

and double exposure holographic interferometry have been extensively used in the visualization of structural deformations and vibrations. The conventional techniques using a two-beam geometry involves the separation of the transmitted object beam and the image-bearing diffracted beam. So the quality of the interference pattern depends heavily on the transmission of the hologram and the suppression of the background intensity. The four-wave mixing (FWM) geometry employed by us helps in obtaining a PC image of the object which is free from distortions because of its aberration compensation property. The importance of the present work lies in the fact that by preparing a nonlinear medium, in the way suggested by us, one can attain a contrast of unity.

A new approach to combine the efficiencies of a photorefractive crystal and the fast response times offered by dye thin film, is discussed. This novel composite material gives two phase conjugate signals differing in their growth and decay times. It has been exploited in a simple four-wave mixing geometry to perform phase conjugate interferometry. The technique is free from the phase change problems associated with dye thin films alone and a very high contrast interferogram can be obtained by properly choosing suitable material and geometric parameters.

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## Investigations of the fullerene hydride $C_{60}H_{36}$

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Under Birch reduction conditions,  $C_{60}$  predominantly forms  $C_{60}H_{36}$ . Spectroscopic results are consistent with the structure predicted by calculations, involving four benzene rings distributed tetrahedrally in a spheroidal framework.

SINCE the discovery of the fullerene, there has been considerable effort to study the chemistry of these

fascinating molecules<sup>1,2</sup>. A variety of reactions have been carried out on  $C_{60}$  generally giving rise to a mixture of products. Birch reduction of  $C_{60}$  has been reported<sup>3</sup> to yield a mixture of  $C_{60}H_{18}$  and  $C_{60}H_{36}$ , while controlled hydroboration<sup>4</sup> followed by protonolysis gives  $C_{60}H_2$ . Calculations have been carried out on  $C_{60}H_{60}$ , with isolated double bonds<sup>5-8</sup>. Considering that several of the derivatives studied so far conform to the general formula  $C_{60}X_{60-6n}$  ( $X = H, Br, \text{etc}$ ), it is tempting to speculate whether some of these derivatives consists of  $n$  distinct benzene rings distributed in the fullerene cage<sup>9</sup>.  $C_{60}H_{36}$  seems to be the most promising candidate to adopt such a structure with four isolated benzenoid rings.

The preparation of fullerene was carried out by contact arc vapourization of graphite<sup>10,11</sup>. Separation and purification of  $C_{60}$  were accomplished by a simple filtration technique using a charcoal-silica-gel mixture<sup>12</sup>.  $C_{60}H_{36}$  was obtained by Birch reduction of  $C_{60}$  as follows. To excess Li/liquid  $NH_3$ , a solution containing 30 mg of  $C_{60}$  and 5 ml of *tert*-butanol in 200 ml methyl cyclohexane was added and stirred vigorously. The temperature of the reaction mixture was maintained at minus  $-33^\circ C$  for 6-7 h by using a liquid ammonia refluxing condenser. The product was quenched with excess of ammonium chloride, washed with water, dried over anhydrous  $MgSO_4$  and passed through a silica column to remove possible amine addition products. The new product in TLC showed a single spot (iodine-active) with an  $R_f$  value of around 0.37 in 30%  $CH_2Cl_2$ /hexane. After removing the solvent, a white solid product was obtained. This product was characterized by FAB and EI mass spectrometry, FTIR, NMR and UV spectroscopy.

Although the FAB and EI mass spectra of the purified product of Birch reduction show a distribution of mass peaks, the main line is at  $m/z = 756$  (Figure 1) corresponding to a hydride  $C_{60}H_{36}$ . There was no feature to indicate the presence of a  $NH_2$  group in the FTIR spectrum (KBr pellet). The FTIR spectrum showed characteristic frequencies associated with aliphatic C-H

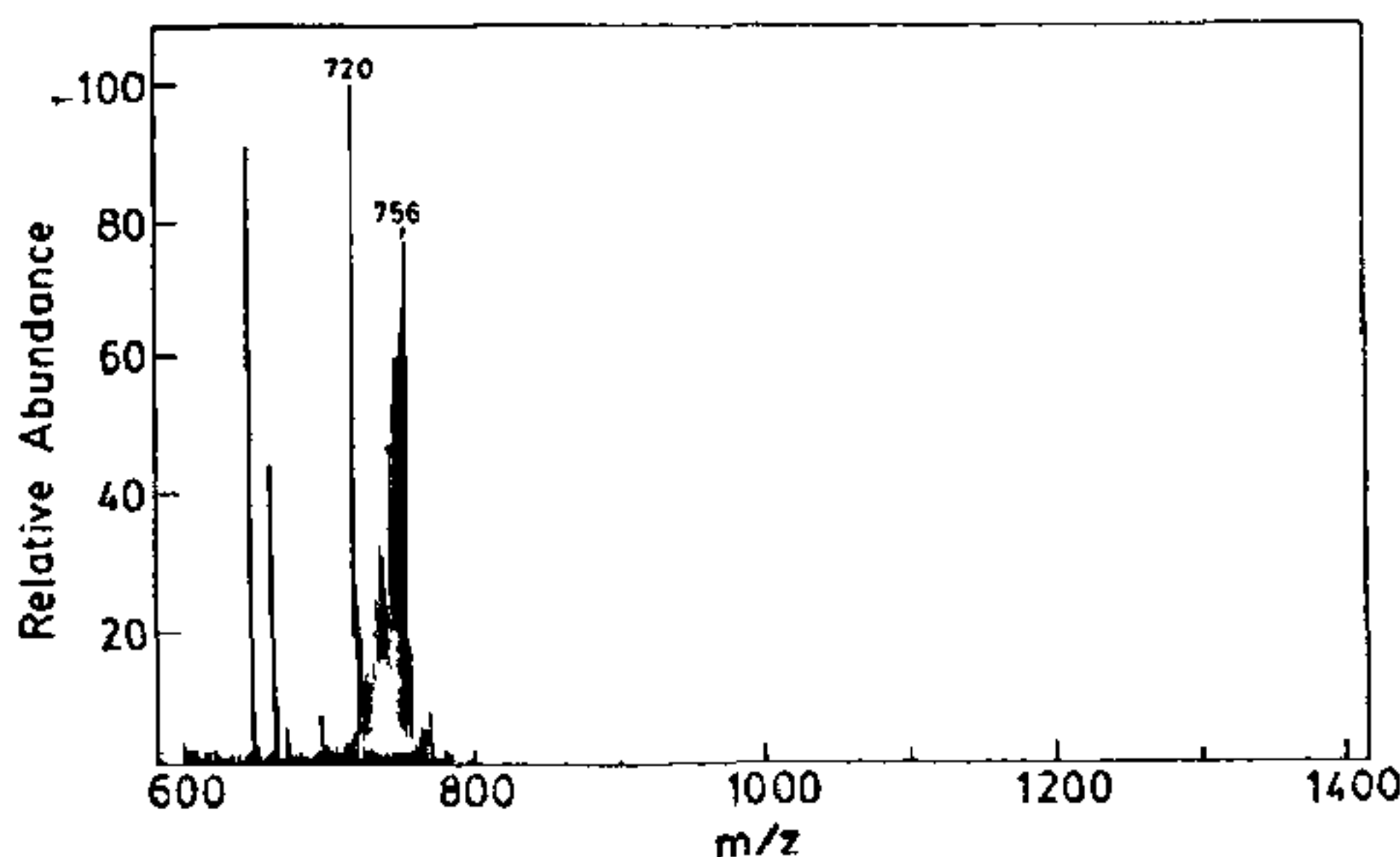


Figure 1. Electron impact mass spectra of  $C_{60}H_{36}$

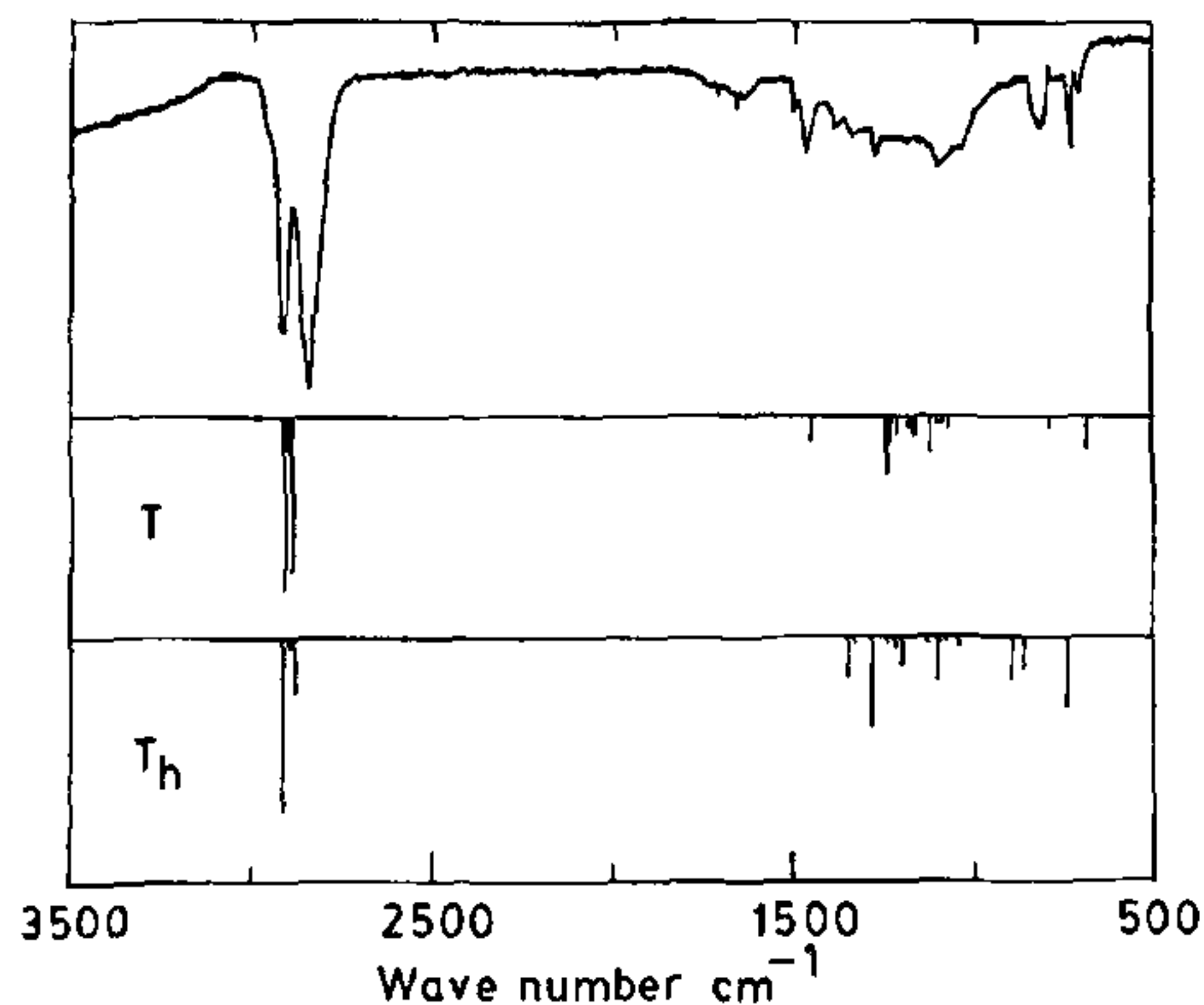


Figure 2. Experimental infrared spectrum (FT) of  $C_{60}H_{36}$  along with the spectra predicted for T and  $T_h$  structures (scaled by 0.9)

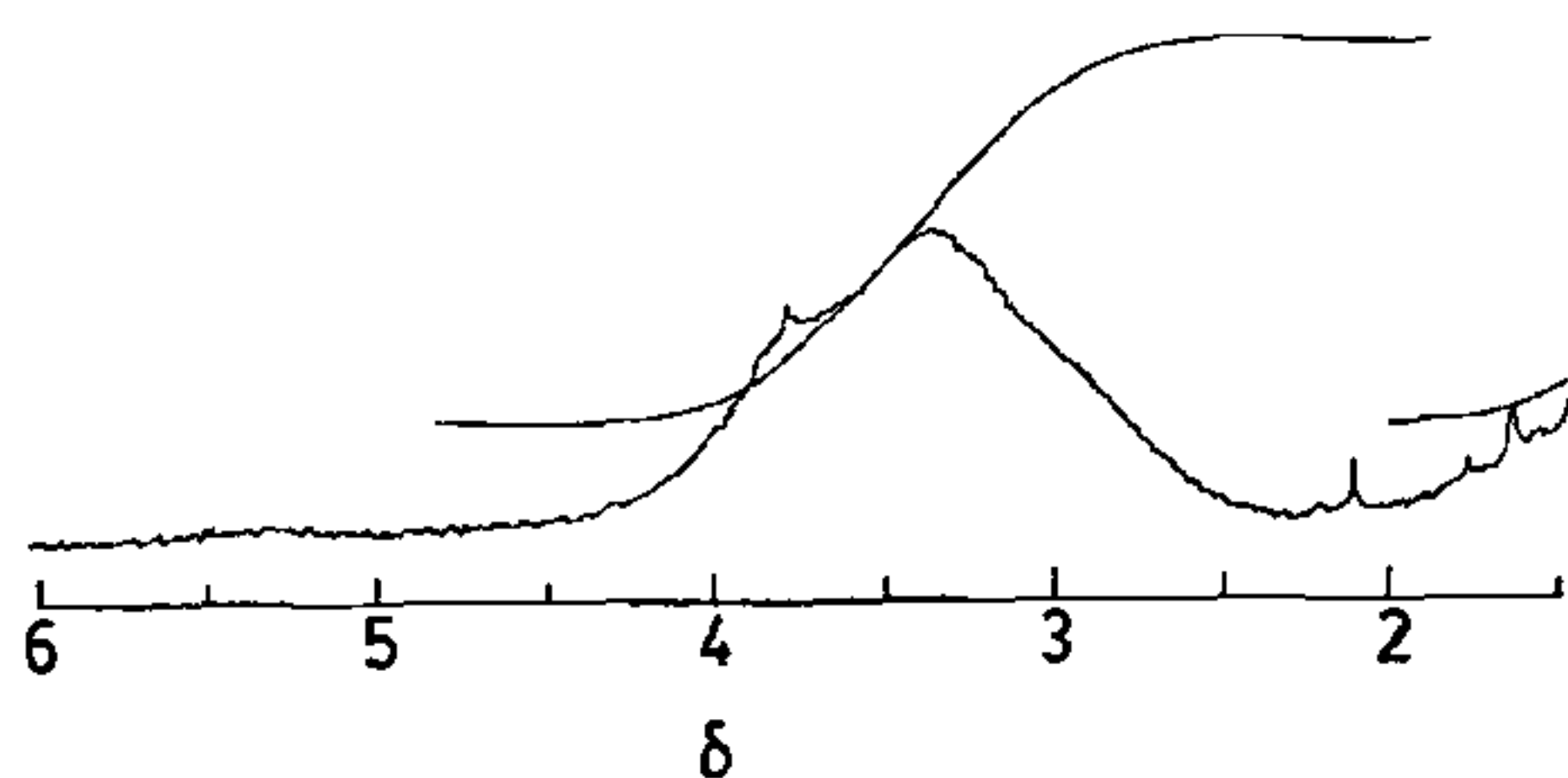


Figure 3. Proton NMR spectrum of  $C_{60}H_{36}$  (in  $CDCl_3$ )

stretching as well as aromatic C=C skeletal vibrations (Figure 2). The  $^1H$  NMR spectrum in  $CDCl_3$  (Figure 3) showed a broad band in the 2.5–4.3 ppm range. The  $^{13}C$  NMR spectrum showed distinct bands around 140 ppm and 40 ppm which can be assigned respectively to benzenoid and saturated carbons (insert of Figure 4). The signal due to the benzenoid carbons is weak because of the quaternary nature of these carbons. Although the NMR signals are relatively broad, their positions support the structure to be discussed later. The hydrocarbon showed a band at 218 nm and another around 275 nm in the UV spectrum (in cyclohexane solution), characteristic of benzenoid rings (Figure 4a). All these spectroscopic data of  $C_{60}H_{36}$  are consistent with a structure containing isolated benzene rings. Further evidence for the presence of benzene rings comes from the observation of a charge-transfer band of  $C_{60}H_{36}$  with tetracyanoethylene around 305 nm (Figure 4b). The benzene – TCNE system<sup>13</sup> shows a charge transfer band at 300 nm.

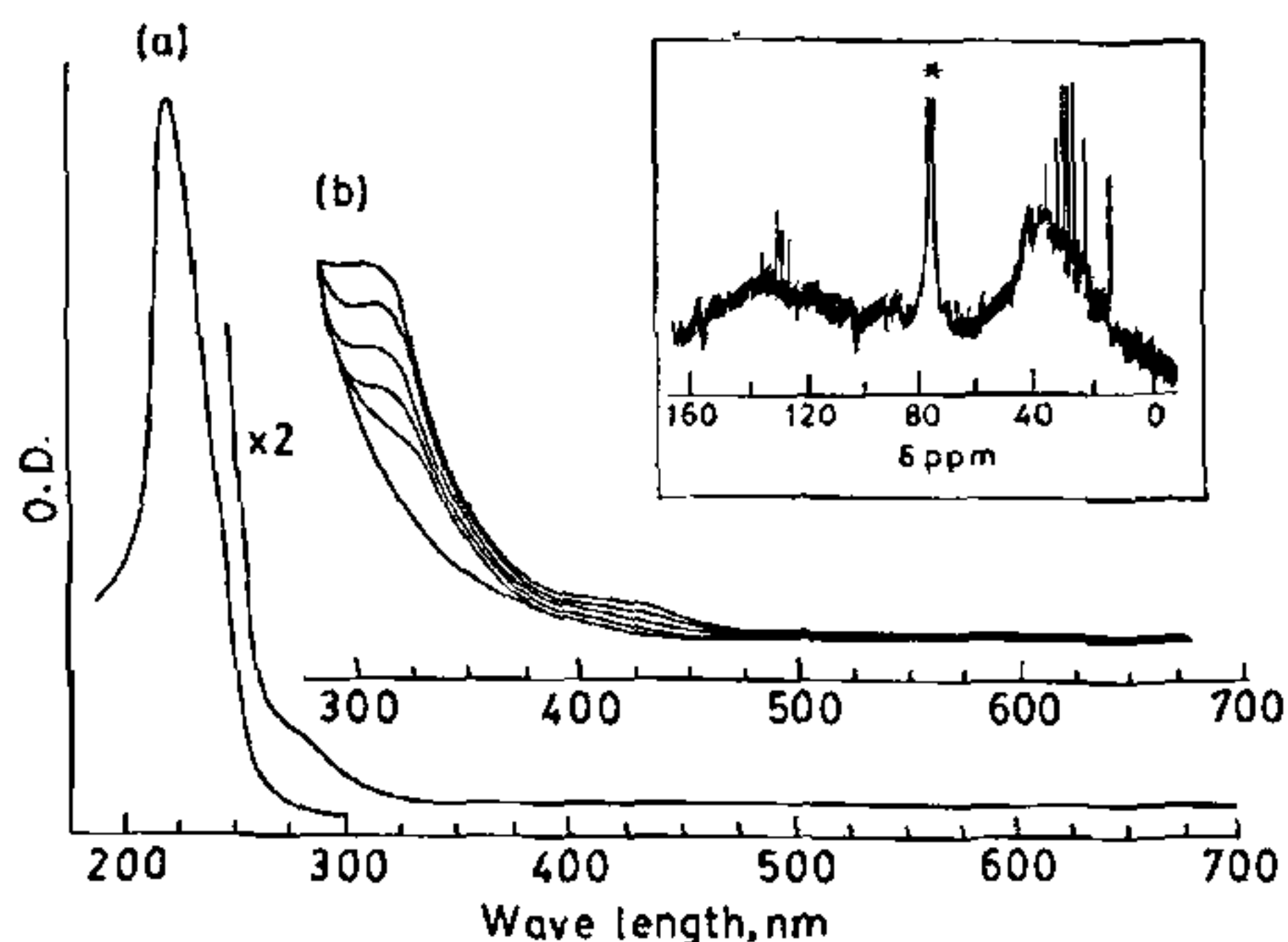


Figure 4. Electronic absorption spectrum of (a)  $C_{60}H_{36}$  along with (b) the spectra of TCNE and the complex with TCNE. Inset shows the  $^{13}C$  NMR spectrum in  $CDCl_3$  (The asterisk indicates the signal due to the solvent)

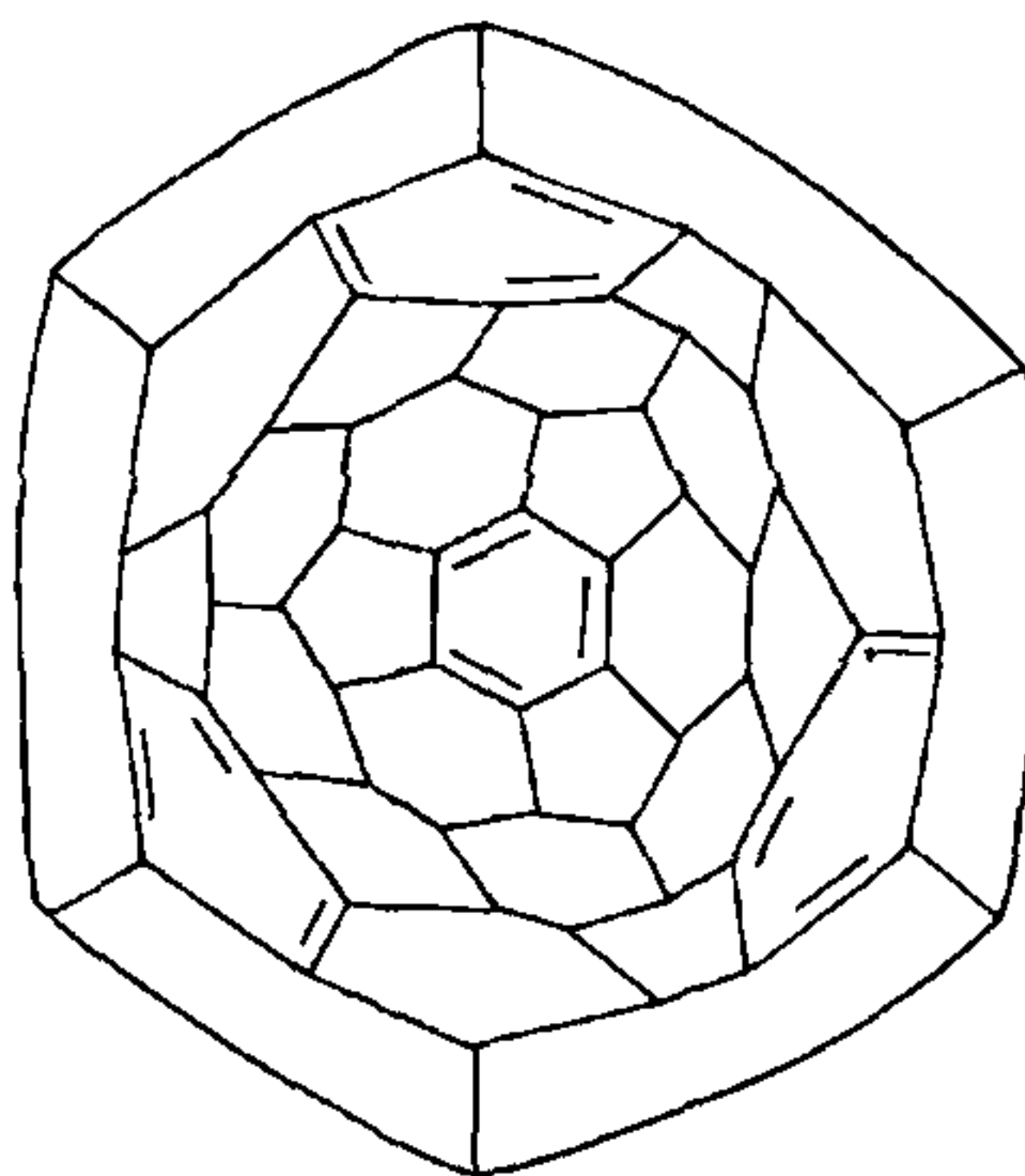


Figure 5. Projection of  $C_{60}H_{36}$  (T) structure down a three-fold axis

MNDO calculations<sup>14</sup> have shown that a structure with four tetrahedrally disposed benzene rings as shown in Figure 5 (T symmetry) is more stable for  $C_{60}H_{36}$  than that with isolated double bonds ( $T_h$  symmetry). MNDO calculations distinguished the T structure with benzenoid rings from the  $T_h$  structure with isolated double bonds in terms of vibrational frequencies. The observed IR spectrum of  $C_{60}H_{36}$  is compared with the spectra predicted by calculation for the T and  $T_h$  structure. The experimental spectrum seems to correspond more closely to the spectrum of the T rather than the  $T_h$  structure (Figure 2). This structure of  $C_{60}H_{36}$  suggests that factors such as angle strain, degree of conjugation, the number and magnitude of eclipsing interactions as



well as the strain associated with cage distortions are important factors in the reduction of  $C_{60}$ . The simple explanation offered earlier<sup>3</sup> for the structure of  $C_{60}H_{36}$  was based on the consideration that 36 is the number of hydrogens required to leave a single unconjugated double bond in each pentagon of  $C_{60}$ . We feel that it is not unreasonable to postulate a structure of  $C_{60}H_{36}$  as one with four tetrahedrally disposed benzene rings. It is possible that a structure with isolated double bonds first formed transforms to the thermodynamically more stable structure with the benzenoid rings via sigmatropic shifts. Thus with the four symmetrically spaced benzene units in the spheroid, the shape of the cage permits an effective elimination of angle strain at both the  $sp^2$  and  $sp^3$  carbon atoms. The overall angular distortions are marginally higher for the T isomer than the  $T_h$  form. It appears that the aromatic character of the benzenoid units is responsible for the greater stabilization of the former isomer. It is also likely that under conditions of Birch reduction with *tert*-butanol as the proton source only partial reduction of  $C_{60}$  occurs leaving four hexa-substituted benzene rings.

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## Evolution of basin boundaries during onset of chaos

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The evolution of basin boundaries in a system with multiple attractors is analysed numerically as the system develops period doublings, crises and tangles. The disappearance of the basin of attraction of a chaotic attractor during a boundary crisis as well as the erosion of the bounded basin by the escaping basin due to a heteroclinic tangle are displayed in a series of basin portraits.

IN the study of nonlinear systems, we often come across systems with multiple attractors, i.e. with more than one asymptotically stable states coexisting for one particular set of system parameters. In such cases, each attractor will be having its own separate basin of attraction, the basin being the set of initial points that lead to the attractor as time  $t \rightarrow \infty$ . The boundary of the closure of this region can in general be smooth or fractal. As the attractor undergoes a bifurcation, the basin boundary evolves, either going from a smooth to a fractal or disappearing. Therefore, studies related to the location as well as the nature of these boundaries and their changes as the system parameters evolve have significance because of their implications in the onset of chaos in the system<sup>1-4</sup>. An *a priori* knowledge about how the attractor basins evolve can be of use when we address the question of control mechanisms too, since suitable control is normally applied to bring the system within the basin of a periodic attractor<sup>5</sup>. So, also the extent of basin erosion due to forcing can tell us how far a system has chances of remaining constrained in a noisy environment, and this is a useful criterion in engineering and applied sciences<sup>6, 7</sup>.

In this communication, a detailed display of the evolution of basin boundaries of a system with multiple attractors is presented. By concentrating on parameter regimes where interesting phenomena like crises and tangles occur, we study numerically the reorganization of the basin structure as the parameters pass through their critical values. In this context, we note that basin boundary analysis has been carried out extensively in discrete dynamical systems<sup>8-10</sup>. The attractor-basin portraits have been explored in detail recently by Ueda<sup>11</sup> for the Duffing equation, while Thompson *et al.*<sup>12-15</sup> have analysed basin organization prior to escape in a single-well or double-well oscillator.

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