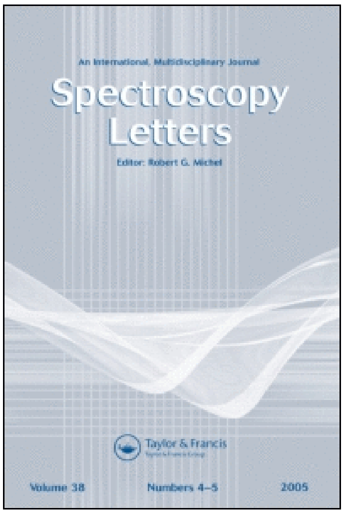

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Chemistry in Lasers. I. The Role of the Stokes O-O Loss

Csaba P. Keszthelyi[a]
[a] Department of Chemistry, Louisiana State University-BR, Baton Rouge, Louisiana

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CHEMISTRY IN LASERS. I. THE ROLE OF THE STOKES 0-0 LOSS.

Csaba P. Keszthelyi
Department of Chemistry
Louisiana State University-BR
Baton Rouge, Louisiana 70803

ABSTRACT

In this first paper in a series aimed at studies of chemistry in lasers, the molecular states in a dye laser are compared to those in the same solution under ordinary fluorescence conditions. Significant differences are found to exist which are readily apparent in case of molecules whose normal fluorescence is characterized by a sizeable Stokes 0-0 loss. Such differences are traced to the invalidity of the Born-Oppenheimer separation approximation for these molecules when the excited state lifetimes are greatly altered as in dyes lasers at high photon density. Representation of this particular type of Stokes shift requires an extension of the usual model based on only two hypersurfaces, namely, a time-ordered sequence of quantum states.

In media having a negative optical absorption coefficient[1] ($\varepsilon < 0$) '<u>l</u>ight <u>a</u>mplification by the <u>s</u>timulated <u>e</u>mission of <u>r</u>adiation' (laser) is predicted by the Beer-Lambert relationship,

$$\text{Intensity}_{(\text{out})} = \text{Intensity}_{(\text{in})} \cdot 10^{-\varepsilon lc} \qquad (1)$$

also called the fundamental law of spectrophotometry.[2] Experimental realization of the proper conditions for $\varepsilon < 0$ is more than a decade old,[3,4] and lasers have already made important contributions to chemistry as coherent and powerful light sources. However, 'chemistry-in-lasers', the specific study of chemical processes occurring in an optical resonant cavity, and their comparison with related results obtained under ordinary conditions, has been largely in the form of scattered reports. The ACP ("axiomatic cum pragmatic") approach to problem solving developed by Matsen[5] suggests that a review and perhaps revision of the pertinent axioms is a timely undertaking. The Stokes loss is an ideal starting point for such an inquiry.

The origin of the terms "Stokes loss" or "Stokes shift" can be traced to the last century, when Stokes reported[6] that the fluorescence emission is often 'red shifted' with respect to the excitation spectrum. As Figure 1 indicates, we distinguish between the Stokes loss in general, and a special type of it which, due to lack of a better descriptive term, this author calls the 'Stokes 0-0 loss'. The Stokes 0-0 loss refers to the

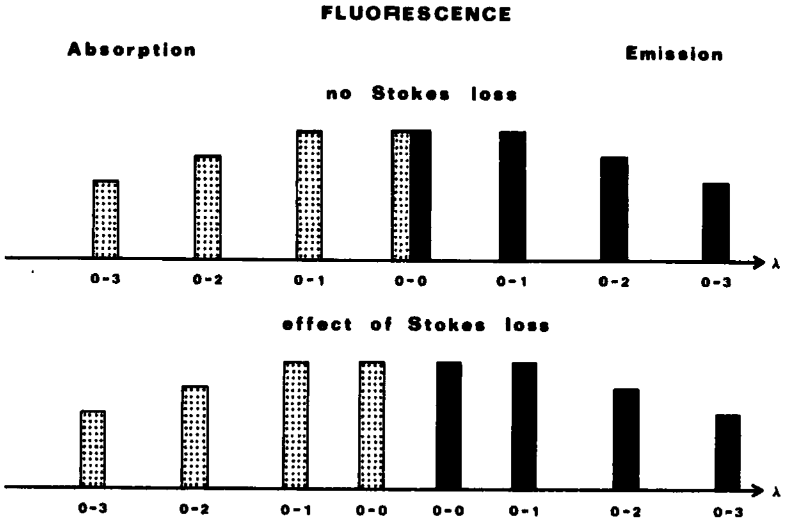
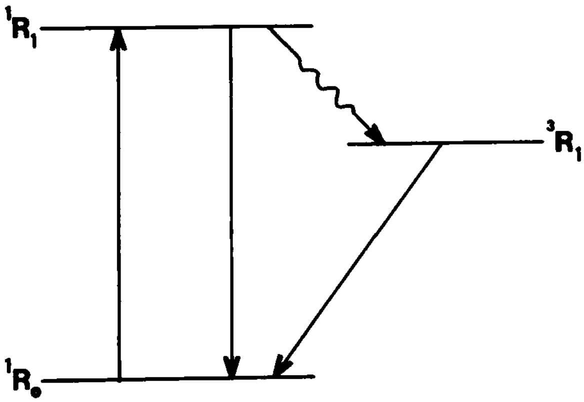


Fig. 1. The 'Stokes 0-0 loss' in generalized representation

separation of the 0-0 bands of the excitation and emission spectra, a phenomenon that is relatively common when the fluorescor is dissolved in fluid solution,[7] but not when it is in the gas phase.[8] A specific example of the Stokes 0-0 loss can be found in Turro's text "Molecular Photochemistry", including reproduction of actual spectra obtained from anthracene fluorescence data.

One of the significant implications of the Stokes 0-0 loss is related to establishing threshold conditions for laser action. We recall that it is impossible to produce a population inversion by optical pumping[9] in a two-level system. In terms of inset 1 this means that we could not



inset 1

achieve the condition $[^1R_1] > [^1R_0]$ by optical pumping, though if $^1R_1$ undergoes non-radiative intersystem crossing to a triplet state for example, a population inversion between the triplet and ground state species becomes possible ($[^3R_1] > [^1R_0]$). It would be still easier to establish population inversion with respect to a terminal state other than $^1R_0$, and such is the situation in 4-level lasers.

The advantages of a 4-level over a 3-level laser are discussed fully elsewhere;[10,11] in essence one can appreciate immediately that it is easier to obtain laser action when population inversion need not be with respect to the ground state (in a 3-level laser $N_3 > N_1$, but in a 4-level laser $N_3 > N_4$, is the required condition). What is of importance here is that a Stokes 0-0 loss converts a 2-level system (cf. $^1R_1$ and $^1R_0$ in inset 1) to a 4-level system. Figure 2 compares 3-level and 4-level lasers with the fluorescence of a scintillator dye that shows a Stokes 0-0 loss.

The usual representation of the Stokes loss in terms of two potential energy hypersurfaces is shown in the second inset. The publications containing a facsimile of inset 2 are too numerous to mention, but the reader may confer the laser related paper by Sorokin, Lankard, Moruzzi, and Hammond as a typical example.[12] The derivation found in standard textbooks[13] is not reproduced here. An attempt to represent the scintillator

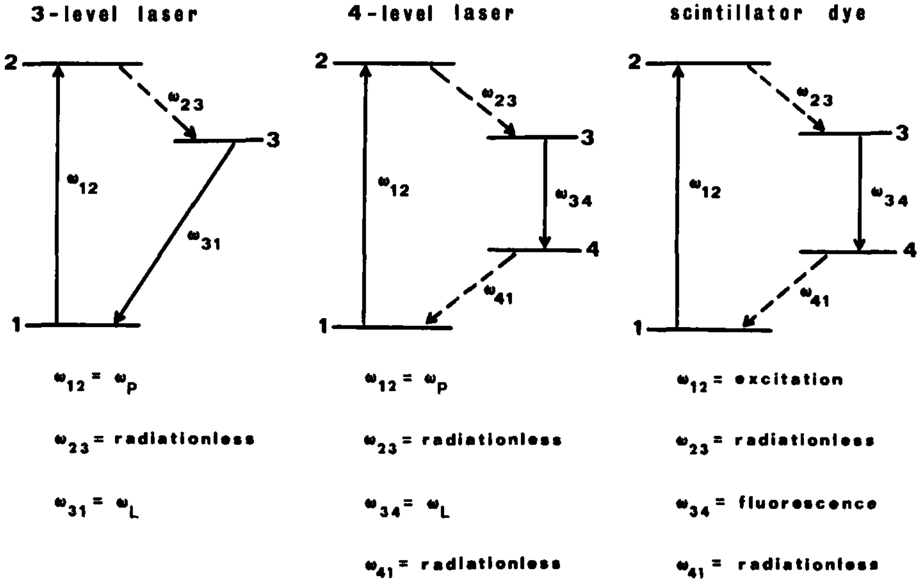
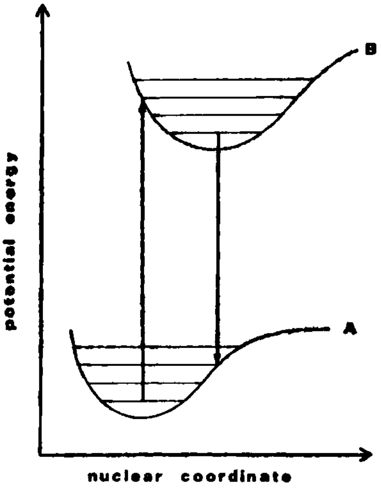


Fig. 2. Comparison of the energy levels of a fluorescor showing a Stokes 0-0 loss with 3-level and 4-level lasers.



inset 2

dye fluorescence (Fig. 2) in terms of the two potential energy surfaces of inset 2 is futile: it is impossible to represent the Stokes 0-0 loss in this manner. In a dielectric medium the zero-point energy of the hypersurface will shift, and in terms of Figure 2 this means that excited molecules (R*) initially created in level 2 will 'coast down' to level 3 (the Franck-Condon relaxed excited state (R^*_{fc}). We estimate about 10^{-10} seconds for completion of a similar process in solution chemiluminescence[14] also involving large molecules, and it must be emphasized that this process is different from the one occurring in case of relaxed molecules, where "nuclear motion leads electronic motion" paraphrases the Born-Oppenheimer separation.[15] The time evolution of molecules in level 2 to level 3 can not be described by states of R* that pertain only to R^*_{fc}, but by 'precursor' states where solvent-solute interaction, solvent dielectric relaxation, and changes in the molecular force constants of R* (i.e. the potential energy surface itself!) have not yet reached steady state. Considering emission from the time-ordered sequence of precursor quantum states, a two-dimensional eigenvalue spectrum matrix is obtained, rather than the usual one-dimensional one which takes into account only the R^*_{fc}

states. Contrary to spontaneous fluorescence, in case of stimulated emission the contribution from 'early' time elements in the 2-D eigenvalue spectrum matrix becomes dominant; this will be discussed subsequently.

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