

### **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 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 [2] 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 [ ]. 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 states and steric interferences.

The 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  $\Delta V_{CH} = 2-5$  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-butanone 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  $CH_b$  bonds of the adjacent methyl group are coincident with the overtones of the independent methyl group, while the overtones of the in-plane  $CH_a$  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  $Sp^3$  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 regions are studied using thermal lens and conventional methods respectively. A high value of the mechanical frequency is observed relative to that in ethylene, which arises from the electron withdrawing property of the halogen atoms. The fifth overtone energy value is used to predict the change in CH bond length from that in ethylene. The  $\Delta V = 3$  region shows Fermi resonance between pure overtone and stretch-bend combination states. The magnitude of the Fermi interaction matrix element is deduced from an analysis of the spectrum.

#### **vi) Monochloro and Monobromo benzenes**

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.