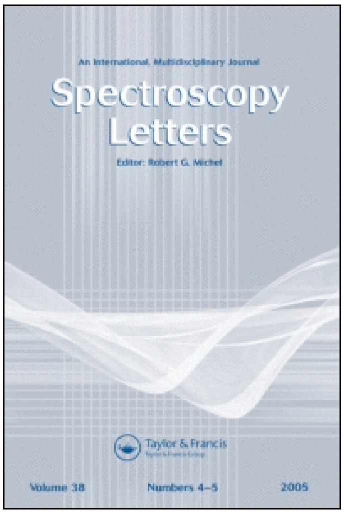

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Chemistry in Lasers. VII. The Effect of Optical Pumping on Local Concentrations in a Cavity

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CHEMISTRY IN LASERS. VII. THE EFFECT OF OPTICAL PUMPING ON LOCAL CONCENTRATIONS IN A CAVITY.

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ABSTRACT

The relationship between spectral line narrowing and diffusion coefficients is extended from previous studies [Part IV of the series]; the interaction between the optically pumped region and surroundings are represented in terms of Bessel functions, and the role of hyper-polarization in the resulting density fluctuation is discussed.

A spectroscopic inquiry into the subject of chemistry in lasers and the proper description of the time oriented sequence of quantum states in terms of a Markoffian chain (1-3) indicated an alteration of usual chemical properties; a close relationship between spectral condensation upon selective optical feedback in a 'tuned' cavity, resulting in spectroscopic line narrowing, the translational freedom of molecules, and diffusion coefficients was subsequently suggested (4) by combining current laser theory (5) with Einstein's original treatment of thermal random motion (6). The following inquiry is organized into two major parts: the first is devoted to a review of Part IV of this series[4] with some extension, and the second, to the formal representation of concentration gradients. Of particular interest at present is the relationship between spectral line narrowing and diffusion coefficients; the restriction of translational movement upon spectral condensation alters the magnitude of the diffusion coefficients of the optically active species, following the original considerations put forth by Einstein who derived D from random thermal motion of particles (6). Accordingly we may represent density fluctuations as

$$f + \frac{\partial f}{\partial t}\cdot\tau = f\int_{-\infty}^{+\infty}\phi(\Delta_x)d\Delta_x + \frac{\partial f}{\partial x}\int_{-\infty}^{+\infty}\Delta_x\phi(\Delta_x)d\Delta_x + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{+\infty}\frac{\Delta^2 x}{2}\phi(\Delta_x)d\Delta_x \ldots \qquad \{1\}$$

$$f + \frac{\partial f}{\partial t}\cdot\tau = f\int_{-\infty}^{+\infty}\phi(\Delta\gamma)d\Delta\gamma + \frac{\partial f}{\partial \gamma}\int_{-\infty}^{+\infty}\Delta\gamma\phi(\Delta\gamma)d\Delta\gamma + \frac{\partial^2 f}{\partial \gamma^2}\int_{-\infty}^{+\infty}\frac{\Delta^2\gamma}{2}\phi(\Delta\gamma)d\Delta\gamma \ldots \qquad \{2\}$$

$$f + \frac{\partial f}{\partial t}\cdot\tau = f\int_{-\infty}^{+\infty}\phi(\Delta_z)d\Delta_z + \frac{\partial f}{\partial z}\int\Delta z\phi(\Delta_z)d\Delta_z + \frac{\partial^2 f}{\partial z^2}\int_{-\infty}^{+\infty}\frac{\Delta^2 z}{2}\phi(\Delta z)d\Delta z \ldots \qquad \{3\}$$

where f is the particle density, τ is the time interval, and Δ is displacement. By making z in the above expressions parallel to the optical cavity axis and letting x be perpendicular to z at any volume element randomly selected, we note that terms containing z and y, i.e. Eq. 2 and 3, correspond to random fluctuations in a dynamic system, and only Δ_x has a vector meaning. Due to the local value of D_x (the diffusion coefficient in the x direction) the even number terms in

Eq. 1 no longer vanish, and net concentration gradients are set up in the system.

The altered diffusion coefficients are in agreement with modern theories concerning anisotropic laser active media, whereby a close relationship between apparently diverse phenomena such as Johnson-Nyquist noise, radiative damping, spontaneous emission, blackbody radiation,brownian motion, thermal noise and optical fluorescence is established, even to the extent that they can be regarded as representing essentially the same physical phenomena (7); our inquiry is devoted to utilizing the well established "textbook" results in chemistry, rather than repeating or further developing them at this point. By necessity specific details pertaining to cavity construction and quantum optics are regarded as somewhat extraneous in this inquiry, and are left for the laser literature proper.

As an example of the effect of nonrandom diffusion, we may consider a separation scheme based on the difference in optical activity. The components separable by the following method must have different optical absorption coefficients at some wavelength, i.e.

$$\epsilon_{\lambda,I} > \epsilon_{\lambda,II} \qquad \{4\}$$

where I and II refer to the chemical species to be separated; in addition other, simpler methods of separation should not be available to make this method an attractive one, that is, I and II should have generally similar chemical properties, as may occur in case of isotopes, or compounds of isotopes, of the same element. The advantage of selecting compounds I and II with permanent dipole moments is the enhanced coupling between the radiation field and the radiative assembly, resulting in a nonisotropic medium where significant difference in local diffusion coefficients can be expected.

Figure 1 refers to a continuously excited (CW) set-up in which a reservoir at ambient temperatures (NL) is in contact with an optical cavity (L), thru porous frits for example. Initially the distribution of the isotopes is uniform throughout the system, i.e.

$$[I]_L = [I]_{NL} \text{ and } [II]_L = [II]_{NL}. \qquad \{5\}$$

Selecting an excitation wavelength such that $\epsilon_{\lambda,I} \gg \epsilon_{\lambda,II}$, a change in the concentration relationship represented by Eq. 5 occurs following CW laser action. From merely the difference in ϵ,

$$\frac{d[I]_L}{dt} \rightarrow 0 \text{ as } \frac{[I]_L}{[I]_{NL}} \rightarrow \frac{\epsilon_{\lambda,I}}{\epsilon_{\lambda,II}} \qquad \{6\}$$

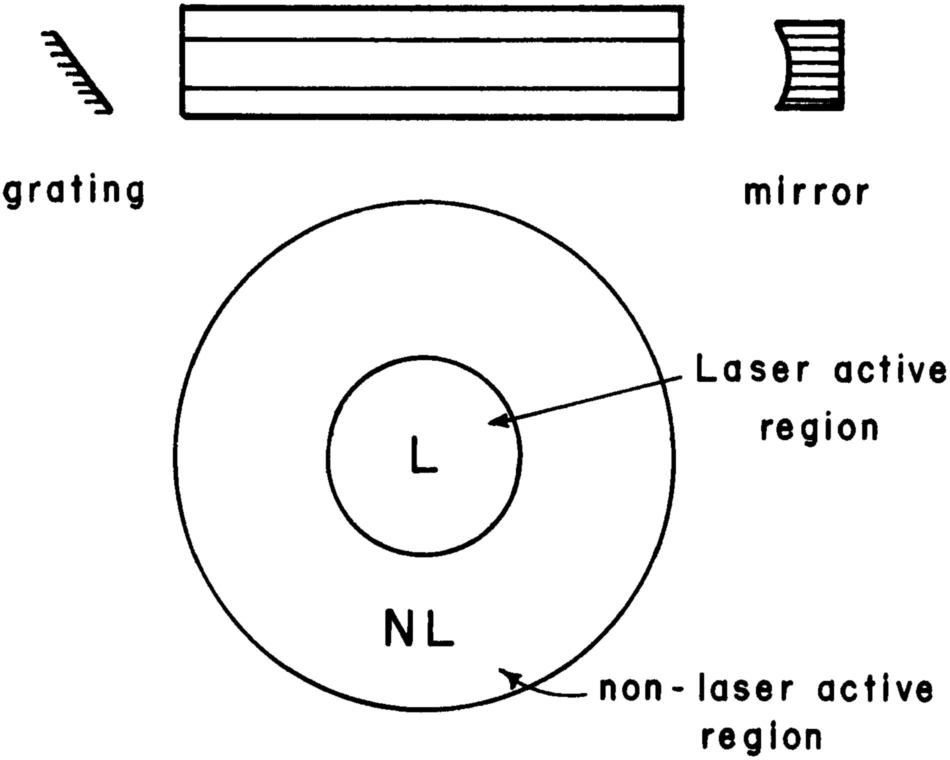

FIG. 1

Side view (top) and end-on view of shematic laser cavity in contact with ambient reservoir. Excitation source is not shown.

and the time required to reach steady state depends on the nature of the permeable barrier between L and NL. Properly speaking this, like so many separations in chemistry, constitutes an "enrichment" of one phase in one of the components, rather than a 'total' separation available in case of macroscopic objects. The maximum degree of enrichment by this technique is seen to be $\epsilon_{\lambda,I}/\epsilon_{\lambda,II}$ at this stage.

As the concentration of I in L increases due to the difference between $D_{I,L}$ and $D_{II,L}$, the density of the sample is also affected. The internal pressure increase in the L, following the increase in density, causes II to diffuse to NL. This produces an enrichment of I in the region L that is greater than was predicted by Eq. 6, and offers a momentum transfer channel. Although we are not primarily concerned with energy density in this paper, it should be remarked that a constant energy density is by no means a necessary or obvious condition. For separations, as we have noted in the foregoing, there are no particular advantages associated with increasing particle and/or energy density in the region L; on the other hand, for processes such as fusion, the cited increases would be of a decidedly beneficial nature.

Continuously introducing a parent mixture of I and II into the region NL at a rate slow enough to allow diffusion of I to L, the efficiency of the separation may be further enhanced. Although the procedure was discussed in terms of separating I from II by condensing the former in the laser active cavity space, a simultaneous increase in the II:I ratio occurs in NL, corresponding to the enrichment of the component having lesser optical activity in that region.

The present study in the following is concerned with the derivation of concentration gradients in an optical resonant cavity. Intimately related to concentration gradients are such fundamental physico-chemical parameters as internal pressure, diffusion and density fluctuations. The results obtained in the present paper are particular only in the sense that one of several possible optical cavities has been selected for solving the problem; yet the results are general in the sense that the derived trends concerning concentration gradients and density fluctuations apply to all optical cavities, and only minor mathematical manipulation is required to adopt the present set of results to another type of optical cavity.

Before considering concentration gradients, the particular optical cavity needs to be defined. Depending on the type of mirrors being employed, common optical resonant cavities may be classified as spherical or cylindrical, or a combination thereof (this last problem offers considerable mathematical complexity, and from an examination of the literature it appears that it has never been examined in detail for special advantages). When the focal length is ∞, the Fabry-Perot cavity results; the great advantage of the Fabry-Perot cavity in terms of a mathematical solution is that it removes a Z-axis ($Z \equiv$ optical cavity axis) dependence from the problem in terms of Z_i coordinates, i.e. the cavity can be assumed to be homogeneous along the Z-direction. The solution given in this paper is in terms of a spherical cavity in the Fabry-Perot limit. Bessel functions are ideally suited to describe the system defined in the aforegoing; as long as the laser active region is assumed to be isolated from the non-laser active surroundings, under CW ('continuous wave') conditions the properties of the system will be homogeneous, and the Bessel function solution mathematically degenerate.

At this point we introduce the non-isolation condition, whereby material outside the Fabry-Perot spatial zone comes into contact with the laser active region. The temperature of the ambient region is

$\mathcal{T}_{n\ell}$, and of the inner, laser region is $\mathcal{T}_{\ell}$. As a matter of convenience we may define a new temperature scale $\mathcal{U}$ such that $\mathcal{U} = \mathcal{T}_i - \mathcal{T}_{n\ell}$; this way the outer boundary condition will be $\mathcal{U} = 0$, which is a trivial simplification, and can always be removed at the final step.

To derive the material transport equations the Laplace transformation (8) can be applied in conjunction with Bessel functions. Using cylindrical co-ordinates (r, θ, z) in their customary meaning, it is immediately obvious that $\mathcal{U} \neq f(\theta)$ and $\mathcal{U} \neq f(z)$, hence $\mathcal{U}(r,t)$ totally defines the variability. Then the boundary conditions are

$$\mathcal{U}(1,t) = 0 \quad \text{and} \quad \mathcal{U}(r,0) = \mathcal{U}_0, \tag{7}$$

and the differential equation for gradients appearing at $t > 0$ is

$$\frac{\partial \mathcal{U}}{\partial t} = k\left(\frac{\partial^2 \mathcal{U}}{\partial r^2} + \frac{1}{r}\frac{\partial \mathcal{U}}{\partial r}\right). \tag{8}$$

In Eq. 7 we have normalized the dimension of the Fabry-Perot region by setting the condition

$$0 < r < 1 \tag{9}$$

It is both convenient and reasonable to assume that the exterior region, with respect to the optical resonant cavity, behaves as an infinite reservoir, and this has in effect been done in selecting the first of the two boundary conditions in Eq. 7.

So that we may apply later on the Bromwich contour technique to find complex inversion integrals with the aid of the equation

$$\mathcal{F}(t) = \lim_{R\to\infty}\left\{\frac{1}{2\pi i}\oint_c e^{\rho t} f(\rho)d\rho - \frac{1}{2\pi i}\int_\Gamma e^{\rho t} f(\rho)d\rho\right\}, \tag{10}$$

we must assume that a constant $\mathfrak{a}$ exists such that

$$|\,\mathcal{U}(r,t)\,| < \mathfrak{a} \tag{11}$$

to satisfy the condition

$$\lim_{R\to\infty}\int_\Gamma e^{\rho t} f(\rho)d\rho = 0, \tag{12}$$

removing the problem of singularities with respect to Eq. 10. (The treatment of branch points, considerably more complex, is not required for the monotonic gradients that appear in solving the problem).

Normalizing Eq. 8 with respect to the constant k and taking Laplace transforms, we obtain the non-partial differential equation

$$\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} - \rho u = - \mathcal{U}_0 \qquad \{13\}$$

with boundary conditions

$$u\,(1,\rho) = 0 \quad \text{and} \quad \left|\, u\,(r,\rho)\,\right| < \frac{a}{\rho}. \qquad \{14\}$$

The Bessel Function solution of Eq. 7 is

$$u\,(r,\rho) = c_1\, \mathcal{J}_0\,(i\,\sqrt{\rho}\; r) + c_2\, Y_0\,(i\,\sqrt{\rho}\; r) + \frac{\mathcal{U}_0}{\rho}. \qquad \{15\}$$

By letting $c_2 = 0$ (required for successful application of the complex inversion formula) and referring to the boundary conditions in Eq. 14, c_1 is evaluated from Eq. 15 as

$$c_1 = \frac{-\mathcal{U}_0}{\rho\, \mathcal{J}_0(i\,\sqrt{\rho})}. \qquad \{16\}$$

Hence Eq. 15 becomes

$$u\,(r,\rho) = \frac{\mathcal{U}_0}{\rho} - \frac{\mathcal{U}_0\, \mathcal{J}_0\,(i\,\sqrt{\rho}\; r)}{\rho\, \mathcal{J}_0\,(i\,\sqrt{\rho})}. \qquad \{17\}$$

By using the technique of Eq. 4 one obtains from Eq. 17 the result in terms of r and t;

$$\mathcal{U}\,(r,t) = \mathcal{U}_0 - \frac{\mathcal{U}_0}{2\pi i} \int_{\gamma\, -i\infty}^{\gamma\, +i\infty} \frac{e^{\rho t}\, \mathcal{J}_0\,(i\,\sqrt{\rho}\; r)\; ds}{\rho\, \mathcal{J}_0\,(i\,\sqrt{\rho})}. \qquad \{18\}$$

The integrand in Eq. 18 has simple poles at $\rho = 0,\ -\lambda_n^2\ (n = 1,2,3\ldots)$ The residues are

$$\lim_{\rho \to 0}\ \rho\, \frac{e^{\rho t}\, \mathcal{J}_0\,(i\,\sqrt{\rho}\; r)}{\rho\, \mathcal{J}_0\,(i\,\sqrt{\rho})} = 1 \qquad \{19\}$$

and

$$\lim_{\rho \to -\lambda_n^2}\ (\rho + \lambda_n^2)\, \frac{e^{\rho t}\, \mathcal{J}_0\,(i\,\sqrt{\rho}\; r)}{\rho\, \mathcal{J}_0\,(i\,\sqrt{\rho})} =$$

$$= \left\{ \lim_{\rho \to -\lambda_n^2} \frac{1}{\mathcal{J}_0'\,(i\,\sqrt{\rho})\, \frac{i}{2\,\sqrt{\rho}}} \right\} \left\{ \frac{e^{-\lambda_n^2 t}\, \mathcal{J}_0\,(\lambda_n r)}{-\lambda_n^2} \right\} =$$

$$= \frac{-2e^{-\lambda_n^2 t}\, \mathcal{J}_0\,(\lambda_n r)}{\lambda_n\, \mathcal{J}_1\,(\lambda_n)}. \qquad \{20\}$$

Hence Eq. 18 becomes

$$\mathcal{U}(r,t) = 2\mathcal{U}_0 \sum_{n=1}^{\infty} \frac{e^{-\lambda_n^2 t}\, \mathcal{J}_0(\lambda_n r)}{\lambda_n\, \mathcal{J}_1(\lambda_n)}. \qquad \{21\}$$

In the Fabry-Perot spatial region, where population inversion exists, the diffusion coefficient has a vector meaning towards the higher negative temperature region (4), and consequently Graham's Law of diffusion, applied in terms of the $\mathcal{U}(r,t)$ profile (Eq. 21), or by shifting back to the original $\mathcal{T}$-scale of temperature, the $\mathcal{T}(r,t)$ profile, indicates a concentration gradient that increases towards z. Density, being proportional to $\mathcal{T}$, also increases towards the main optical cavity axis, a condition which may create favorable conditions for fusion. Although individual molecular states were not involved in the above derivations, we may mention in closing that the coupling of the radiation ($\mathcal{E}$M) field with the molecules results in changes beyond those discussed previously in relation to the time-evolution of electronically excited states(3,9-11). To account for these special effects, we should add as an update, the terms hyperpolarization and optical plasma have been advanced. In contrast to the relatively simple time-evolution problem, the coupling of the $\mathcal{E}$M field and the molecules necessitates the consideration of non-Born-Oppenheimer states (12).

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