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Enhancement of absorption spectra by dye-laser quenching, III: Quantitative aspects and a comparison of flash-lamp-pumped and cw systems under high resolution

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The enhancement of the detectability for trace absorptions by placing samples inside the laser cavity was found to be a factor of 100 for a flash-lamp-pumped dye laser and one thousand for a cw dye laser. High-resolution spectra showed that the holes in the laser output were as narrow as the absorptions that caused them. An approximately linear relationship (rather than the step-function behavior often associated with threshold phenomena) exists between pressures necessary to produce visually identical absorption spectra from samples placed inside and outside of the laser cavity. If such a relationship is of general occurrence, it will greatly facilitate the use of intracavity absorption for quantitative analysis, determination of relative absorption cross sections, and for the study of the kinetics of appearance and disappearance of transient species.

Index Headings: Lasers; Absorption; Spectra.

It has been shown that the detectability of trace absorptions can be enhanced by several orders of magnitude when the absorbing species is placed inside the cavity of a broad-band organic-dye laser.[1–6] The species observed by this technique include (a) gas phase[1,5,6]—Na, I_2, Ar^+, HCO, NH_2; (b) solution[2]—$Eu(NO_3)_3$ dissolved in methyl alcohol; and (c) flames[3]—Ba^+, Sr.

The gain of sensitivity was reported to be about 100 by Keller, Zalewski, and Peterson using a flash-lamp-pumped dye laser.[2] Hänsch, Schawlow, and Toschek used a cw dye laser to detect I_2 molecules inside the laser cavity and reported a gain in sensitivity of about 10^5.[4] They detected absorption by monitoring fluorescence from an I_2 sample placed outside the cavity, which, in effect, eliminated problems associated with detector resolution.

Klein observed absorptions from Ar^+ in the output of a cw dye laser when the pumping Ar^+ laser and the dye laser were part of the same optical cavity.[5] They noted that the holes in the laser output were much wider than absorption linewidths and could not explain this.

We have studied the enhancement of the high-resolution spectrum of I_2 placed inside the optical cavity of both a flash-lamp-pumped dye laser and a cw dye laser. Detector resolution was approximately equivalent for both systems. A linear correspondence was found between the appearance of the absorption spectra inside and outside the laser cavity. The slope of this ratio was approximately 100 for the flash-lamp-pumped laser, indicating that an increase of sensitivity of 100 was realized by placing the sample inside the laser cavity. The increase of sensitivity for the cw system was found to be approximately 1000. Some of the observed absorption lines were very narrow and appeared to be less than the resolution of the detector.

EXPERIMENTAL

The experimental parameters for the flash-lamp-pumped system are: (a) coaxial configuration; (b) output energy greater than 1 J; (c) pulse width less than 1 μs; (d) dye solution composed of 10 mg of rhodamine 6 G dissolved in a liter of absolute ethyl alcohol; (e)

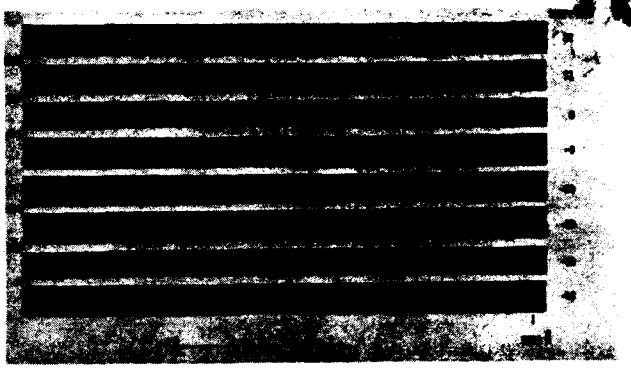

FIG. 1. Intracavity I_2 absorption as a function of the I_2 pressure in a flash-lamp-pumped dye laser, 10-cm sample cell.

Temperature (°C)	22	11	0
Pressure (torr)	2.5×10^{-1}	8.9×10^{-2}	3.2×10^{-2}
Temperature (°C)	−9	−20	−9
Pressure (torr)	1.3×10^{-2}	3.7×10^{-3}	1.2×10^{-3}
Temperature (°C)	−39	−46	
Pressure (torr)	3.2×10^{-4}	1.1×10^{-4}	

70-cm cavity length; (f) back mirror—1-m radius of curvature and reflectivity of 97%; (g) output mirror—planar with a 30′ wedge and a reflectivity of 65%; (h) 10-cm-long absorption cell with wedged, nonparallel windows; (i) spectrograph used in 10th order with resolution greater than 250 000.

The experimental parameters for the cw system are: (a) configuration followed that of Dienes, Ippen, and Shank[8]; (b) 200-mW output power; (c) dye solution composed of rhodamine 6 G dissolved in water containing 4% Ammonyx LO; (d) 2-m cavity length; (e) back mirror—10-cm radius of curvature and greater than 97% reflectivity; (f) intermediate reflector—10-cm radius of curvature and greater than 97% reflectivity; (g) output mirror—planar with a 30′ wedge and reflectivity of 94%; (h) 26-cm-long absorption cell with Brewster windows; (i) spectrum analyzer—2-mm gap and resolution equal to less than 250 000.

Iodine was sublimed into an evacuated sample cell, condensed in a cold finger at ice temperature and all residual gas pumped off. The concentration of I_2 in the cell was maintained and measured by controlling the temperature of a cold finger on the cell. Cold-finger

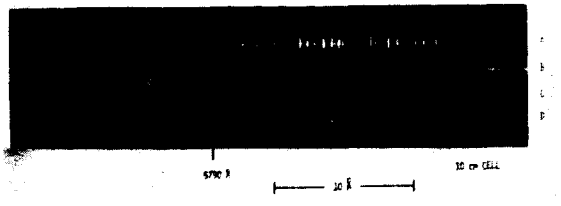

FIG. 2. Comparison of intracavity and extracavity I_2 absorption in a flash-lamp-pumped dye laser, 10-cm sample cell. A and D—sample inside the laser cavity; B—sample outside the laser cavity; C—Hg calibration. Pressure −0.25 torr in A and B and 3×10^{-3} torr in C.

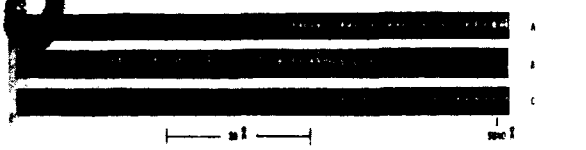

FIG. 3. Comparison of intracavity and extracavity I_2 absorption in a flash-lamp-pumped dye laser. Internal cell was 10 cm and external cell was 71 cm. A and C—sample inside the laser cavity; B—sample external to laser cavity. Optical path; A is 0.32 torr cm, B is 19.0 torr cm, C is 0.13 torr cm.

temperatures were obtained with thermo-electric cooling or liquid nitrogen formed slushes of various organic solvents. Temperatures were measured with a thermometer or thermocouple.

RESULTS

Laser spectra at several I_2 pressures are shown in Fig. 1. Iodine absorption features are visible at a pressure of 10^{-4} torr. The effect of lowering the concentration of I_2 in the cell is to make the holes in the laser output slowly disappear. Close inspection of Fig. 1 shows that some of the intracavity absorptions are very narrow and are probably limited by the resolution of the spectrograph.

A comparison of the spectrum inside and outside the cell is shown in Figs. 2 and 3. In Fig. 2, the same cell is placed inside and outside the laser cavity. The increase in the observed spectrum is striking. Also shown in Fig. 2 is the spectrum of a sample, with the cold finger at −23 °C, inside the cavity. This spectrum appears equivalent to the room-temperature spectrum outside the cavity and indicates that a gain of sensitivity of approximately 100 is realized by placing the sample inside the laser cavity. Similar conclusions are obtained

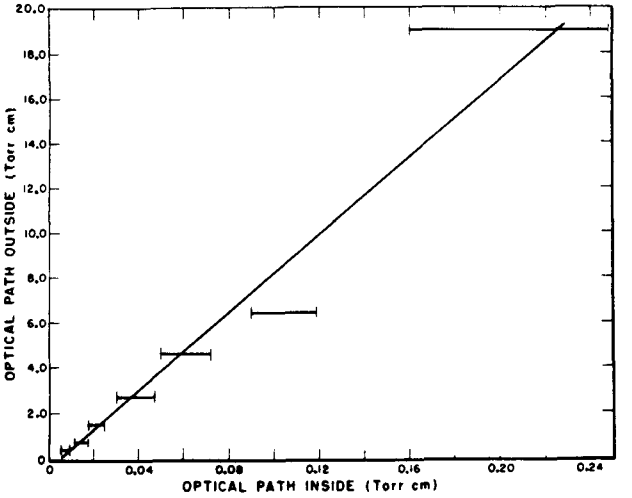

FIG. 4. Visually equivalent I_2 absorption spectra internal and external to the flash-lamp-pumped laser cavity, as a function of the optical path length.

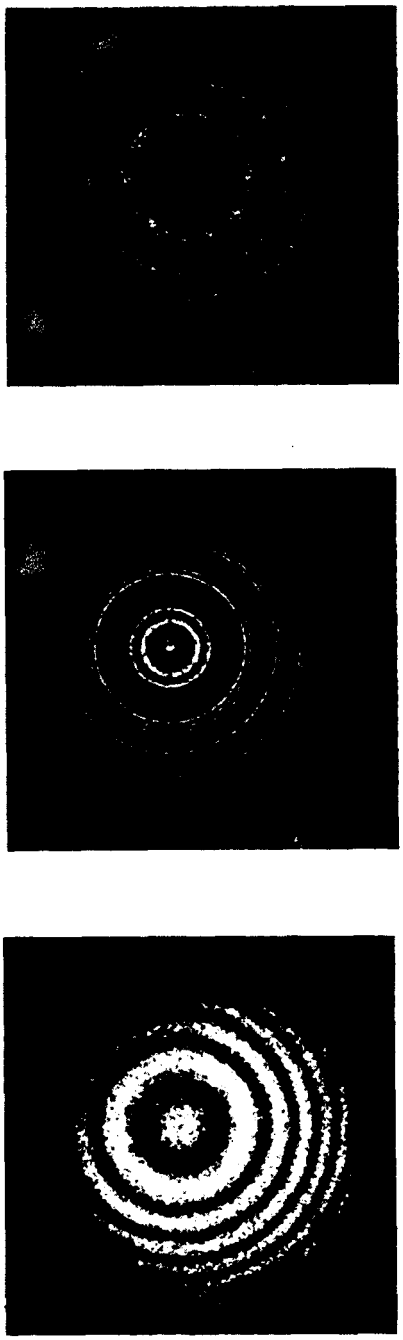

FIG. 5. Intracavity I_2 absorption as a function of the I_2 pressure in a cw dye laser. Top: temperature—77 K, pressure—0; middle: temperature—300 K, pressure—10^{-1} torr; bottom: temperature—210 K, pressure—10^{-5} torr.

from Fig. 3, which shows a comparison of the absorption spectrum between a 76-cm cell at room temperature outside the optical cavity and a 10-cm cell at reduced pressure inside the optical cavity. Again the increase of sensitivity is about 100.

Substitution of a 65% reflectance mirror for the total reflector did not effect the detectability limit, in agreement with previous results[1,2] that the sensitivity of the system does not depend upon the reflectance of the cavity resonators.

Comparisons of the type in Fig. 3 were used to determine the relationship that exists between the spectrum observed when the sample is inside the laser cavity and the normal spectrum observed for samples outside the cavity. A plot of the optical path lengths for visually equivalent internal and external spectra is shown in Fig. 4. This plot is linear, within rather large error limits, over two orders of magnitude and indicates that the intracavity technique can be used to determine ratios of absorption intensities and for quantitative estimations of concentrations. The error limits shown indicate our estimate of the validity of the visual matching.

A photograph of the interference fringes that result when the output of the cw dye laser was passed into a Fabry–Perot interferometer with 2-mm plate spacing is shown in Fig. 5. The laser bandwidth (approximately 0.5 Å) is the cause of the wide bands observed in the photograph. Iodine absorptions are distinguished by the dark concentric circles observed in the laser output (middle photograph). Close inspection of the bottom photograph shows that absorptions are still visible even at a pressure of 10^{-5} torr. This is a factor of 10 better than was obtainable with the flash-lamp-pumped system.

DISCUSSION

There are presently two theories developed to account for the increased sensitivity of detection of trace absorptions when samples are placed inside the cavity of a broad-band organic-dye laser. The first of these theories, developed by Keller, Zalewski, and Peterson,[2] ascribes the limit of sensitivity to fluctuations of the laser power (primarily the initial surge over threshold when the flash-lamp is turned on). The second theory, developed by Hänsch, Schawlow, and Toschek,[4] ascribes the limit of sensitivity to spatial inhomogenities of the laser saturation. Both theories predict a linear enhancement of the absorption process for samples inside laser cavities. This is apparent in Hänsch *et al.*'s, theory from Eq. (6) of Ref. 4. Keller *et al.*, did not develop analytical solutions, but from Fig. 10 of Ref. 2 it is easy to see that for weak absorptions, $(\tau_b/\tau_0 \sim 1)$,

$$\log\Phi_b/\Phi_0 \sim \delta(1-\tau_b/\tau_0), \tag{1}$$

where δ represents the slope of the various lines and is roughly proportional to $1/\tau_0$. Substitution of $\tau_b/\tau_0 \sim 1-\beta(C\tau_0/l\sqrt{R})$ from Eq. (6) of Ref. 2 into Eq. (1) above gives

$$\log\Phi_b/\Phi_0 \sim \delta'\beta C/l\sqrt{R}, \tag{2}$$

where β is the absorbance, C is the velocity of light, l is the cavity length, and R is the geometric mean of the mirror reflectances and $\delta' = \delta\tau_0$. This is a modified

form of Beer's law, where the term $\delta' C/l\sqrt{R}$ represents the linear enhancement. Note that, to the first approximation, τ_0 does not appear in Eq. (2) in agreement with experimental observations. Substitution of the calculated values of δ' into Eq. (2) ($\delta' \sim 1 \times 10^{-6}$, $l = 100$ cm, $R = 1$) gives the value of 300 for the enhancement, in good agreement with our experimental results. In summary, both theories predict a linear enhancement and, although the experimental observations of this work show a linear enhancement, as predicted, the results cannot be used to distinguish between the two theories.

The factor-of-10 improvement for cw systems over flash-lamp-pumped systems probably results from the absence of the large initial surge over threshold of the concentration of the first excited singlet state as the flash lamp turns on.[2] Smaller fluctuations, such as are caused by bubbles and thermal gradients, limit the sensitivity of the cw system. The resolution of the detection system does not seem to be the important factor in the difference of sensitivity of the two systems, because the resolution of the spectrograph in the flash-lamp-pumped system was greater, if anything, than the resolution of the Fabry–Perot étalon used as the detector in the cw system.

It is interesting to note that Hänsch *et al.*,[4] who detected intracavity absorption by monitoring changes of fluorescence intensity from an iodine cell external to the cavity did observe a greater intensity enhancement than we did.

The sensitivity was independent of the cavity life time for the flash-lamp-pumped system, in agreement with previous results.[1,2] It should be emphasized again that the increased sensitivity gained by placing the sample inside the laser cavity is not simply due to an increase of the number of transits through the sample cell by the photon beam. With a 65% reflectance output mirror, the average number of transits through the sample cell is less than 3. This is far short of the factor-of-100 gain of sensitivity.

The gradual disappearance of the I_2 spectrum shown in Fig. 1 demonstrates that the disappearance of the internal spectrum is not a step function. Figure 4 shows that the correspondence between external and internal spectra may be linear. These relationships improve the status of intracavity enhancement of trace absorption, from a system that can merely be used to find wavelength positions of weak transitions, to a system that can eventually be used for quantitative analysis, characterization of relative absorption cross sections, and as a tool for studying rates of appearance and disappearance of transient species for kinetic analysis. Improvements of technique will improve the quantitative aspects of the method.

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