mechanisms for onset of chaos in many systems is the period doubling bifurcations. This route to chaos is characterised by a universal behaviour described by two
universal indices viz. the bifurcation rate and the scaling factor \( \alpha \) as well as the
universal function \( g(x) \). These are usually computed numerically.

The thesis reports a new analytic algorithm developed using a perturbative
scheme to compute \( \alpha \),
and \( g(x) \) for general one hump maps of the form
\( x_{n+1} = 1 - a \times n^x \) where \( z \) is the order of the local maximum. For a given \( z \), it
is possible to carry out the calculations to any order of accuracy. However the
perturbative series is not highly convergent but asymptotic in nature and so the
use of Padé approximants is found to give reliable results. When \( z \) is not an
integer, but \( z = z' \pm \epsilon \) with \( z' \) the integer nearest to \( z \), the expressions for \( \alpha \)
and \( g(x) \) can be expanded in powers of \( \epsilon \).

At the accumulation point of the bifurcations \( \alpha_s \), the iterates of \( g(x) \) form
a nearly self-similar Cantor set. The first three dimensions \( D_0 \), \( D_1 \), \( D_2 \) of this set
are computed using our method and their variation with \( z \) is studied.

The latter part of the thesis deals with investigations on the onset of chaotic
behaviour in a driven pendulum with van der Pol like dissipation. We apply
Melnikov criterion to predict the onset of chaos in this system, followed by a
detailed numerical analysis. We observe that at low frequencies, the system has
a strange attractor while at medium frequencies, the limit cycle develops a
stochastic band. Inside the band, subharmonic bifurcations can be observed.

The effect of an additive white noise in this system is to wash out the

S.p.37. Abdul Rasheed, T.M.—Laser induced thermal lens and
near infrared absorption studies of CH overtones in some
organic compounds—1988—Dr. V.P.N. Nampoori

With the advent of laser technology and parallel developments in detection
techniques, research in spectroscopy has attained new dimensions. Measurement
of weak absorptions arising from vibrational overtone and weakly allowed electronic
transitions is one such area. Two optothermal techniques namely photoacoustic
and thermal lensing are now-a-days used to detect such weak absorptions.
Vibrational overtone spectroscopy of X-H (X = C, N, O) containing molecules is
an area of considerable interest and both the above mentioned experimental
techniques are being used for overtone spectroscopy. The following specific
reasons are seen as the motivation for the interest in X-H overtone spectroscopy.

(1) It is recognised in the study of nonradiative electronic relaxation processes
that highly excited vibrational levels in the ground electronic state actively
participate in the intramolecular energy relaxation. (2) The conventional normal
mode description, which is widely and successfully used to describe fundamental
molecular vibrations fails to provide a satisfactory description of the very anharmonic
overtones. One can in principle introduce anharmonic coupling terms in the
Hamiltonian and can predict the overtone spectra. But such an approach is
shown to predict complicated spectral features, and is contrary to what is
experimentally observed. This led to the introduction of the local mode model
for describing the highly excited vibrational states of X-H containing molecules.

(3) An understanding of highly excited vibrational states is an essential part
of the development of a satisfactory theory of multiphoton photochemistry. (4) The
spectroscopic and theoretical studies of anharmonic oscillators are concerned
with the excitation of chemical bond dissociation energies. Thus they provide
properties and chemical reactivity.

This thesis presents a detailed account of the

The experimental set up uses a Rhodan
argon laser. The pump beam (50-100
(10-25 Hz) causes a time dependent thermal
index gradient within the sample. A probe
through the sample gets modulated by this
of the modulation depends on the absorption
pump wavelength. Also, this signal is linear
levels. The signal is detected in the far field
with a He-Ne laser line filter and pinhole. The
detected using a lock-in amplifier. Scanning
the lock-in signal yields the overtone

The experimental configuration used in the
of the configuration used by Swofford et al. to
suit the present set up and also to obtain
work of Swofford. For successful measurement
transitions, several important experimental con
of experimental set up takes into account all
while the spectra in the fifth overtone (\( \alpha \) thermal lens technique, the spectra upto these
are recorded in a Hitachi Model 330 UV-VIS
pointed out that even the fourth overtone
recorded in spectrophotometers and the fifth
sensitivity techniques such as the thermal lens.
The overtone data from \( \Delta V = 2 \) to \( \Delta V =
the infrared and the high sensitive thermal lens
using the local mode model. The model treats
anharmonic oscillators. For the X-H oscillators
coupling terms are introduced in the local model
which characterise a local mode are the
anharmonicity. These parameters are very
environment, conformation states and stereo

The spectroscopic and structural information
and thermal lens spectroscopic studies of C
organic compounds are summarised below.
any systems is the period doubling bifurcations,
d by a universal behaviour described by two
rate and the scaling factor \( \lambda \) as well as
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\( k \) for general one hump maps of the form
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ions to any order of accuracy. However the
revertent but asymptotic in nature and its
it to give reliable results. When \( z \) is not an
integer nearest to \( z \), the expressions for \( x\)
of \( E \). 

- The conventional normal
nonradiative electronic relaxation processes
in the ground electronic state acti-
ve in this system to wash out the random
approach to chaos is accelerated by noise.

- The overtone transitions are very weak in intensity compared with the fundamental
measurements and both the above mentioned ex-
perimental and theoretical studies of highly excited vibrational levels are
concerned with the excitation of chemical bonds to a significant fraction of
their bond dissociation energies. Thus they provide an important link between spectral
properties and chemical reactivity.

This thesis presents a detailed account of the work done by the author during
the past few years in the Department of Physics, Cochin University of Science
and Technology. The main experimental work that has been carried out is the
setting up of a dual beam cw laser induced thermal lens spectrometer and
measuring the fifth CH overtone spectra of several liquid phase organic compounds.
The overtone transitions are very weak in intensity compared with the fundamental
transitions (the fifth overtone transition being a million times weaker than that of
the fundamental) and the recording of such spectra requires high sensitivity
experimental techniques. Important among them are thermal lensing and
photoacoustic detection. Of these the thermal lens technique is ideal for liquid
phase measurements [1] which has been used for the present studies.

The experimental set up uses a Rhodamine 6G dye laser pumped by an
Argon ion laser. The pump beam (50-100 mW) chopped at a low frequency
(10-25 Hz) causes a time dependent thermal lens resulting from the fluctuating
index gradient within the sample. A probe He-Ne laser beam passing collinearly
through the sample gets modulated by this fluctuating thermal lens. The strength
of the modulation depends on the absorptivity of the sample at the particular
pump wavelength. Also, this signal is linear in pump power for moderate power
levels. The signal is detected in the far field from the sample using a PMT fitted
with a He-Ne laser line filter and pinhole. The output of the PMT is synchronously
detected using a lock-in amplifier. Scanning the dye laser and power normalizing
the lock-in signal yields the overtone absorption spectrum.

The experimental configuration used in the present study is a modified version
of the configuration used by Swofford et al. [2]. The modifications were made
to suit the present set up and also to obtain certain advantages over the earlier
work of Swofford. For successful measurement of the extremely weak overtone
transitions, several important experimental considerations are required. The present
experimental set up takes into account all these factors.

While the spectra in the fifth overtone \( \Delta V = 6 \) region are obtained by the
thermal lens technique, the spectra upto the fourth overtone regions \( \Delta V = 2-5 \)
are recorded in a Hitachi Model 330 UV-VIS-NIR spectrophotometer. It is to be
pointed out that even the fourth overtone \( \Delta V = 5 \) is extremely weak to be
recorded in spectrophotometers and the fifth overtone necessarily requires high
sensitivity techniques such as the thermal lens spectroscopy.

The overtone data from \( \Delta V = 2 \) to \( \Delta V = 6 \) obtained by the conventional near
infrared and the high sensitive thermal lens spectroscopic technique are analysed
using the local mode model. The model treats a molecule as a set of uncoupled
anharmonic oscillators. For the X-H oscillators belonging to a common X atom,
coupling terms are introduced in the local mode Hamiltonian. The two parameters
which characterise a local mode are the mechanical frequency and the
anharmonicity. These parameters are very sensitive to the type of the oscillator,
environment, conformation stats and steric interferences.

This spectroscopic and structural information obtained from the near infrared
and thermal lens spectroscopic studies of CH overtones recorded here in some
organic compounds are summarised below.
i) 1, 2-Dichloro and Dibromo ethanes

The near infrared overtone spectra of liquid phase 1, 2 dichloro and 1, 2 dibromo ethanes in the spectral regions of \( \Delta V = 2-5 \) are studied. The observed spectral features are assigned using the local mode model. Local mode frequencies and diagonal local mode anharmonicities are obtained from an analysis of the spectra. The local-local combinations observed are interpreted on the basis of a coupled CH oscillator model Hamiltonian. Local normal combinations show complex structures and their possible assignments are also given.

ii) Acetophenone and Benzaldehyde

Overtone spectra of Acetophenone and Benzaldehyde in the visible and near infrared regions are studied by the dual beam thermal lens and conventional absorption techniques respectively. The observed increase in the mechanical frequency of aryl CH bonds from that of benzene is attributed to the decrease in aryl CH bond length caused by the electron withdrawing property of the substituents. It is also shown that the main influence arises from the carbonyl group in the substituents. Overtone spectra also demonstrate that acetophenone contains two types of methyl CH bonds arising from the anisotropic environments created by the oxygen lone pair and carbonyl \( \pi \) electron interactions. The local mode parameters of the two types of methyl CH modes are compared with those of acetone and acetaldehyde reported by other workers earlier. The possible factors influencing the methyl CH bonds in acetophenone are discussed.

iii) 2-Butanone

The near infrared absorption spectrum of liquid phase 2-butane in the overtone regions \( \Delta V = 2-5 \) is studied. The main peaks observed in the spectrum are assigned to pure overtones of the methyl group away from the carbonyl group. This methyl group is shown to maintain \( C_3v \) symmetry. The calculated peak positions of the overtone spectrum using \( C_3v \) local mode Hamiltonian agree with the observations. It is also shown that the overtones of the out-of-plane CH bonds of the adjacent methyl group are coincident with the overtones of the independent methyl group, while the overtones of the in-plane CH bond are on the high energy side.

iv) Styrene and Polystyrene

The vibrational overtone spectra of styrene (liquid) and polystyrene (solid) are studied in the visible and near infrared regions using dual beam thermal lens and conventional absorption techniques respectively. A local mode analysis of the spectra has shown that the prominent absorption bands in both the compounds are aromatic CH overtones. The local mode parameters of the two compounds are found to be close to those of benzene. For polystyrene, the overtones of the \( S_p^1 \) CH bonds appear on the low energy side of the aryl CH overtones. This work presents the first thermal lens overtone observation in a polymer. This is also the first thermal lens overtone study in a solid.

v) Trichloroethylene

As a good candidate containing a single CH oscillator, the overtone spectrum of trichloroethylene in the visible and near infrared thermal lens and conventional methods respectively. The frequency is observed relative to that in withdrawing property of the halogen atoms used to predict the change in CH bond. The fifth overtone region shows Fermi resonance between combination states. The magnitude of the deduced from an analysis of the spectrum.

vi) Monochloro and Monobromo benzene

The fifth overtone spectra of these compounds and conventional absorption were have reinvestigated these spectra using the thermal lens and conventional absorption techniques respectively. Thus the present overtone spectroscopic and structural details of the molecules are presented in seven chapters.

S.p.38. RAMACHANDRAN, T. - K. Sathanandan

Pulsed uv lasers and tunable dye laser applications as sources for various physical, chemical physics, and medicine. The demands on the laser power, stability and repetition rate become more important as technology advances. The first chapter begins with a brief analysis of nitrogen laser action in nitrogen gas. It is shown that molecules are a pre-requisite for population of laser transitions in a medium. The optical pumping of a medium by the laser light can be incorporated into a laser amplifier with other types of discharge circuits in a
spectra of liquid phase 1, 2-dichloro and 1, 2-ethanes of \( \Delta V_m = 2-5 \) are studied. The observed shift in the local mode model. Local mode frequencies

Corrections are obtained from an analysis of the

theoretical results on the basis of the Hamiltonian. Local normal combinations show possible assignments are also given.

bonds arising from the anisotropic environments

So that of benzene is attributed to the decrease

in the visible region using dual beam thermal lens and conventional techniques respectively. A local mode analysis of the two compounds

infrared regions using dual beam thermal lens and conventional absorption were reported earlier by other workers. We

have reinvestigated these spectra using the cw dual beam thermal lens technique. The physical mechanism of CH bond strengthening resulting from the halogen substituents is also proposed.

Thus the present overtone spectroscopic studies using laser induced thermal lens and conventional absorption techniques have yielded several spectroscopic and structural details of the molecules studied.

The fifth overtone spectra of these compounds detected by pulsed thermal lens and conventional absorption were reported earlier by other workers. We

have reinvestigated these spectra using the cw dual beam thermal lens technique. The physical mechanism of CH bond strengthening resulting from the halogen substituents is also proposed.

Thus the present overtone spectroscopic studies using laser induced thermal lens and conventional absorption techniques have yielded several spectroscopic and structural details of the molecules studied.

Pulsed uv lasers and tunable dye lasers pumped by them find important applications as sources for various experiments in spectroscopy, solid state physics, chemical physics and medicine. As the experiments advance to higher sophistication, the demands on the laser characteristics such as power, pulse width, stability and repetition rate become more stringent. The present thesis reports the work carried out by the author on the design, fabrication and optimisation of a high power nitrogen laser and a tunable dye laser with an oscillator-amplifier configuration. The studies also include applications of the above lasers to the investigations on solvent effects of Rhodamine 6G dye laser, energy transfer studies on mixed dye systems and radiative decay characteristics of Ho\(^{3+}\) ions in CaF\(_2\) lattice. The above problems have direct applications on laser physics itself, since studies on solvents and mixed dye systems can lead to better designs of active media for dye lasers. Also, since CaF\(_2\) Ho\(^{3+}\) is one of the few solid state materials having laser transitions in green region, considerable importance is attached to its detailed study. The investigations outlined above are presented in seven chapters.

The first chapter begins with a historical survey on the various designs of nitrogen lasers followed by a brief analysis of the theoretical considerations for laser action in nitrogen gas. It is shown that a very fast excitation of nitrogen molecules is a pre-requisite for population inversion. This is accomplished by a fast electrical discharge which dictates a very low impedance pulse circuit. A Blumlein circuit with transverse excitation is ideal for this, since with a moderate voltage it is possible to excite the gas at high pressures. Details of how a Blumlein circuit can be incorporated into a nitrogen laser is given. A comparison with other types of discharge circuits is also presented.