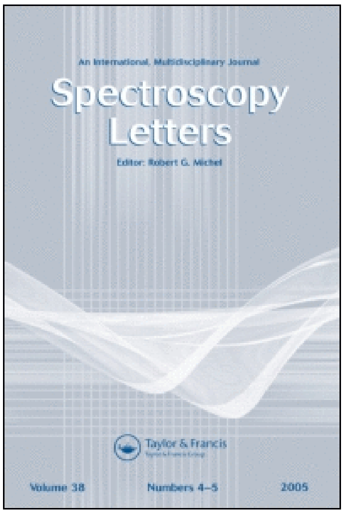

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Chemistry in Lasers. II. Contribution from Precursor States: A Comparison of the Time Evolution of Electronically Excited States Under Spontaneous and Stimulated Emission Conditions

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CHEMISTRY IN LASERS. II. CONTRIBUTION FROM PRECURSOR STATES: A COMPARISON OF THE TIME EVOLUTION OF ELECTRONICALLY EXCITED STATES UNDER SPONTANEOUS AND STIMULATED EMISSION CONDITIONS.

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ABSTRACT

The relative importance of the time-ordered sequence of precursor states is examined; their contribution to the ensemble is negligible for spontaneous emission, but under stimulated emission conditions at high photon density the dominant terms in the sequence, determining the ensemble properties, are different from the Franck-Condon relaxed state. The 'chirp' of a traveling wave laser is shown to be related to time-resolved spectroscopic measurements.

The results of Part I[1] can be summarized briefly by recalling that in case of a fluorescor whose excitation and emission spectra are characterized by a Stokes 0-0 loss, the molecular relaxation processes involve a time-ordered sequence of quantum states; by definition, the properties, including chemical properties, of different terms within the sequence differ. The very important question: what contribution do the precursor states make in terms of the total assembly, is considered in this Part II.

It is worth noting that spectroscopic data in the literature for quite some time has warranted a multiple hypersurface representation. As examples, Figure 1 shows the temperature dependent spectra obtained by Lippert, Lüder and Moll back in the 1950's, and Figure 2 shows time-resolved spectra taken by Ware and co-workers in the 1960's. To represent these processes in a manner that is closely related to the customary (cf. inset 2 in Part I), one needs to distinguish excited and ground electronic states in various stages of their time evolution; this is shown in Figure 3 where the absorption (emission) of a photon at t_1 results in an energetically unfavorable excited (ground) state that will, through re-organization of the solvent cage and altering the molecular geometry, relax to the t_3 state. Though only one intermediate state (labeled t_2) is shown in Figure 3, it is a time-ordered sequence of states that is invol-

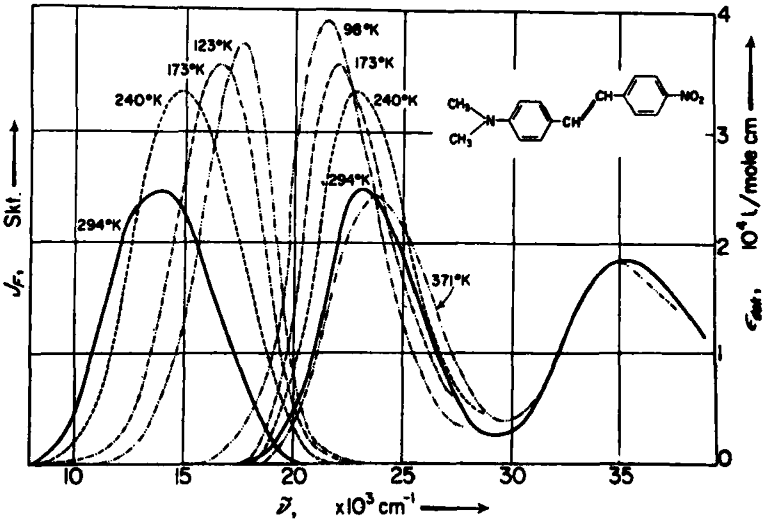

FIG. 1
Temperature dependent spectral shifts (cf. Fig. 3 for multi-potential energy hypersurface representation) reported by E. Lippert, W. Luder and F. Moll, Spectrochim. Acta, 15, 858 (1959); (reproduced by permission).

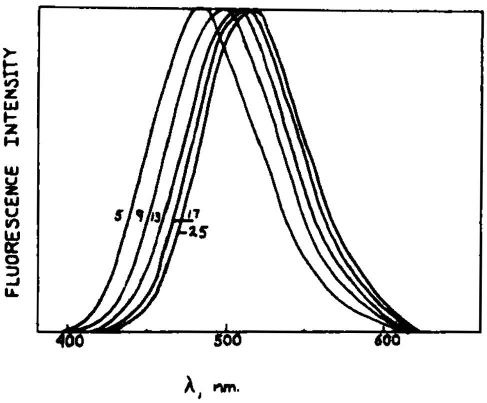

FIG. 2
The time evolution of electronically excited states detected by nanosecond time-resolution. (Figure reproduced by permission: W. R. Ware, P. K. Chow and S. K. Lee, Chem. Phys. Lett., 2, 357 (1969).)

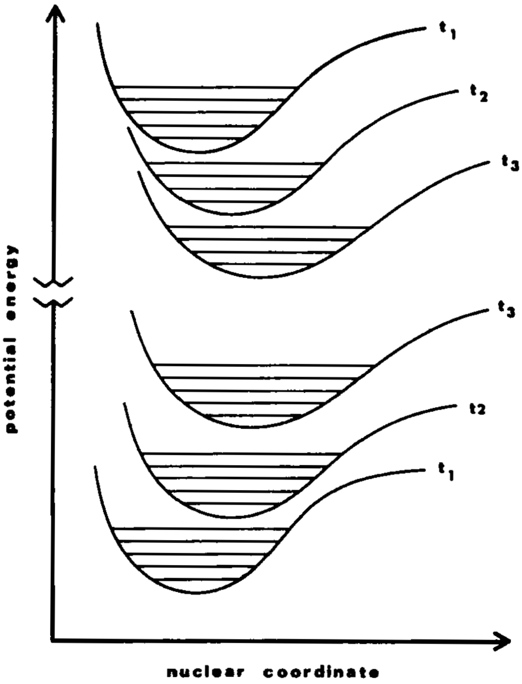

FIG. 3
Time oriented sequence of potential energy hypersurfaces, including virtual ground state manifolds. Emission of a photon results from transition between excited and ground state manifolds having the same time-evolution coordinate.

ved in the relaxation process, both for the excited and ground state species.

From the expression $N_t = N_o e^{-t/\tau}$, where τ is the fluorescence lifetime of the excited state,[2] one can obtain an estimate of the relative population of various precursor states in comparison to the relaxed excited state population; the results, shown in Figure 4, reveal that under spontaneous fluorescence conditions the overwhelming fraction of the electronically excited assembly is properly characterized by t_3-type relaxed molecules, hence contribution from precursor states to the assembly properties would be negligible (the Figure 4 also includes triplet species for comparison, for which a similar conclusion holds; one nanosecond and one millisecond were chosen as representative lifetimes for the singlet and triplet species, respectively).

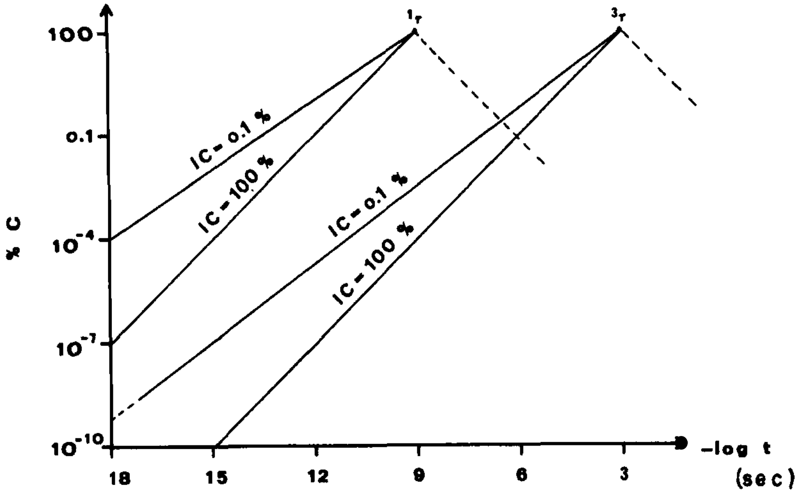

FIG. 4

Weighting factors for various time elements in the evolution of metastable states; ordinate is normalized with respect to predominant time element (100%). IC is the internal conversion efficiency from level 2 to 3 under spontaneous fluorescence conditions.

The most elementary consequence of laser action is an alteration of the excited state lifetime; by opening an additional reaction channel for the process $R^* \rightarrow R$, τ will be shortened (note that τ was not identified as the spontaneous fluorescence lifetime in the foregoing). Depending on the relative importance of stimulated emission, the new value of τ may differ drastically from its value under spontaneous emission conditions (τ_{sp}). When this happens, the majority of molecules in the excited assembly is no longer characterized by quantum states appropriate to describe the spontaneous assembly, but by some of the former 'precursor' states. The properties of the assembly will change in an observable manner as τ changes; for example in a traveling wave laser the frequency of the emitted light will sweep toward higher frequency as τ shortens, a phenomenon known as "the laser chirps". This sweep of the emission wavelength is readily understood in terms of Ware's time-resolved spectra (Figure 2), since altering the excited state lifetime in the laser in effect corresponds to observing selective precursor states.

In addition to the alterations in the radiative lifetime, there are special molecular ordering processes in a tuned laser which affect the properties of the radiating ensemble in more involved ways than the mere necessity of using a time-ordered sequence of quantum states;[3] these can directly involve activation energies of chemical reactions, and relate to utilizing a laser cavity as a special 'catalyst' in carrying out certain processes. The role of the ordered assembly of particles will be discussed in IV., subsequently.

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