following result:

$$\dot{n}_3 = C_0 + C_1 n_3 + C_2 n_3^2 \quad [8]$$

with

$$\begin{aligned} C_0 &= B \cdot \rho^0 \cdot n \\ C_1 &= (\frac{1}{2})P(N - 2n) - A - 2B\rho^0 + B\rho' n \\ C_2 &= -2B\rho' \end{aligned}$$

and the notations of Appendix II.

This equation is the fundamental relation describing the dynamics of exciplexes, resulting in a permanent photon emission \dot{n}_3 . It has to be considered that Eq. [8] represents a nonlinear differential equation with time-dependent factors.

Since under most obvious conditions, by use of the maximum entropy formalism (34), this system stabilizes around the laser threshold (35) (Appendix III), let us confirm this point of view by expanding Eq. [8] near the threshold. We then take $\rho^0 = \rho_0$, which does not depend on time. A metastable state of exciplex formation in laser action is then obtained (Appendix II).

For $\rho' = 0$ (in contrast to the case of Appendix III), Eq. [8] reduces to a linear differential equation with a solution, which shows an exponential growth of the number of exciplexes, provided the pumping rate is

greater than the rate of spontaneously induced transitions. This increase breaks down as soon as the nonlinear term of Eq. [8] plays a role. When, on the other hand, the pumping rate becomes lower than that of spontaneous and induced transitions, the self-excitations by means of induced radiation density compensate the natural decay. Thus, we have a feedback scattering of radiation (see Appendices I and III), which stabilizes a metastable state of exciplex matter for a wide range of ρ' .

In the DNA this feedback coupling may not be ignored. In particular, the appreciable occupation of level 2, which is different from the usually random-distributed exciplexes in solution, plays a dominant role. It is also necessary to consider interactions between the DNA-lattice systems and phonons, giving rise to transitions from and to level 2. As a consequence, the feedback scattering of the radiation field may become coherent if, and only if, the photons are coupled to the phonons of the DNA lattice. Regarding Appendices I-III, the DNA laser model may then work in the following way: The pumping energy that is taken up either chemically or by resonance absorption of a photon dissipates from the monomer state to exciton states. These states become metastable as soon as the energy density is high enough ($f \approx 1$ according to Appendix III). As an example, let us consider an allowed optical transition of the exciton state that is governed by the rule of vanishing momentum \vec{K} of the envelope function of the exciton (36). This means that the corresponding lattice section over which the exciton is distributed exhibits a standing vibrational mode. Consequently, the vertical distances of the base pairs are then stationarily distributed over a definite range of amplitudes depending on the density of phonon energy. At the same time, the transitions of the different exciplexes within this lattice system take place simultaneously, corresponding to coherent emission and rescattering (Appendix I). However, the different distances of base pairs give rise to a continuous spectral distribution of emitted photons because of the dependence of the transition energy on the distance r between the base pairs (Fig. 6). Such a mode coupling has in fact been observed (20). The measured distribution $f \approx \text{const.}$ (20) may well reflect this behavior. Besides all the arguments already advanced, let us add the following thermodynamical consideration. The photons that are stored within DNA exciplexes have to work against the phase space in order to expand to more delocalized excitons. This natural quantum theoretical effect does not depend on a definite interaction with matter, but always takes place when the distance r of the containing volume is smaller than the wavelength λ (37). Hence, the condition of Eq. [9] holds:

$$(\partial U/\partial V)_{\lambda, T} dV + (\partial U/\partial g)_{V, T} dg = 0 \quad [9]$$

where U , V , and g represent the energy of the photon gas, the volume within the exciplexes, and the number of degenerate states within the phase space, respectively. T is the excitation temperature of the exciplex system (12). From Eq. [9] we obtain for $\delta U = 0$ the additional condition, Eq. [10]:

$$(\partial U/\partial T)_{\lambda, \nu} dT + (\partial U/\partial \lambda)_{g, \nu} d\lambda = 0 \quad [10]$$

After straightforward calculations this yields, finally, $f = \text{const.}$

A more detailed thermodynamical analysis has been presented in ref. (38). Biological consequences corresponding to these findings and considerations have been discussed in (38,39).

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APPENDIX I

We start with the well-known oscillation equation of an oscillator, which may represent a coupled system of single oscillators.

$$\ddot{x} + 2\beta\dot{x} + \omega_0^2x = 0 \quad [I.1]$$

x is the amplitude, ω_0 the eigenfrequency, and β the decay constant of the system. For electronic transitions in the optical range, we usually have $\omega_0 \approx 10^{15} \text{ s}^{-1}$ and $\beta \approx 10^9 \text{ s}^{-1}$.

In order to take into account the couplings within the system, we assume β to be a slowly varying function of time t . Obviously, this assures the general validity of our solution. We ask which conditions have to be fulfilled by $\beta(t)$ and $x(t)$ to keep $\omega = \omega_0$ a constant of the oscillation.

This requirement is possible since phase and amplitude restrict each other to some extent. This stabilization of phase, corresponding to coherent relations, can be only achieved if a definite damping, or increase, of amplitude takes place.

Since we cannot exclude the possibility of slow alterations of the oscillator during the relatively long decay time T , we have to extend the conditions for frequency stabilization to the case of possible changes (i.e., deformations) in oscillator structure. Although such deformations may be coupled to the amplitude itself, they are considered not to take part in radiation emission. As an example, we note the decondensation of chromatin during photon emission because of the decay of exciplexes. Obviously, the exciplex ground states are repulsive and do not contribute to radiation emission.

Thus, we find a solution of the form

$$x(t) = x_0(t) [1 + d(t)]e^{i\omega_0 t} \quad (\text{I.2})$$

providing

- (1) Frequency stabilization by means of the rapidly oscillating function $\exp(i\omega_0 t)$
- (2) "Radiation damping," originating from the slowly varying amplitude $x_0(t)$ only
- (3) Radiationless deformations described by the slowly varying function $d(t)$.

Let us restrict ourselves to a definite class of deformations that depend on the potential energy content of the oscillator system. This potential, in turn, may determine whether oscillations take place at all. They are defined by Eq. [I.3]:

$$d(t) = bx_0^{\mathcal{H}} + d_0 \quad (\text{I.3})$$

where b , d_0 and $\mathcal{H} > 0$ are constants, b reflects the coupling of single oscillators that are contributing to the total amplitude, and \mathcal{H} is caused by the distribution of the potential energy x_0^2 over the system. For $b \rightarrow 0$ (decoupling), we consequently require $x(t) \rightarrow 0$, resulting in $d_0 = -1$.

Hence, we obtain

$$\dot{d}(1 + d) = \mathcal{H} \dot{x}_0/x_0 \quad (\text{I.4})$$

As a consequence, we have also

$$\ddot{d}(1 + d) = \mathcal{H} \ddot{x}_0/x_0 + \mathcal{H}(\mathcal{H} - 1)(\dot{x}_0/x_0)^2 \quad (\text{I.5})$$

Inserting the special frequency-stabilized solution, Eq. [I.2], into Eq. [I.1] results in Eq. [I.6] and, after eliminating the unknown $\beta(t)$ by using Eqs. [I.4] and [I.5], and combining Eqs. [I.6a] and [I.6b], we finally obtain Eq. [I.7]

$$\ddot{x}_0 + 2\dot{x}_0\dot{d}(1 + d) + x_0\ddot{d}(1 + d) = -2\beta(\dot{x}_0 + x_0\dot{d}(1 + d)) \quad (\text{I.6a})$$

$$\dot{x}_0 + x_0\dot{d}(1 + d) = -\beta x_0 \quad (\text{I.6b})$$

$$\ddot{x}_0 x_0 = (2 + \mathcal{H})\dot{x}_0^2 \quad (\text{I.7})$$

Equation [I.7] has a clear physical meaning. It predicts that at any instant a definite fraction of the kinetic energy $(\dot{x}_0)^2$ has to be transformed into potential energy in order to achieve a constant oscillation frequency. This term, which is subject to storage of rescattered energy, increases with increasing \mathcal{H} .

It may be expressed in terms of a chemical potential μ , for example by Eq. [I.8]

$$\mathcal{H} + 1 = \mu/kT \quad (\text{I.8})$$

The solution of Eq. [I.7] takes for $\mu \neq 0$ the form

$$x_0(t) = A(t + t_0)^{-kT/\mu} \quad (\text{I.9})$$

For $\mu = 0$ it can be seen by insertion of $x_0(t) = \exp(i\omega t)$, with an arbitrary ω , into Eq. [I.7] that a purely exponential decay takes place. This accounts in this case for the equality of kinetic and potential energy within the system.

The radiation damping $I(t)$, which for sufficiently long time intervals is due to

$$d/dt x_0^2 = 2x_0\dot{x}_0$$

it then follows that

$$I(t) \sim kT/\mu (t + t_0)^{-\gamma}$$

with

$$\gamma = 2kT/\mu + 1$$

For the measured values γ with $1 < \gamma < 3$, we have $\infty > \mu > kT$.

APPENDIX II

In the following, we refer to Fig. 5 and its notations.

The net rate of exciplex formation, resulting from occupation of level 4, is determined by two processes, namely (1) the collisions between n_1 unexcited and n_1 excited monomers, pairing to exciplexes: $(\frac{1}{2})Pn_1n_1^*$ (1), and (2) the radiationless transitions from level 4 to level 3. Hence we get

$$\dot{n}_4 = \frac{1}{2}Pn_1n_1^* - k_4n_4 \quad [\text{II.1}]$$

The rate equation of level 3 accounts for (1) decay of level 4, (2) spontaneous and induced transitions from level 3, and (3) induced transitions from level 2, where we have to take into account that two molecules of level 2 form one of level 3.

$$\dot{n}_3 = k_4n_4 - (A + \rho B)n_3 + \frac{1}{2}\rho Bn_2 \quad [\text{II.2}]$$

Analogically we then can write

$$\dot{n}_2 = 2(A + \rho B)n_3 - k_2n_2 - \rho Bn_2 \quad [\text{II.3}]$$

$$\dot{n}_1 = k_2n_2 - Pn_1n_1^* \quad [\text{II.4}]$$

Because energy levels 4 and 3 are in the same potential gap of excimer states (Fig. 5), the rate parameters k_4 and k_2 are much greater than all others throughout transition processes. Thus they represent the so-called "overdamped motion" in Haken's sense (2). Consequently, taking $\dot{n}_4 = \dot{n}_2 = 0$, we get the following relations:

$$k_4n_4 = \frac{1}{2}Pn_1n_1^* \quad [\text{II.5a}]$$

$$k_2n_2 = Pn_1n_1^* \quad [\text{II.5b}]$$

Inserting Eq. [II.5a] into Eq. [II.2], and Eq. [II.5b] into Eq. [II.3], we obtain

$$\dot{n}_3 = \frac{1}{2}Pn_1n_1^* - (A + \rho B)n_3 + \frac{1}{2}\rho Bn_2 \quad [\text{II.6a}]$$

$$\dot{n}_2 = 2(A + \rho B)n_3 - Pn_1n_1^* - Bn_2 \quad [\text{II.6b}]$$

From these equations follows

$$n_3 + \frac{1}{2}n_2 = n = \text{constant} \quad [\text{II.7}]$$

$$d/dt (n_3 - \frac{1}{2}n_2) = Pn_1n_1^* - 2(A + \rho B)n_3 + \rho Bn_2 \quad [\text{II.8}]$$

Equation [II.8] is just one of the famous laser equations describing the dynamic inverse population of matter. It may be rewritten in the known form

$$\dot{\sigma} = \gamma (\sigma_0 - \sigma) - 2B\rho\sigma \quad [\text{II.9}]$$

with $\sigma \equiv n_3 - n_2/2$ and the definition in Eq. [II.9a]

$$\gamma(\sigma_0 - \sigma) \equiv Pn_1n_1^* - 2An_3 \quad [\text{II.9a}]$$

The other equation is that of the radiation field

$$\dot{\rho} = 2B\rho\sigma - K\rho \quad [\text{II.10}]$$

where K represents the loss factor of the system under investigation. These coupled equations, [II.9] and [II.10], are completely identical to that of O'Shea et al. (3).

Now let us concentrate our interest to the exciplex dynamics. The basic equation is given by Eq. [II.6a] with the additional condition of Eq. [II.11].

$$n_1 + n_1^* + n_2 + n_3 + n_4 = N \quad [\text{II.11}]$$

where N represents the total number of bases. Since $n_4 \approx 0$ because of its rapid decay, and consequently because of $n_3 \approx n_1^*$, we then obtain after taking account of Relation [II.7]

$$n_1 = N - 2n = \text{constant} \quad [\text{II.12}]$$

Hence, Eq. [II.2] can be rewritten in the form

$$\dot{n}_3 = \{\frac{1}{2}P(N - 2n) - A\}n_3 - \rho B(2n_3 - n) \quad [\text{II.13}]$$

Inserting the solution of ρ of Eq. [II.10] into Eq. [II.13], we get an integro-differential equation with time-dependent factors. It cannot be solved exactly. However, after expansion of ρ in power series of n_3 at $n_3 = (\frac{1}{2})(\sigma_0 + n)$, which corresponds to the expansion of ρ in series of σ at σ_0 , we can write:

$$\rho = \rho^0 + \rho'n_3 + \rho''n_3^2 + \dots \quad [\text{II.14}]$$

With

$$\rho^0 = \rho_0 \exp[(2B\sigma_0 - K)t]; \quad \rho' = (K - 2B\sigma_0)2B\sigma_0$$

we then obtain

$$\dot{n}_3 = B\rho^0n + \{\frac{1}{2}P(N - 2n) - A - 2B\rho^0 + B\rho'n\}n_3 - 2B\rho'n_3^2 \quad [\text{II.15}]$$

Near threshold ($2B\sigma_0 \approx K$), taking $\rho^0 = \rho_0$, we obtain

$$\dot{n}_3 = c_0 + c_1 n_3 + c_2 n_3^2 \quad [\text{II.16}]$$

whereby c_0, c_1, c_2 representing constants:

$$\begin{aligned} c_0 &= B\rho^0 n \\ c_1 &= \frac{1}{2}P(N - 2n) - A - 2B\rho^0 + B\rho' n \\ c_2 &= -2B\rho' \end{aligned}$$

Obviously, we then have a metastable state of exciplex formation in laser action.

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APPENDIX III

Let us consider a homogeneous, finite, and stationary system of radiation and matter that is not at thermal equilibrium. Consequently, we have a chemical potential attributed to the deviations from Bose-Einstein statistics.

Besides the well-known Einstein's relation Eq. [III.1], we then have a balance equation, [III.2].

$$\dot{\rho} = h\nu [AN_2 - \rho B(N_1 - N_2)] \quad [\text{III.1}]$$

$$kTN_1 + [\mu(\nu) + c_1(\nu)]N_2 = c_0(\nu) \quad [\text{III.2}]$$

where ρ is the spectral photon density, N_1 and N_2 are the numbers of unexcited and excited molecules (e.g., monomers and exciplexes), respectively, $h\nu$ represents the photon energy, and A and B are the Einstein's coefficients of spontaneous and induced transitions, respectively. Equation (III.2) means that the total free energy $c_0(\nu)$ is divided into two parts, one of them representing the mean thermal energy of monomers after decay (kT), the other the binding energy of exciplexes including their excitation (pumping). The term $\mu(\nu)$ accounts for the energy necessary to break an exciplex state, that is, to liberate a photon. It has, therefore, the meaning of a photochemical potential. $c_1(\nu)$ takes into account the coupling with other stationary systems; $\rho(\nu)$ is generally given by Eq. [III.3]

$$\rho(\nu) = A/B \exp[\mu - c_2(\nu)]kT \quad [\text{III.3}]$$

For black body radiation we have there $\mu = 0$ and $c_2(\nu) = h\nu$.

After insertion of μ from (III.3) into (III.2) we obtain

$$kTN_2 = \rho B c_0(\nu)(A + \rho B[1 + \ln(\rho B/A) + (c_2 - c_1)kT]) \quad \text{[III.4]}$$

For mixing a photon gas with a homogeneous system of matter exhibiting a photochemical potential, the entropy takes a maximum for the highest possible excitation of states, since in this case the photon gas is distributed most homogeneously over the matter.

We get therefore

$$(\partial N_2 / \partial \rho)_{\rho_0} = 0 \quad \text{[III.5]}$$

Equation [III.5] provides at the same time that the photon density is used with highest effectiveness for exciting exciplexes.

Straight forward calculation yields then

$$\rho_0 = A/B = 8\pi h\nu^3/c^3 f_0 \quad \text{[III.6]}$$

where $f_0 = 1$.

As a consequence, it follows that a stable state is reached for $f_0 = 1$, corresponding to the laser threshold.