In this present study, spectral and laser gain studies on some aminocoumarin laser dyes have been carried out using nitrogen laser excitation.

Dual ASE is observed in aminocoumarin dyes which have a free mobile amino group at the seventh position. The normal ASE is from the planar form of the excited state of the dye molecule, whereas the anomalous ASE is from the twisted intra molecular charge transfer (TICT) form of the excited state of the dye molecule. A complete charge transfer from the benzo ring to pyrone ring accompanies the twisted form of the excited dye.

Earlier reports stated that the twisted form is non-emissive or at the best weakly emissive. Under our excitation conditions, using a pulsed nitrogen laser of pulse width 10 ns as the pump source, it is possible to pump a large number of dye molecules to the excited states. Within their life time a sufficient number of molecules may transfer to the TICT state from the locally excited normal state of the excited dye molecules. This produces optical gain in the medium, and ASE may thus be obtained from this TICT form also, even if there is no detectable or noticeably different fluorescence on this transition from the TICT state.

The TICT states of the aminocoumarins can apparently be reached through two path ways of excitation. One of the
path ways is the excitation of the molecule from its ground singlet state to the first excited singlet state of the planar conformation and then transiting over the polarity controlled potential energy barrier into the TICT state. The second path way of excitation of the molecule is from its ground singlet state to the second excited singlet state of the planar conformation and then making a barrier less transition from this high lying energy level to the TICT state.

The TICT process appears to be relatively more favored in coumarin molecules having a strong electron donating substituent at the seventh position and a strong electron withdrawing substituent at the fourth position. For example dye C35 emits anomalous ASE in all the solvents studied.

TICT formation could be enhanced by solvent induced charge separation from the ICT state. For example in benzene which is non-polar, the normal ASE alone is emitted by the dye C1. In weakly polar aprotic solvents such as chloroform, n-butyl acetate etc., apparently both normal and anomalous forms coexist. In highly polar aprotic solvents such as acetonitrile only anomalous ASE from the twisted form exists. These polar solvents are capable of offering stronger stabilization to the TICT state owing to the enlarged dipole moment of the TICT state. In other words, the role of the solvent is to enhance the TICT formation and to stabilize it rather than to determine the formation, of the TICT state. This is confirmed from the fact that dye C35 emits anomalous ASE even in non-polar solvents like benzene, with the dye molecule itself becoming more polar on excitation.
The rate of variation of gain with temperature where the normal ASE alone is emitted is much less than the rate of variation of gain with temperature where the anomalous form alone is emitted. Thus, the method of measuring variation of gain with temperature, seems to be useful in identifying and classifying the emission as either from the normal form or from the twisted form since these two forms have different slopes of gain versus temperature.

In the dyes Cl and C445, where dual ASE is simultaneously observed, the small signal laser gain of the normal ASE form increases linearly with temperature and that of the anomalous ASE form decreases linearly with temperature. The rate of variation of gain with temperature from the normal (planar) form and the anomalous (twisted) form are equal and opposite indicating an apparent conversion from the normal form to the anomalous form.

This increase of gain of the anomalous ASE band with decrease of temperature appears to be due to two possible reasons. One is the increase of the polarity of the solvent when the temperature is decreased, the second is due to the variation of the rates of population of the TICT state from the excited second singlet state, as the temperature is varied.

In hydrogen bonding solvent like methanol the variation of gain with temperature has much higher values than those found for non H-bonding solvents. Therefore, the method of measuring the variation of gain with temperature can apparently be used to identify specific interactions such as H-bonding.
Since no solvent bonding is possible with benzene, the identical values of the rate of variation of gain with temperature for the dye C35 in benzene and chlorobenzene derivatives apparently indicates the absence of any specific bonding of the TICT molecule and the solvent molecule.

An attempt was made to understand the characteristics of the dual ASE bands of the aminocoumarin dyes by calculating the Forster and radiative type transfer rates from the normal and anomalous states of the donor dye in different binary dye mixtures. The study revealed that the total Forster type energy rate is independent of temperature whereas the total radiative type transfer rate varied with temperature. If the radiative transfer from the TICT state predominates the acceptor gain drops with increase of temperature and if the radiative transfer from the normal state predominates the acceptor gain increases with increase of temperature. Amongst the various dye mixtures studied in the case of the dye C515 energy transfer from Cl enabled us to obtain the normal ASE from this dye which otherwise displays only the anomalous ASE when pumped by the nitrogen laser. This seems to further confirm that the anomalous ASE is a non equilibrium transient phenomenon which occurs only under intense short pulse excitation. This technique of energy transfer seems to be quite useful for studying the ASE from the ICT and the TICT states.

The excitation of the normal ASE from the dye C515 via energy transfer to its first singlet band and the excitation of the normal ASE of the dye C35 using the third harmonic Nd:YAG laser and pumping into the singlet band of C35, seems to also confirm the postulate of populating the
TICT state via a barrierless crossing from the second singlet excited state of the dye molecule.

10.1 SUGGESTIONS FOR FURTHER WORK:

To further establish the validity of the TICT hypothesis proposed in this study it is suggested that the following investigations can be carried out further:

1. Synthesis of more coumarin dyes with different electron donor and acceptor groups at different position and carrying out gain studies and energy transfer studies will help to generalize and confirm the hypothesis proposed.

2. Time resolved studies of different excited states (excited state absorption as well as excited state ASE), can be carried out to obtain additional evidence for these TICT states. Excitation into both $S_1$ and $S_2$ states and their correlation with the TICT states can be studied using time resolved spectroscopy.

3. With the help of molecular orbital theory, one can attempt to study theoretically the twisting of the substituent group at different positions and correlate them with observed TICT energy levels.

4. The gain study can further be extended to other polar and also H-bonding solvent.

5. Energy transfer studies can be made to obtain normal ASE from dyes which display only anomalous ASE
(e.g. the fluorinated coumarin dyes C35, C485 etc.,) by using these fluorinated dyes as acceptors and choosing suitable donors and pumps so as to preferentially pump their first singlet state instead of the second singlet state (as happens with a N₂ laser pump).