

CHEMISTRY IN LASERS, V
Electrogenerated Chemiluminescence and Electrochemistry
in a Laser Cavity

By

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(Received May 10, 1974)

The effect of the optical resonant cavity on molecular assembly parameters is examined, in an extension of previous studies. The spectroscopic line width narrowing observed in tuned dye lasers also leads to a reduction of the "electrochemical line width", and shift of the laser wavelength is accompanied by alteration of the standard oxidation and reduction potentials. The results suggest novel chemical separations unattainable except in the laser cavity itself.

The availability of blue emitting electrogenerated chemiluminescence (ECL) systems with quantum efficiency better than 10% [1] adds practical significance to the novelty aspect of an ECL pumped dye laser. Two investigations are on record that attempted to construct such a dye laser; neither has succeeded in obtaining documented laser action [2, 3]. The following inquiry has been organized into three parts: preliminary requirements, documenting laser action, and a comparison of electrochemical and ECL properties before and during laser action. This final and third phase of the inquiry is of particular interest, as it appears to be, based on a thorough examination of the literature, to be the first of its kind, relating the spectroscopic line width to "electrochemical line width" in an extension of earlier inquiries [4] concerning chemistry in lasers.

Among the preliminary requirements, a system providing intense chemiluminescence ranks foremost, because a high photon density cannot be achieved in a system that has a low Φ_{ECL} , nor in one where Φ_{ECL} is high but the low solubility of the parent compounds keeps the radiant power output low (an example of this latter adversity would be rubrene in ACN—TBAP, and to a lesser degree, DPA in ACN—TBAP; in both cases incorporating a second solvent component such as toluene or benzene removes the solubility problem, hence Φ_{ECL} is the more fundamental index for evaluating prospective ECL systems). Determination of the ECL quantum efficiency in itself is a major and time consuming undertaking [1], yet it is only a starting point in this case for calculating the excited state population density, N^* . The ECL process, assuming that linear diffusion conditions govern the annihilation of electrochemically generated A^- and D^+ in the vicinity of the electrode, has been successfully treated by computer simulation [5]. Attempts by SCHWARTZ *et al.* [6] to utilize Fourier transforms to simulate ECL have been unsuccessful on the

quantitative level, as pointed out previously by the present author [7]. None of the simulations in the literature have included the effect of double layer charging on the annihilation process; in effect double layer charging will alter the concentration profiles significantly, especially at high pulse rates [8]. This is a particularly important point in the present context, because as the annihilation zone oscillates in the diffusion layer following the electrochemical pulsing, the excited state population density N^* varies significantly as the annihilation zone geometry changes. There are a number of quenching possibilities one could consider, but these are usually insignificant in altering the excited singlet lifetimes, and Φ_{ECL} gives a good first approximation for N^* without taking specific quenching into account. A final preliminary requirement is a flat electrode, because even a very intense ECL system might be incapable of supporting a reasonable N^* when the simulation volume elements ("boxes") are correlated with real space of the optical resonant cavity axis. The minute dimension of the annihilation zone, even in comparison to the diffusion layer thickness, indicates how flat the electrode should really be to obtain maximum optical gain. Furthermore, one is faced with the problem of the electrode acting as a quencher for R^* [9]; this complication is most severe at very fast pulse rates due to the decreased width of the diffusion layer, suggesting that useful electro-generation frequencies should be in the low audio range (DC potentials applied to a network of submicron dimension microelectrodes offer another promising method [10], free of double layer charging and oscillation of the annihilation zone also, shown to be important problems in the preceding).

Detection and documentation of laser action, should it indeed occur, also involve formidable problems. Two principal techniques of recognized utility are the spatial non-randomness test using a partially reflective mirror ($1/r^2$ law should not be obeyed), and spectral resolution of the emitted light for evidence of line narrowing. It is in this second technique that lack of *a priori* information presents a major problem: the sensitivity and frequency-gain characteristics of the detector useful in analysing fast trains of light pulses are not the same as would be desirable in case of CW laser action.

MATSUDA and AYABE [11] have shown that the absolute temperature enters into the expression for the "electrochemical line-width" as

$$(E_s)_r = E'_{1/2} - 1.11 \frac{RT}{n\mathcal{F}} \quad (1)$$

and

$$(E_{s/2})_r = E'_{1/2} + 1.09 \frac{RT}{n\mathcal{F}} \quad (2)$$

NICHOLSON and SHAIN confirmed these results approximately a decade later with very minor exceptions¹.

The relationship between electrochemical line width and spectroscopic line width can be illustrated in a most obvious fashion by comparing an AC rather than a DC polarogram with a fluorescence peak (Fig. 1). Under the usual laboratory conditions a typical temperature such as 25°C causes considerable broadening

¹ In Analytical Chemistry 36, 706 (1964), NICHOLSON and SHAIN give 1.109 ± 0.002 in Eq. (1).

(Fig. 1, *a*); on the other hand, in a tuned dye laser the spectroscopic line-width may decrease by as much as a factor of 10^5 (Fig. 1, *c*), and the effective Gaussian temperature² also reduces the calculated electrochemical line-width to a very narrow one. It is significant to note that the conclusion holds not only for an ECL pumped dye laser, but also for well established optically pumped ones utilizing selective optical feedback. The changing slope of polarographic waves or the narrowing of electrochemical line-widths appears to have little practical significance within the context of Fig. 1 only. An additional property of dye lasers, however, leads

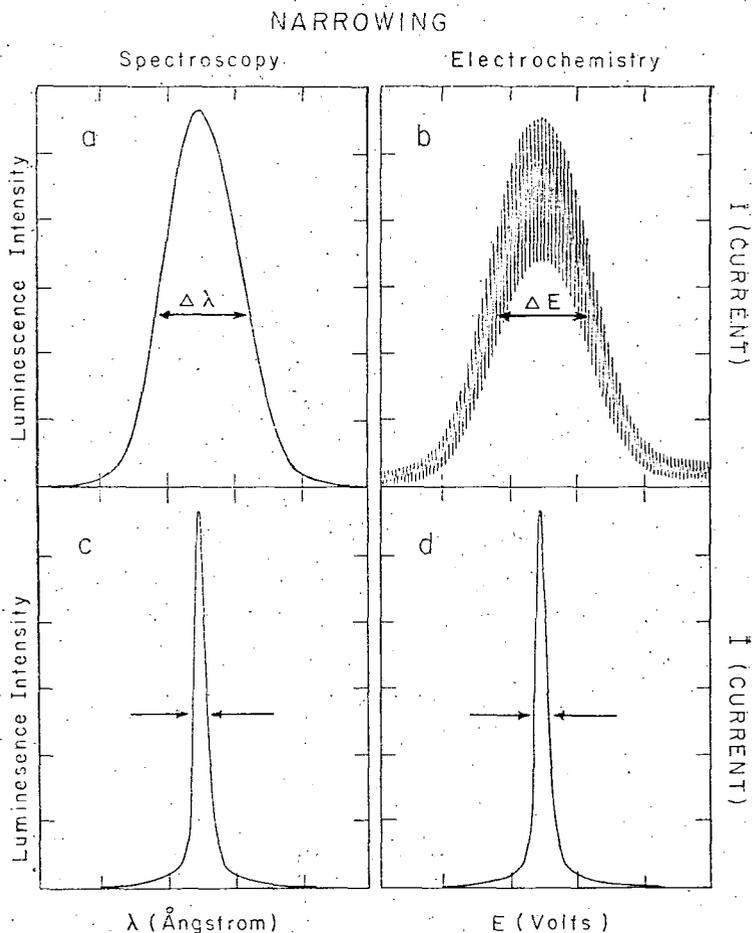


Fig. 1. Spectroscopic and electrochemical line-narrowing: *a* and *b* commonly observed line widths at ambient temperatures, *c* and *d* reduced line-widths associated with the ordered ensemble.

² The use of an "effective Gaussian temperature" has been discussed by the present author in "Statistical Aspects of Spectroscopic Line Narrowing", Paper presented at the 1974 Meeting of the Louisiana Academy of Sciences, Mathematics and Statistics Section.

to an extension of the above results which pertain to novel electrochemical separations or reactions that can only be carried out under laser action.

The tunability of the narrow spectral output *vs.* wavelength (λ) is well established, and is illustrated in Fig. 2, *a*. The relationship between E_s (the excited singlet energy) and E^0 for many compounds indicates a usual proximity of the two energy values. Altering E_s , as in Fig. 2, *a*, is also expected to alter E^0 , indicated in Fig. 2, *b*. In a

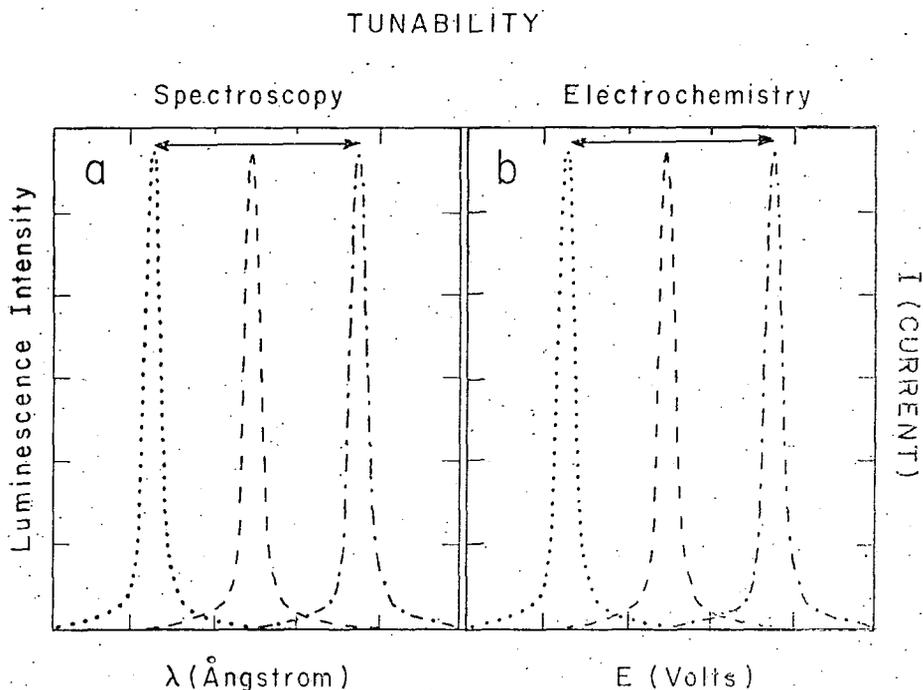


Fig. 2. Spectroscopic and electrochemical tunability in the ordered ensemble: *a* variation of λ , *b* variation of E^0 . (cf. Fig. 1, *c* and *d*).

mixture of two electroactive species having close E^0 values, but one of them being optically inactive while the other laser active (L), the shift of $E^0(L)$ provides an electrochemical selectivity previously unattainable by conventional means. A fuller treatment of the subject including details of the derivations and the results of planned experimental confirmation of the trends will be given in this journal subsequently.

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This was Paper No. 293 presented at the San Francisco Meeting of the Electrochemical Society, May 1974.

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ХИМИЯ В ЛАЗЕРАХ, V

Хемилюминесценция, возбуждённая электрическим путём,
и электрохимия в резонаторе лазера

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В статье, которая является продолжением предыдущих исследований, рассмотрено влияние оптического резонатора на параметры молекулярного ансамбля. Сужение спектральной ширины линии в перестраиваемых лазерах на красителях также приводит к уменьшению «электрохимической ширины линии» и смещение длины волны лазера сопровождается изменениями стандартного окислительного и восстановительного потенциалов. Результаты указывают на новый метод химического разделения в самом лазерном резонаторе.