

Infrared spectroscopic study of the structural transitions of $C_{60}Br_{24}$

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Abstract

Variable temperature infrared spectroscopy and differential scanning calorimetry measurements show that $C_{60}Br_{24}$ undergoes two structural transitions at 171 and 180 K with ΔH values of 0.87 and 3.94 kJ mol⁻¹ respectively. Only one transition is clearly visible in IR which is manifested by the hardening of certain IR peaks and narrowing of the 1400 cm⁻¹ transition. The results support an orientational change although ordering of the solvated bromine molecules could also be a reason for the observed changes. © 1997 Elsevier Science B.V.

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1. Introduction

The 249 K orientational ordering transition of C_{60} [1,2] has generated considerable attention in the recent past. Calorimetric, spectroscopic and structural investigations of this phase transition have conclusively established the existence of a simple cubic orientationally ordered state below the transition temperature. The near-spherical symmetry of some of the derivatives of the buckminsterfullerene may cause phase transitions in such systems which could be orientational in nature. One of the ideal examples to probe such an ordering is $C_{60}Br_{24}$, because of its near spherical symmetry and the ease of preparation of a pure compound devoid of partially brominated molecules. The $C_{60}Br_{24}$ crystal is indeed soft, having a near neighbour distance of 3.55 Å [3,4]. Although the possibility of a dynamic disorder has not been established

in this system, the material could undergo a quasi-crystalline, glassy or ordered crystalline transition upon cooling.

In the variable temperature infrared spectroscopic studies of C_{60} and C_{70} major changes are observed in the line-widths of certain bands during the orientational ordering. For C_{60} [5], the 1183 cm⁻¹ mode narrows somewhat continuously and shifts from a centre frequency of 1183.1 to 1183.4 cm⁻¹ around 240 K. For the 1429 cm⁻¹ mode, a splitting is observed around 245 K. The observed splitting pattern has been ascribed to differences in local crystal field which arises when solid C_{60} goes into a rotationally locked phase below 250 K. In the case of C_{70} also [6] at the orientation temperatures of 276 and 337 K, major changes in the line-widths of the IR bands at 577, 643, and 674 cm⁻¹ are observed. The band at 795 cm⁻¹ showed a splitting when the temperature was lowered from 370 to 296 K through the first phase transition. This is assigned as being due to a

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band splitting occurring in the more ordered low temperature phase.

This article describes our experiments on $C_{60}Br_{24}$ and $C_{60}Br_8$ using variable temperature infrared spectroscopy and differential scanning calorimetry. Both of these experiments suggest possible structural transitions in the bulk solid which is manifested in the enhancement of certain vibrational modes, shift in certain frequencies and narrowing of some of the infrared peaks. Differential scanning calorimetry reveals two phase transitions with low ΔH values. $C_{60}Br_8$, however, does not show any change in the variable temperature infrared studies.

2. Experiment

$C_{60}Br_{24}$ was prepared by adding excess bromine to about 5 mg of C_{60} and the reaction was allowed to proceed overnight. After pumping away the excess bromine, the product was separated as a yellow powder [3,7]. Purity of the product was checked with FTIR spectroscopy.

For the temperature-dependent IR studies, the 10% (by weight) pellet of the sample was made by mixing it with pure KBr powder. A commercial Leybold closed-cycle helium cryostat, associated with a heater and a Perkin Elmer 983 dispersive IR spectrometer were used for the measurements. The spectra were recorded in the scan range of $1800\text{--}400\text{ cm}^{-1}$ under a dynamic vacuum of 10^{-6} torr in the temperature range of $12\text{--}300\text{ K}$. All reported spectra are averages of five scans. Using a 10% polyethylene pellet of the sample, far IR studies in the scan range $600\text{--}180\text{ cm}^{-1}$ were also carried out in a similar fashion. Differential scanning calorimetry thermograms of $C_{60}Br_{24}$ samples were obtained with the DSC(++) instrument of Rheometric Scientific Ltd., UK, on a sample size of 1.79 mg encapsulated in an aluminium crucible against an empty one. The samples were heated from 133 to 293 K at rate of 10 K min^{-1} . Transition temperature and enthalpy were measured after calibration with indium, against a baseline of empty pans and sapphire, with the help of a thermal software version 5.40.

$C_{60}Br_8$ was prepared by treating a solution of C_{60} in CS_2 with bromine in CS_2 [7]. The crystals were separated, recrystallised in CS_2 and dried. The temperature

dependent IR studies were carried out in the range of $1800\text{--}400\text{ cm}^{-1}$.

3. Results and discussion

$C_{60}Br_{24}$ belongs to the T_h point group [3]. In the T_h symmetry, the C–C stretching modes span T_u irreducible representation. The C–Br stretches correspond to three infrared active modes which are observed in the room temperature spectrum. The room temperature infrared spectrum shows vibrational bands at $1409, 1392, 1248, 914, 850, 752, 776, 721$ and 549 cm^{-1} ; only certain characteristic vibrations have been assigned so far in terms of symmetry classification [3,8]. The origin of the modes have not been

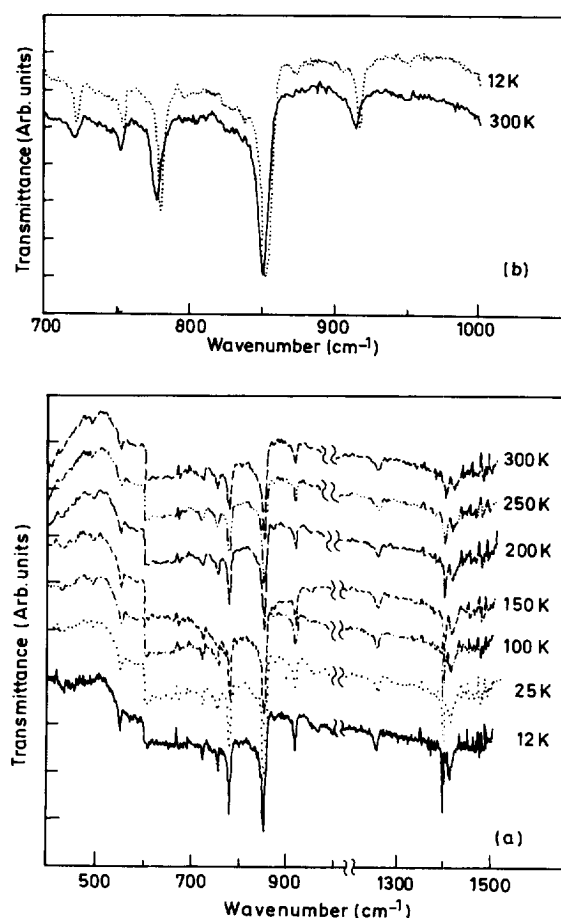


Fig. 1. (a) Infrared spectra of $C_{60}Br_{24}$ in the temperature range of $12\text{--}300\text{ K}$. (b) The spectra at 300 and 12 K.

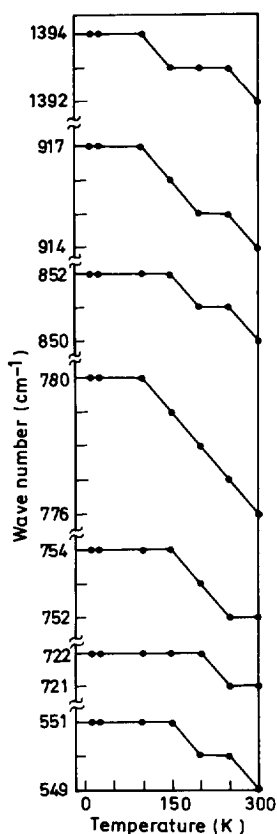


Fig. 2. Shift in the frequencies of various peaks in the infrared spectra of $C_{60}Br_{24}$ as a function of temperature.

suggested owing to the complexity imposed by the low symmetry. In Fig. 1, we show the infrared spectrum of $C_{60}Br_{24}$ in the temperature range of 12–300 K. All the reported IR peaks are clearly visible in the spectrum. As the temperature decreases we observe hardening of most of the modes as in the case of C_{60} and C_{70} . The observed shifts can be as large as 4 cm^{-1} in this temperature range. Certain vibrations indeed show drastic reduction in peak-width. In the temperature region investigated, we have not seen the appearance of any major structure.

The most interesting aspect of the infrared spectrum is that the peak shifts occur within a narrow temperature window (Fig. 2) indicating the possibility of a structural ordering. The 249 K transition of C_{60} is manifested in the infrared spectrum as sharp shifts in the vibrational modes in a narrow temperature window [5,9]. It has been reported that the width of the

temperature window can be as small as 1 K depending upon the sample preparation conditions. However, for C_{70} the shift occurs in a much larger temperature window of 50 K [10]. It has also been reported that upon making a KBr pellet containing dispersed C_{70} powder, the abrupt shifts in the peaks are not observed [10].

In Fig. 2 we show the shift in the various IR peaks as a function of temperature. It is apparent from the figure that the 780 cm^{-1} peak shows the most drastic change. The width of the temperature window during which the transition occurs is the same for all vibrations. In order to understand the origin of frequency shift, we carried out DSC measurements of the sample (Fig. 3). The DSC endotherm indicates two abrupt transitions around 171 and 180 K. Onset of the transitions occurs at a higher temperature possibly owing to a large heating rate. The area under the endotherm gives ΔH values of 0.87 and 3.94 kJ mol^{-1} for the transitions at 171 and 180 K respectively. It may be noted that the ΔH values of the transitions are very close to the reported values of C_{60} and C_{70} [1]. Although two distinct transitions are not discernible from the infrared spectrum, such a behavior is not unexpected. For example, both C_{60} and C_{70} are shown to possess two structural transitions, but both IR and Raman indicate only one major transition [3,9–13]. In C_{60} the C–C vibrations around 1400 cm^{-1} are the most affected ones owing to rotational ordering [5,12]. The observed splitting pattern of the 1429 cm^{-1} band is related to changes in local crystal field arising out of the interaction of the electron-rich 6–6 bond of one molecule with the electron deficient pentagonal ring of the adjacent molecule; which is manifested in the low temperature structure [14].

In Fig. 4, we show the variation of the peak-width for the 1400 cm^{-1} band as a function of temperature. As in the case of parent fullerene, the line-width goes through a continuous change where DSC suggests a structural transition. The IR line-width is determined by the life-time of the vibrational state which is strongly dependent upon vibration-rotation coupling. A strong coupling between the two will reduce the life-time and correspondingly increase the peak-width. It is also possible that the peak-width undergoes a change owing to vibration-phonon coupling as a result of reduced lattice spacing at lower temperatures.

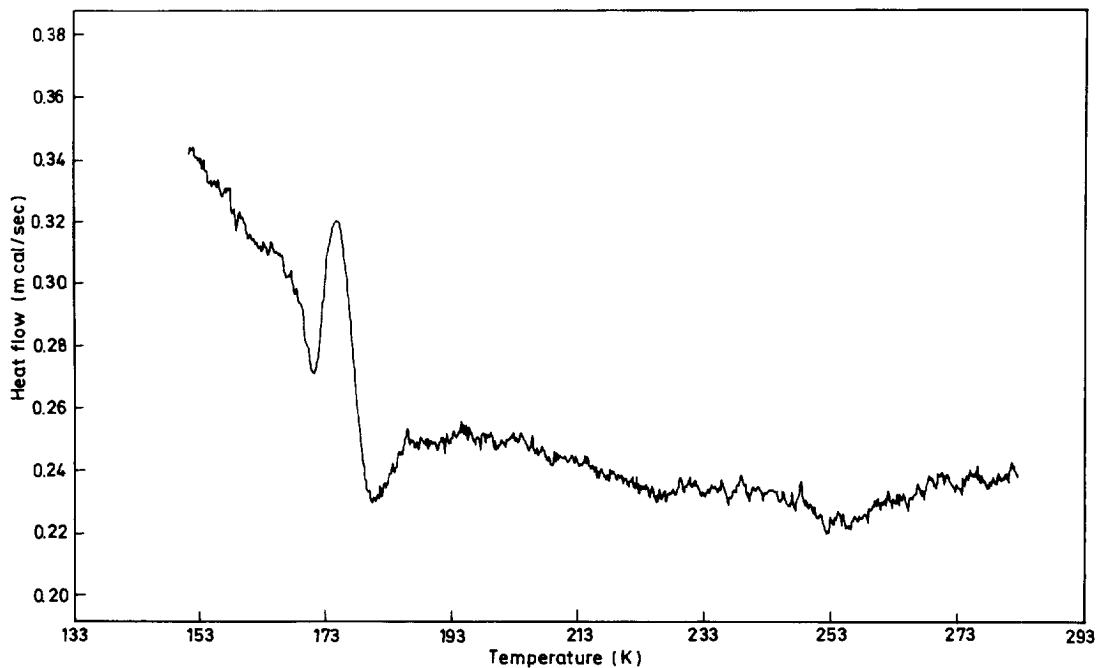


Fig. 3. The DSC endotherm of C₆₀Br₂₄ in the temperature range of 133–293 K.

A decreasing lattice constant can indeed result in increasing electrostatic and other possible interactions between the molecules. This effect is more prominent in C₆₀Br₂₄ where a large C–Br dipole moment and the high polarizability of Br atoms would indeed result in

strong intermolecular interactions. Such intermolecular interactions would be a major hindrance to the possible free rotation of the molecule. A possible freezing of the rotations would therefore eliminate the vibration–rotation relaxation thereby increasing

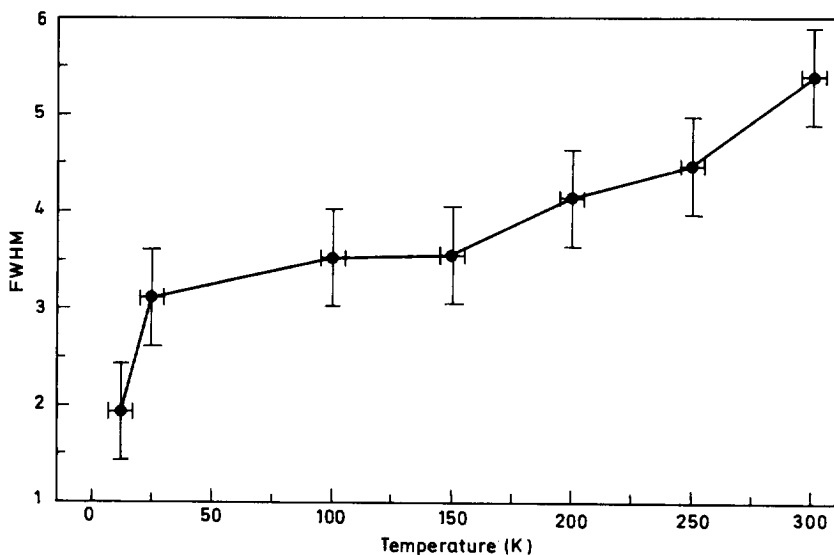


Fig. 4. The variation of peak-width for the 1400 cm⁻¹ band as a function of temperature.

the lifetime of the vibrational quanta. Such a possible elimination of the relaxation channel would lead to sharp reduction in the vibrational peak-width in a narrow temperature window. It may be mentioned that the possibility of such a peak-width reduction depends not only on the vibration–rotation coupling terms, but also on the density of the available rotational states.

The changes observed could also be interpreted in terms of the movement of the solvated bromine molecules. The relatively low ΔH values, small shifts in the peak positions and the absence of any new major structure in the infrared spectrum do, indeed, support such an interpretation. Structural studies within the temperature region would be necessary to get an unambiguous answer.

The present experiments suggest that $C_{60}Br_{24}$ undergoes structural transitions around 171 and 180 K which is manifested in the hardening of certain characteristic vibrations. Reduction in line-width of the 1400 cm^{-1} peak in the same temperature window seems to suggest that the phase transitions are orientational in nature although other possibilities are not excluded. The temperature instability of the material does not permit us to make an evaporated film to perform better quality experiments.

It is important to note that nearly all the peaks in the IR spectrum show blue shifts at low temperatures. This suggests shrinkage of the unit cell which makes molecular vibrations more difficult. It is noteworthy that the shifts observed are comparable to those of C_{60} and C_{70} .

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