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OVERTONE SPECTRUM OF POLY BENZYL AMINE-ANALYSIS USING LOCAL MODE MODEL

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Abstract:

Overtone Spectrum of Poly benzyl amine prepared by RF plasma polymerization method is analyzed using local mode model. The analysis of the observed CH and NH local mode mechanical frequency values show that donation of electron density does not take place from NH_2 group to the phenyl ring. So the ring CH mechanical frequency of benzyl amine remains unchanged compared to that of benzene. Due to polymerization through NH, the NH mechanical frequency of poly benzyl amine decreases compared to that of benzyl amine.

Keywords: Vibrational spectrum, local mode model, Benzyl amine, Poly benzyl amine.

Introduction:

Vibrational overtone spectra of molecules containing X-H bonds (X = C,N,O) in the near infrared region and their interpretation by local mode model is now, a well established tool for drawing information on molecular structure and dynamics [1-4]. The local mode model treats the molecule as a set of loosely coupled anharmonic oscillators and the overtone transition energies generally obey the relation

$$\Delta E_{0\rightarrow v} = Av + Bv^2$$

Where 'v' is the quantum level of excitation. A-B $=X_1$ is the mechanical frequency and B= X_2 is the anharmonicity of the X-H bond. The X_1 and X_2 parameters are sensitive not only to the bond type but to conformational state of the molecule and the inter intra molecular environment to which the X-H bond is subjected. This has made overtone spectroscopy an important tool for structural analysis [5-9]. The local mode model in which the X-H oscillators are considered to be loosely coupled anharmonic oscillators has been widely used for the interpretation of overtone spectra. The local mode parameters X_1 and X_2 vary for nonequivalent X-H bonds and are sensitive to the inter and intramolecular environment on the X-H oscillator.

In the present paper we report the CH and NH overtone spectra of polymer poly benzyl amine. The analysis of the spectra shows that plasma polymerization of benzyl amine occurs through NH bond thereby decreasing the NH mechanical frequency of poly benzyl amine. The present result clearly shows that overtone spectroscopy can be an effective tool in probing polymerization and understanding bond linkage in polymers.

Experimental:

(a) Preparation of polymer thin film.

The thin film of poly benzyl amine is obtained by high frequency discharge. An ac power supply operating at 4.5 MHz is utilized through capacitive coupling for high frequency plasma polymerization. The samples are prepared on clean optically flat glass substrates which are cleaned by chemical and ultrasonic methods prior to placing in the plasma polymerization chamber. The polymerization chamber is initially pumped to ≈ 10^{-2} torr and then the monomer benzyl amine is allowed to enter the chamber. After a steady monomer pressure of ≈ 0.5 torr is maintained, the RF is applied to obtain a glow discharge between the electrodes. Polymerization takes place and the polymer is deposited on the substrates placed between the electrodes. A uniform polymer film of sufficient thickness is obtained.

(b) Overtone Spectra

The near infrared absorption spectra of poly benzyl amine is recorded using a Hitachi UV-VIS-NIR dual beam spectrophotometer in the wavelength range 650-2000 nm. This region contains CH and NH overtone bands from second through fourth quantum level of excitation along with associated combination bands.

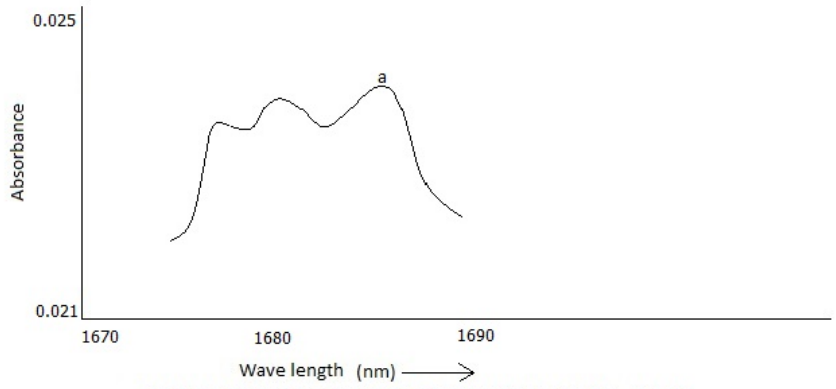

Fig.1 CH Overtone spectrum of poly benzyl amine in the Δv = 2 region

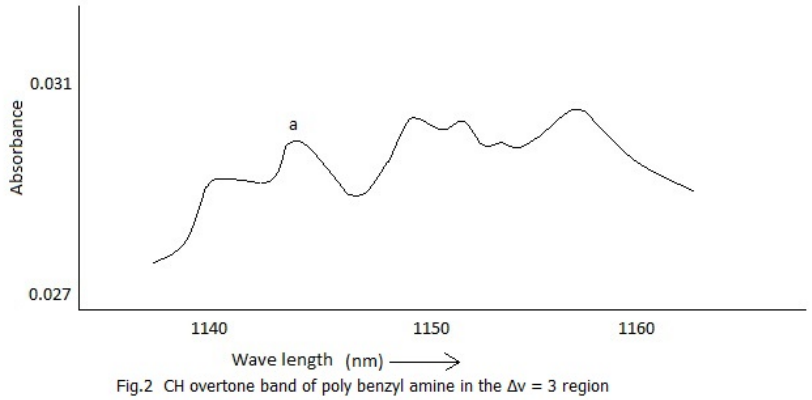

Fig.2 CH overtone band of poly benzyl amine in the Δv = 3 region

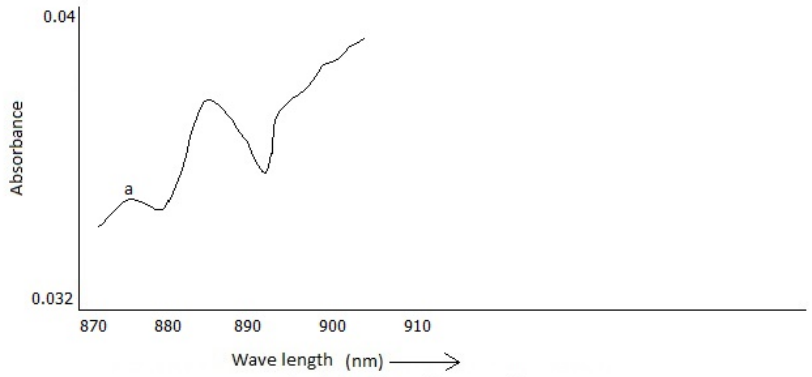

Fig 3 CH overtone band of poly benzyl amine in the Δv = 4 region

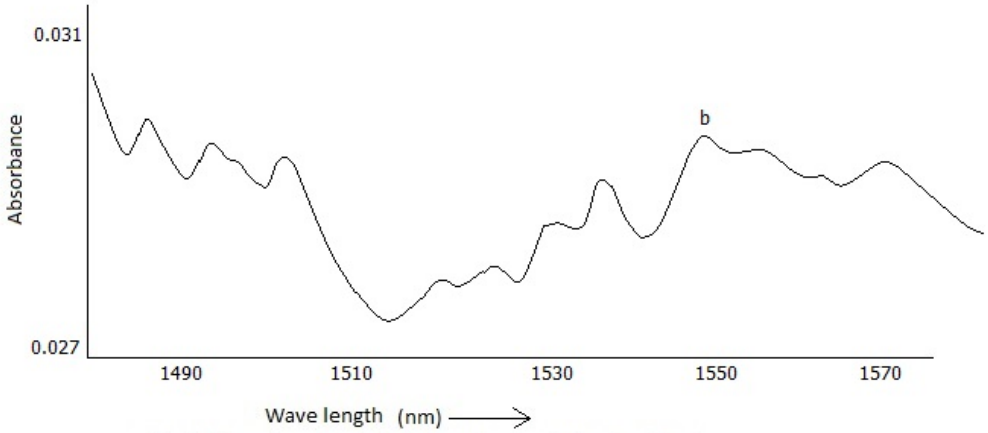

Fig 4. NH overtone band of poly benzyl amine in the Δv = 2 region

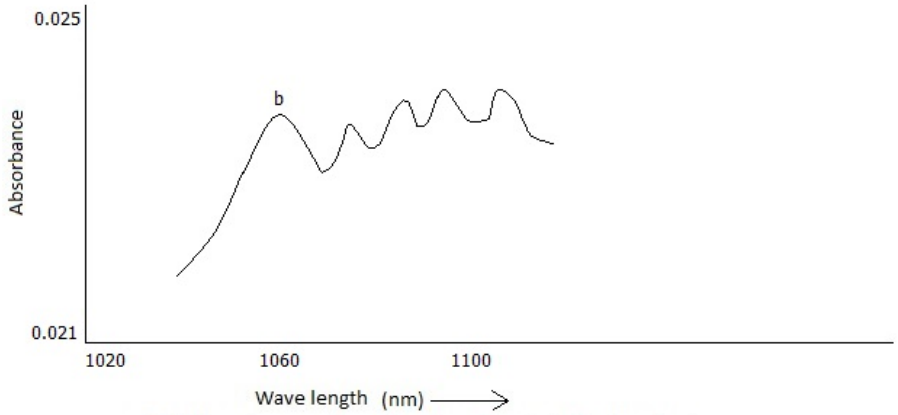

Fig 5 NH overtone spectrum of poly benzyl amine in the Δv = 3 region

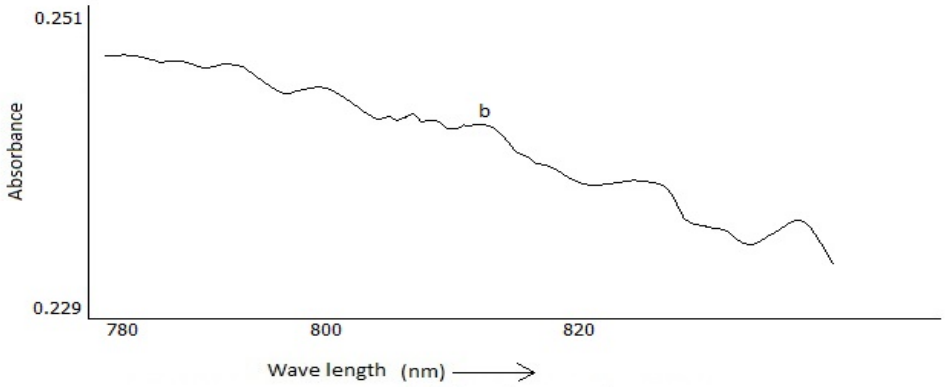

Fig 6. NH overtone spectrum of poly benzyl amine in the Δv = 4 region

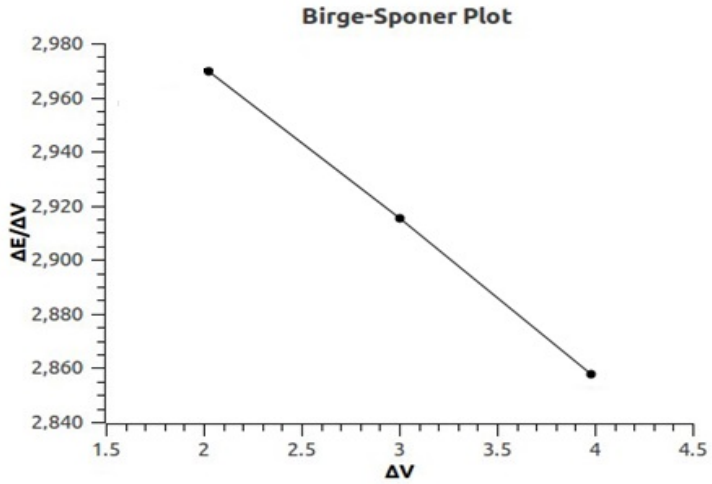

Fig.7 (Birge- Sponer Plot for CH)

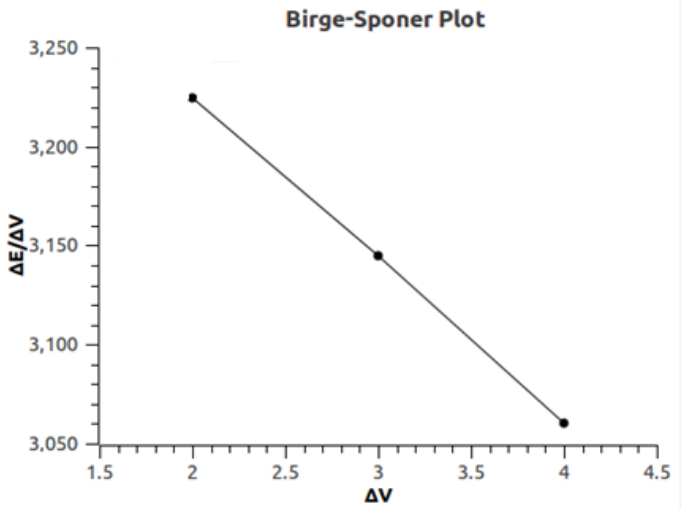

Fig 8 Birge – Sponer Plot for NH

Table 1.

Observed overtone energies (cm^{-1}), mechanical frequencies X_1 cm^{-1}, anharmonicities (X_2) of CH and NH local modes of poly benzyl amine. The least square correlation coefficient (Υ) are also given.

Molecule	Δv = 2	Δv = 3	Δv = 4	X_1	X_2	Υ
Poly benzyl amine						
Ring CH	5945.3	8738.2	11423.35	3147.17	-58.41	-0.99989
NH	6448.7	9433.96	12239.9	3472.36	-82.37	-0.99982
Liquid benzyl amine						
Ring CH				3139	-58.71	-0.9998
NH				3505	-74.16	-1.0000

1. Results and Discussion

The CH and NH overtone spectrum of poly benzyl amine thin film in the region Δv=2-4 is shown in figure 1-6. In these figures "a" represent CH overtones and "b" represent NH overtones. The spectrum of poly benzyl amine is very complex. The overtone region shows multiple peaks. These multiple peaks occur due to the existence of many combinations having comparable energy and oscillator strength to those of pure overtones. The pure overtone peaks of poly benzyl amine are assigned after trying many peaks in the regions for the Birge-Sponer plot. The assignments of pure overtones are given in table 1. The CH local mode parameters obtained from the Birge-Sponer plot are X_1 = 3147.17 cm^{-1}, X_2 = -58.41 cm^{-1} with very good correlation Υ = -0.99989. The NH local mode parameters obtained are X_1 = 3472.36 cm^{-1}, B = -82.37 cm^{-1} and Υ = - 0.99982.

A comparison of the local mode parameters of benzyl amine and poly benzyl amine shows that the ring CH mechanical frequency of benzyl amine [10] is less than that of poly benzyl amine. Extensive studies reported in substituted benzenes have shown that an electron withdrawing substituent causes an increase while an electron donating substituent causes a decrease in aryl CH mechanical frequency. The reduced value of aryl CH mechanical frequency in benzyl amine with respect to poly benzyl amine occurs due to electron donation from NH_2. In poly benzyl amine donation of electron from NH bond to the phenyl ring does not take place

owing to polymerization. Therefore the NH mechanical frequency of poly benzyl amine compared to that of benzyl amine decreases due to increased electron density.

In conclusion, we have reported the NIR vibrational Overtone Spectra of poly benzyl amine. The reduced value of ring CH mechanical frequency in benzyl amine compared to poly benzyl amine is explained as due to donation of electron from NH to aryl CH bond.

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