Determination of Thermo Physical Parameters of C_{60} Using Fourier Transform Infrared Photoacoustic Spectroscopy

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The thermo physical parameters thermal effusivity (e) and thermal diffusivity (α) have been measured using Fourier transform infrared (FTIR) Photoacoustic spectroscopy (PAS) for two different purities of C_{60} fullerenes (99.5 % , 98.5%) samples in the powder form. The experimental results shows that the values of thermal diffusivity is less then that obtained for crystalline C_{60} fullerenes. The data obtained are comparable with those obtained by microscopic infra-red radiometry

1. Introduction:

The C_{60} molecule was discovered as peak in the mass spectra of quenched carbon vapor [1]. In order to explain the stability of this molecule Krtoto et al.[2] proposed the highly symmetric soccer-ball- like molecular shape coined Buckminsterfullerene. The unique geometry of this compound, known as an icosahedra structure, and its possession of superconductivity attract attention of several groups the world over with a view to understand the chemistry, physics of this material. Because of its usually high symmetry, C_{60} is expected to have only four infrared active modes [3]. Thermal characteristics of such materials play a major role in the development of newer applications. Many spectroscopic properties of this compound have been already reported in a short time through the experimental investigation investigations such as IR, UV [3] and Raman spectroscopy [4].

Fourier transform infra read (FTIR) Photoacoustic spectroscopy (PAS) is a nondestructive technique for measuring the sample's absorbance directly with controllable depth and with no sample preparation. In this technique The PAS signal generation sequence starts with the infrared beam of the FTIR spectrometer being incident on the sample and the nonreflected beam component penetrating into the sample a distance approximately equal to $1/\beta$

where β is the absorption coefficient. Absorption and thermalization of light with intensity modulated by the interferometer, results in instantaneous temperature oscillation within the sample. The instantaneous temperature oscillation generate thermal waves with a decay coefficient $a_s = (\pi f/\alpha)^{1/2,}$ where f is the modulation frequency and α is the sample thermal diffusivity. These absorption- generated thermal waves propagate back in part to the incident beam surface and also cause the gas atmosphere in contact with the surface to oscillate in temperature. The temperature oscillations produce pressure oscillations in the small volume sample chamber of the PA detector which are detected by a sensitive microphone as the photoacoustic signal.

Several authors dealing with thermal properties of C_{60} have used laser, flash method and microscopic infrared radiometers [5,6]. In the present work we have been employed the FTIR PA to measure the absorption spectra of C_{60} . We also demonstrate the application of this technique for nondestructive evaluation of thermal effusivity (e) and thermal diffusivity (α) of the same samples. Where $e = \sqrt{k\rho c}$ and α = k/ ρc, k, ρ and c are the thermal conductivity , mass density and specific heat respectively.

The thermal effusivity (e) of the sample can be determined by employing the FTIR PA technique, where (for optically opaque and thermally thick sample) the PA signal amplitude is given by [7]

$$q = A/fe \tag{1}$$

$$A = \frac{I_o \gamma P_o \alpha_g^{1/2}}{4\pi \ell_g T_o} \tag{2}$$

I_o is the intensity of the incident radiation, T_o and P_o are the ambient pressure and temperature respectively, γ is the ratio of gas specific heats, ℓ_g is the length of the gas column of the PA cell. Using the powder Si as a slandered material of Known effusivity, the constant A can be determined and applied to determine the effusivity for the C_{60} samples.

2. Experiment:

The FTIRPA data reported here have been obtained at room temperature by the use of an FTIR 600 spectrometer (Jasco - Japan). The intensity modulation of the IR beam is produced by a path difference modulation via a Michelson interferometer .Typically 100 scans at resolution 8 cm^{-1} , scan speed 0.5 mm /sec and maximum aperture (7.1 mm), were used to collect the spectra from 400 to 2000 cm^{-1} range. The modulation frequency (f) depends on the mirror velocity of the spectrometer's interferometer according to the formula f = v υ where v is the optical path difference velocity and υ is the wave number of the incident IR beam. An MTEC model 300 photoacostic cell (MTEC photoacoustic Ames Iowa, USA) with its accompanying preamplifier was used to obtain all spectra. The PA window is KBr has a transmission range from 385 to 40,000 cm^{-1}. The sophisticated design of MTEC 300 PA detector allows changing of various samples by removing only the sample carrier, while the optical microphone always remain in the same arrangement. For normalizing the acquired spectra a carbon black standard (MTEC) was used. Two C_{60} samples of purities 99.5 % and 98 % in the powder form have been used. The two samples were obtained from a commercial supplier.

3. Results and Discussions:

For each measurement the sample was placed in the sample holder and inserted in the PA cell. Spectra were recorded on FTIR spectrometer between 400- 2000 cm^{-1} at mirror speed 0.05 cm/sec and resolution 8 cm^{-1}. All spectra were normalized to carbon black reference. The PA FTIR spectra obtained from C_{60} of purity 99.5 % is shown in Fig (1a). From the figure we observe that the presence of four characteristic strong bands (1429, 1182, 573, 491.75 cm^{-1}) as expected for the free truncated icosahedra model with its usually high symmetry. These bands are the same as those obtained by Donald et al. for IR spectra [3]. However, the band at 1000 cm^{-1} may be due to some contamination. Fig. (1-b) shows The FTIR PA spectra obtained from C_{60} of purity 98 %. From the figure we also observe the same four vibration active modes are obtained.

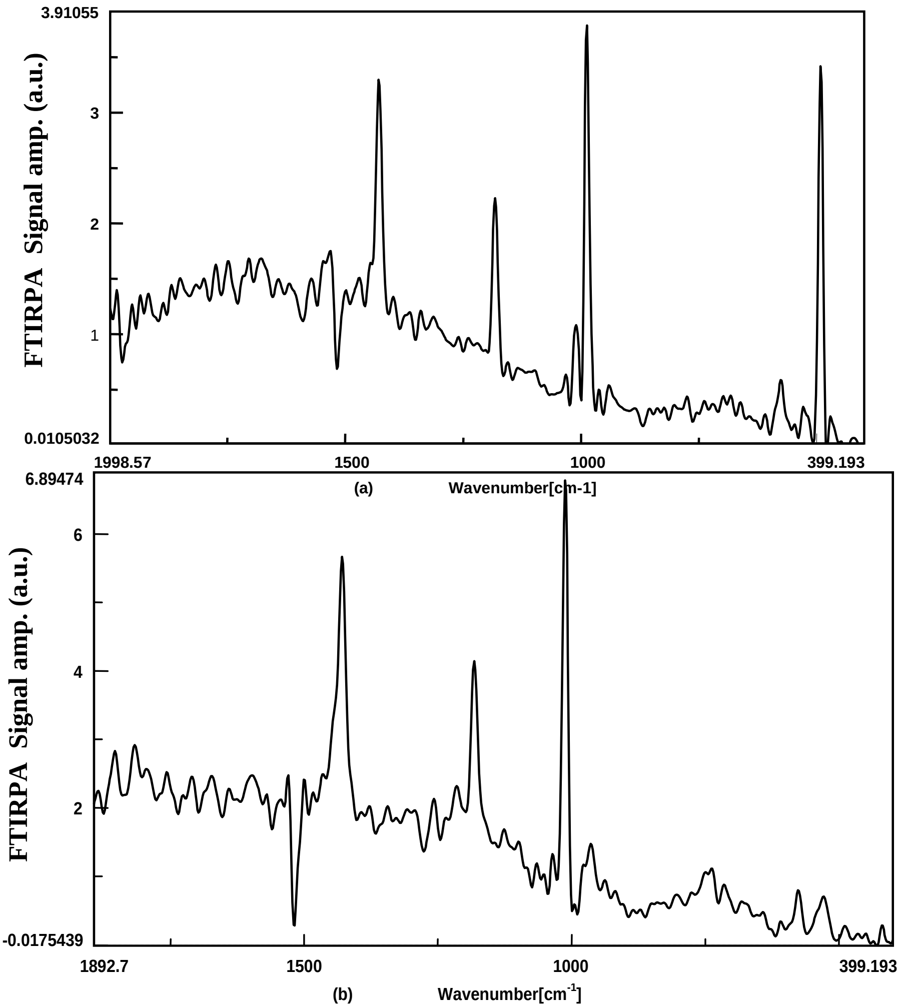

Fig (1): FTIRPA spectra for C_{60} normalized to carbon standard at resolution 8 cm^{-1}, scan speed 0.5 mm/sec and aperture 7.1 mm (a- purity 99.5% , b- Purity 98 %).

For thermal parameters measurements the FTIRPA spectrum were recorded for each C_{60} samples (99.9 %, 98 %) at different modulation frequency. The modulation frequencies used ranged from 390 Hz to 25 KHz. Fig. (2) shows the FTIRPA spectra of C_{60} of purity 99.5 % and at wave number 1429 cm^{-1} for different modulation frequency (390 Hz – 25 kHz). The same specta are also recorded at the same modulation frequencies for the second C_{60} (98 %) sample and given in Fig. (3). It is easily observed that as the modulation frequency increases the signal amplitude decreases due to the reduction in propagation length of thermal wave within the material. The amplitude of the FTIRPA signal at wave number 1429 cm^{-1} for the two C_{60} samples are determined for each modulation frequency used. The variations of the FTIRPA signal amplitude vs the inverse of the modulation frequency for C_{60} of purity 99.9 %, are plotted in Fig. (4). Using equation (1) and effusivity for amorphous Si ($e_{a\text{-}si}$ = 0.2 $Ws^{1/2}$ /cm^2 K) [8], the thermal effusivity was determined for the first C_{60} (99.5 %) sample as e = 0..17 $Ws^{1/2}$ /cm^2 K. Using relation $e = \sqrt{k\rho c}$ and the specific heat (c = 0.52 x 10^3 J/ kg K) and the mass density of C_{60} (ρ = 1.72 x 10^{-3} kg/ cm^3), the thermal conductivity k for C_{60} was determined as k =0.37 x 10^{-2} W/cm K . Also the thermal diffusiviy α was determined as α = 0.42 x 10^{-3} cm^2/ sec . Fig. (5) shows The variations of the FTIRPA signal amplitude vs the inverse of the modulation frequency for C_{60} of purity 98 %. The values of e, k and α are also determined for the second C_{60} (98 %) sample e =0.18 $Ws^{1/2}$ /cm^2 K, k = 0.39 W/cm K and α = 0.45 cm^2/ sec. The results show that the values of thermal parameters are very close to each other. The values of thermal diffusivity obtained are less than that obtained by Pandy etal. (3.38×10^{-3} cm^2/sec). [6] for crystalline C_{60} This due to the structural voids/pores on the powder C_{60} pellet are expected to create barrier to heat flow and may be responsible for the low value compared to a single crystallite . The restricted heat flow will depend upon the size and the number of pores per unit area, ie . the Lager the number and the size of the voids, the lesser will be the thermal diffusivity. This study presents a nondestructive method for the determination of thermal diffusivity of C_{60} fullerenes in powder form.

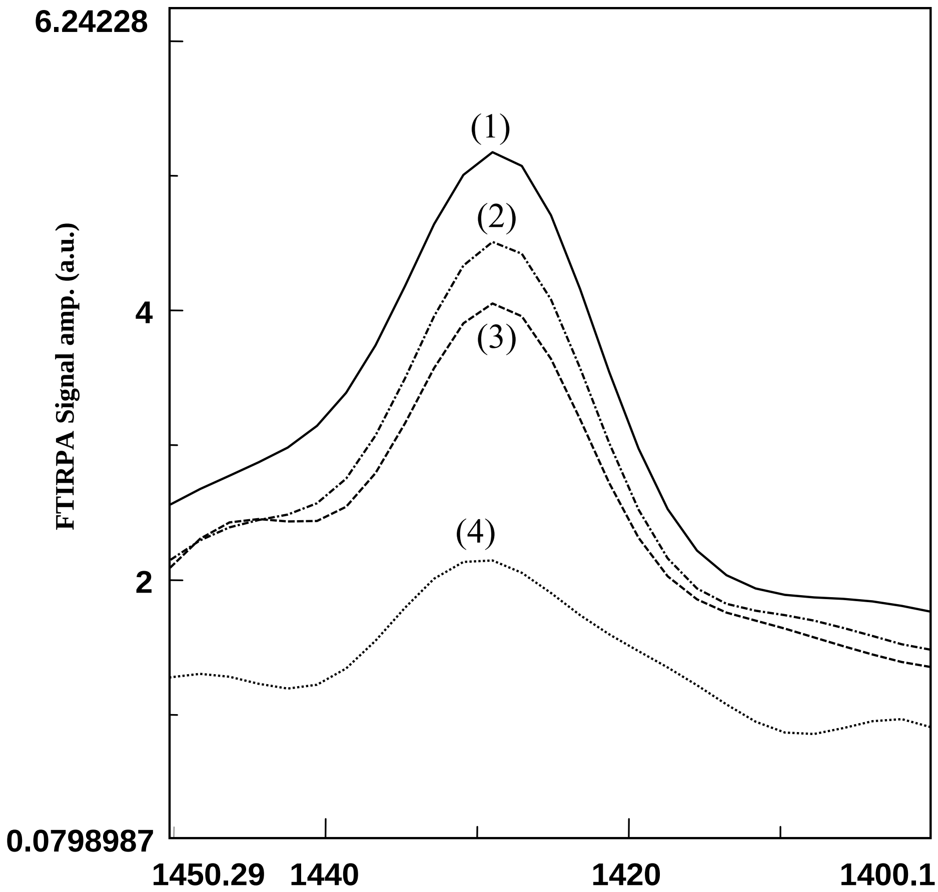

Fig (2): FTIRPA spectra at for C_{60} (99.5 %) at wave number 1430 cm^{-1} at Different modulation frequency (1- 390 Hz, 2- 1560 Hz, 3- 6250 Hz 4- 25 KHz).

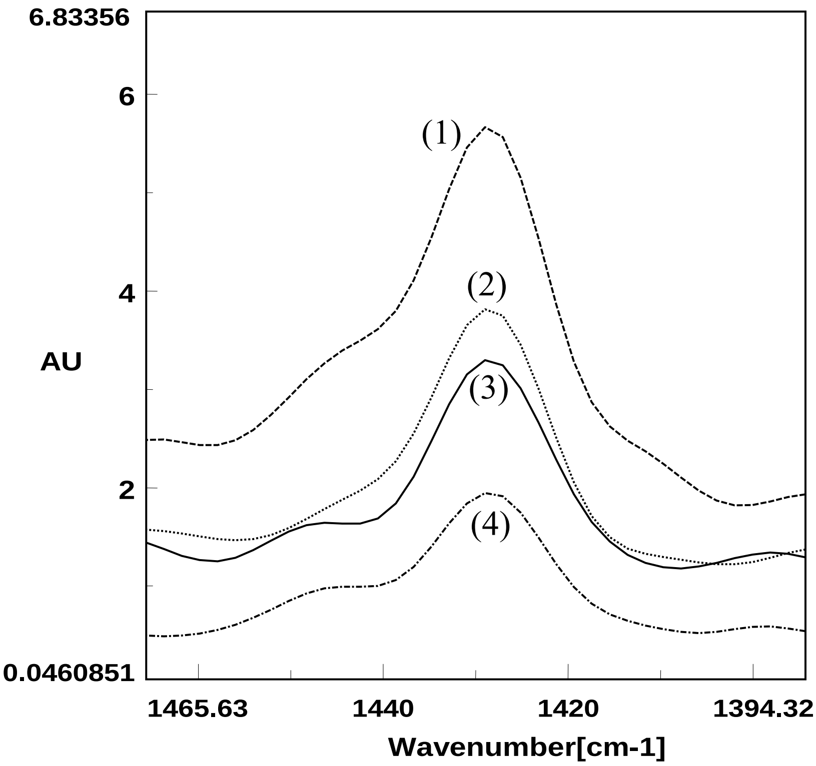

Fig (3): FTIRPA spectra at for C_{60} 98 %) at wave number 1430 cm^{-1} at different

FTIRPA Signal amp. (a.u.)

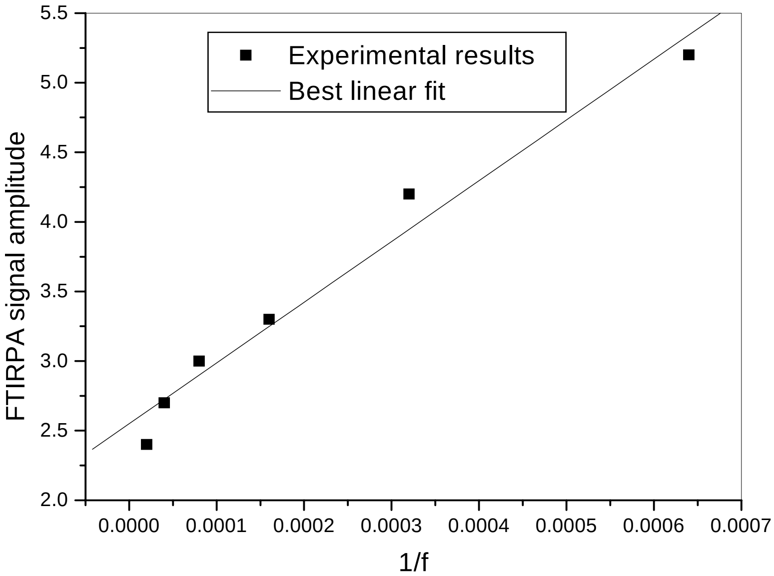

Fig (4): FTIRPA signal amplitude versus the inverse of the modulation Frequency for C_{60} of purity 99.5 % at wave number 1430 cm^{-1}

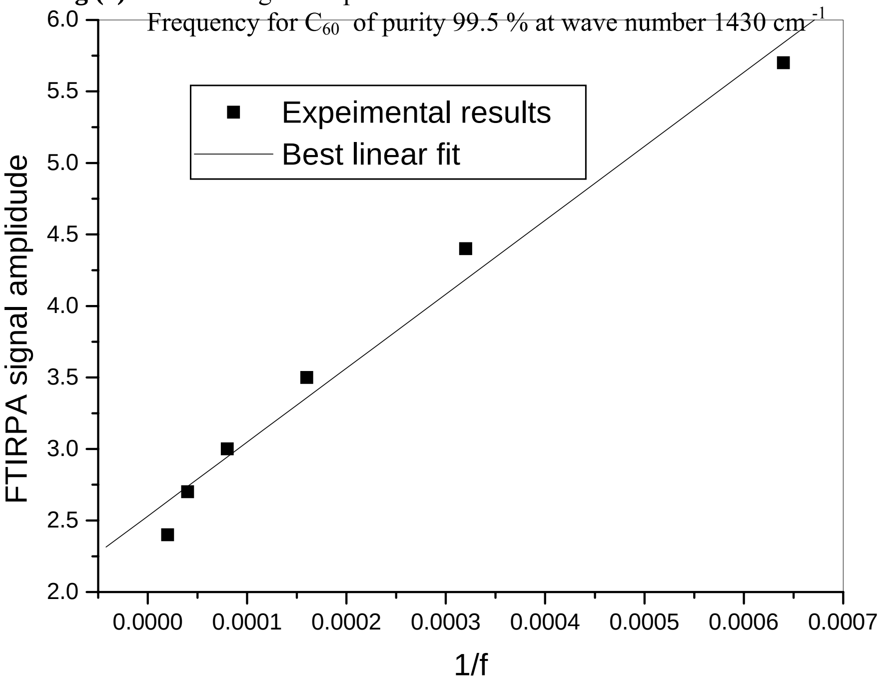

Fig (5): FTIRPA signal amplitude versus the inverse of the modulation Frequency for C_{60} of purity 98 % at wave number 1430 cm^{-1}

4. Conclusion:

Using the nondestructive FTIRPA technique we were able to determine the thermo physical parameters (e, k and α) for two powder C_{60} samples of different purity (99.5 % and 98 %). The values of thermal diffusivity is less than that for crystalline sample due to the structure of pores which create barrier to heat flow in the powder sample.

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