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The Role of the Intradimer C–C Bridge on the Stability of (C₅₉N)₂: A High Pressure Raman Study

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The effect of high pressure (up to 10 GPa) on the phonon modes of azafullerene (C₅₉N)₂ has been studied by means of Raman spectroscopy. The dimeric character of this fullerene derivative is manifested in its Raman spectrum. The pressure dependence of the $\omega(3)$ mode and the H_g(1) squashing mode frequencies exhibit reversible changes in the pressure region (5.0 ± 0.5) GPa. In addition, the A_g(1) breathing mode shows two clear reversible changes in its pressure coefficient at ≈3.0 and ≈5.5 GPa. These results are consistent with the structural modifications of (C₅₉N)₂ due to the existence of the intradimer C–C bridge obtained by other techniques.

1. Introduction

The introduction of heteroatoms into the fullerene cage leads to significant perturbations in the electronic character and geometry of the fullerene cluster; such fullerenes (heterofullerenes) are expected to have applications in superconductivity, photoinduced electron transfer (photoelectric devices), and organic ferromagnetism. As a result of the trivalency of nitrogen, compared to the tetravalency of carbon, carbon substitution by a nitrogen atom in the C₆₀ cage leads to the azafullerene radical C₅₉N[•] which has been found to rapidly dimerize, yielding the (C₅₉N)₂ dimer [1]. Thus, solid (C₅₉N)₂ consists of dimerized molecular units linked by C–C bonds between carbon atoms adjacent to the N atom (the C–N bond is between two six-membered rings) at each monomer [1 to 3].

The samples under investigation had a crystalline hexagonal structure (space group P6₃/mmc or one of its subgroups). At room temperature and normal pressure, the *c/a* ratio is equal to 1.623 (*a* = 9.97 Å, *c* = 16.18 Å), differing marginally from the ideal

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ratio of ≈ 1.633 which is expected in the case of spheres packed in the hexagonal close-packed (h.c.p.) lattice [4]. The stability of the h.c.p. structure of $(C_{59}N)_2$ is evidently driven by the presence of residual solvent molecules in the lattice. Azafullerene has been found to be a less compressible solid ($\kappa = 4.65 \times 10^{-2} \text{ GPa}^{-1}$ [4]) than C_{60} ($\kappa = 5.52 \times 10^{-2} \text{ GPa}^{-1}$ [5]).

In this paper, we present an investigation of the effect of high pressure up to 10 GPa on the phonon modes of $(C_{59}N)_2$ in the low energy region in order to investigate the role of the intradimer C–C bridge in its stability. The high pressure behavior of solid azafullerene is also compared to that of pristine C_{60} .

2. Experiments

The azafullerene samples, in the form of fine dust, used in the present study were prepared from a “holey bucky” [6] and were purified by HPLC on a Cosmosil “Bucky prep” column, using toluene as eluent. Solid $(C_{59}N)_2$ was obtained from a solution in *o*-dichlorobenzene (ODCB), which was evaporated to dryness in a rotary evaporator. Recrystallization from a CS_2 solution led to a highly crystalline material, which was subsequently degassed under dynamic vacuum ($\approx 10^{-4} \text{ Pa}$) at 140°C for 12 h [7].

High pressure was generated using the diamond anvil cell (DAC) of Mao-Bell type [8]. The 4:1 methanol–ethanol mixture was used as pressure-transmitting medium and the well-known ruby fluorescence technique was used for pressure calibration [9]. Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectral width of the system was $\approx 5 \text{ cm}^{-1}$. The 514.5 nm line of an Ar^+ laser was used for excitation, with the laser power kept less than 5 mW, measured directly before the cell, in order to avoid laser heating effects analogous to the ones leading to the softening of the $A_g(2)$ pentagonal-pinch (PP) mode observed in C_{60} [10]. The experimental results were obtained for a number of different cell loadings and data were recorded for both increasing and releasing pressure.

3. Results and Discussion

The Raman spectra of $(C_{59}N)_2$ in the frequency region 100 to 800 cm^{-1} at various pressures and room temperature are illustrated in Fig. 1. At normal pressure, the Raman spectrum of $(C_{59}N)_2$ in this low energy region is similar to that of C_{60} . It contains the five principal molecular modes observed in C_{60} , i.e. $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(3)$ and $H_g(4)$. In addition, three more modes marked by $\omega(1)$, $\omega(2)$ and $\omega(3)$, are observed with frequencies 344, 395 and 730 cm^{-1} , respectively. We note that these modes are also observed in crystalline C_{60} but for pressures higher than 0.4 GPa, where the free rotations of the C_{60} molecules are frozen [11]. Their presence in $(C_{59}N)_2$ is consistent with the freezing of the free rotations caused by dimerization as the $(C_{59}N)_2$ molecule is elongated along the intradimer bridge. In particular, the appearance of the Raman line $\omega(1)$ at 344 cm^{-1} has been proposed as the Raman signature of the polymeric phase of AC_{60} (A: Cs, Rb, K) at room temperature and ambient pressure [12]. The assignment of this mode is still an open question but, as we also observe this Raman peak in the spectrum of azafullerene under normal conditions, we assume that its appearance is due to the existence of the C–C covalent bridge present in both cases.

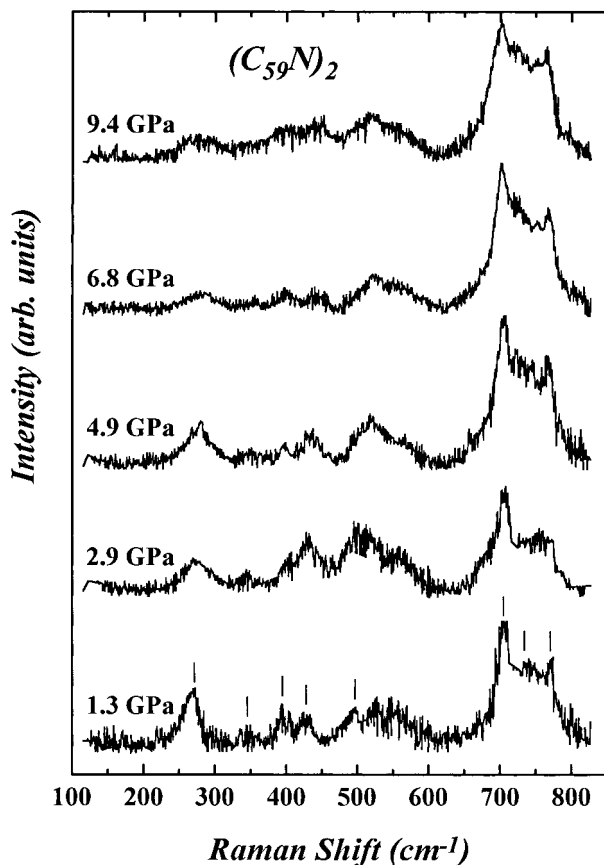


Fig. 1. Raman spectra of $(C_{59}N)_2$ in the frequency region 100 to 800 cm^{-1} at room temperature and for various pressures up to 10 GPa. The vertical lines indicate the observed phonon peaks

The frequencies of the observed intramolecular phonon modes in the Raman spectra of $(C_{59}N)_2$ are close to the corresponding ones of pristine C_{60} [11, 13]. The observed differences do not exceed $\approx 3 \text{ cm}^{-1}$ except for the $H_g(1)$ mode, where the corresponding difference is 7 cm^{-1} . Another interesting observation with this mode in azafullerene is its significant broadening (width $\approx 40 \text{ cm}^{-1}$) and asymmetric line shape with peak frequency at 265 cm^{-1} . In photodimerized C_{60} , the $H_g(1)$ intramolecular mode appears to be split into two components with frequencies of 258 and 271 cm^{-1} [14]. Therefore we believe that the line shape and the frequency shift of the $H_g(1)$ mode in $(C_{59}N)_2$ are connected with the dimerization as in the case of photodimerized C_{60} . The above observations, namely: (i) the appearance of the $\omega(1)$ to $\omega(3)$ modes and (ii) the broad asymmetric peak at the $H_g(1)$ frequency region, are strong indications of the dimeric character of azafullerene manifested in the Raman spectra.

The pressure dependence of the observed phonon frequencies is shown in Figs. 2 and 3. The open (solid) circles correspond to spectra recorded with increasing (decreasing) pressure. The peak positions were determined by fitting of Lorentzian line shapes to the experimental data. The phonon frequencies as well as their pressure coefficients, as obtained by the least-squares fitting procedure, are tabulated in Table 1 along with the corresponding data for pristine C_{60} [11]. All modes, except $H_g(3)$ and $H_g(4)$, exhibit a

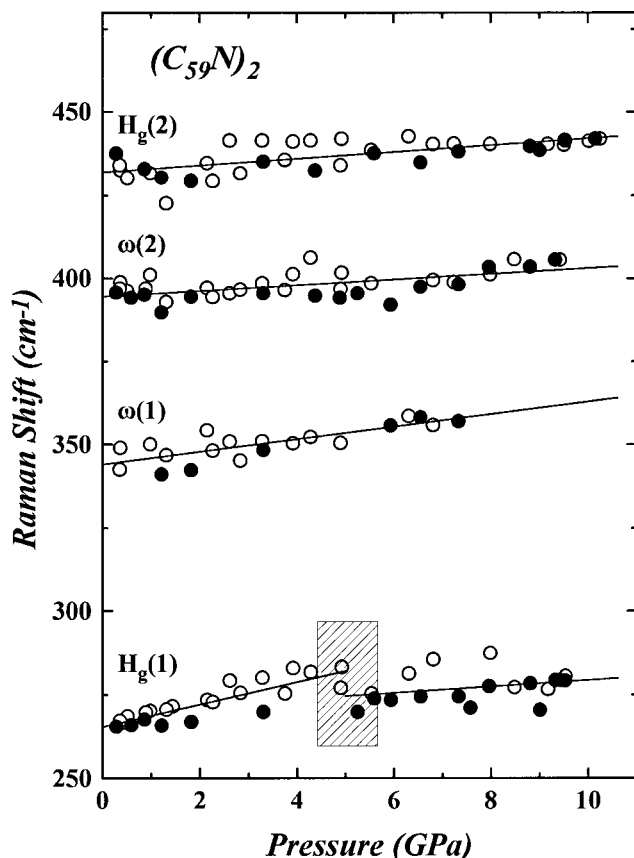


Fig. 2. The pressure dependence of the $H_g(1)$, $\omega(1)$, $\omega(2)$ and $H_g(2)$ intramolecular Raman modes of $(C_{59}N)_2$. The open (solid) circles denote data taken for increasing (decreasing) pressure runs. The shaded area denotes the change in the slope of the pressure dependence for $H_g(1)$ squashing mode

positive response to pressure, in analogy to pristine C_{60} . Note that the $\omega(2)$ and $\omega(3)$ modes exhibit positive slopes (for $P < 5$ GPa) while in the case of fullerite C_{60} their slopes had opposite signs. From Table 1, we see that for $P < 3$ GPa the pressure coefficients ($\partial\omega/\partial P$) of the principal intramolecular modes $H_g(2)$, $A_g(1)$, $H_g(3)$ and $H_g(4)$ are systematically smaller, in absolute values, than those of the corresponding modes of C_{60} . This can be rationalized by taking into account the lower compressibility of $(C_{59}N)_2$ [4, 5] compared to that of pristine C_{60} .

From Figs. 2 and 3, we deduce that $(C_{59}N)_2$ does not exhibit pressure induced phase transitions, driven by changes in the fullerene rotational state, similar to those observed in C_{60} at 0.4 and 2.4 GPa [15]. This behavior may be understood from the fact that the existence of the intradimer C–C bridge in azafullerene prevents such molecular reorientations. These results are consistent with XRD measurements [16].

The pressure dependence of the $H_g(1)$ mode exhibits a reversible abrupt softening by ≈ 7 cm^{-1} and a reversible pressure coefficient change at $P \approx 5$ GPa with smaller slope values at higher pressures (Table 1). Also, the $\omega(3)$ mode exhibits a reversible pressure

Table 1

The phonon frequencies, their assignment and pressure coefficients for the (C₅₉N)₂ Raman active modes in the low energy region. The corresponding values for C₆₀ are also included

mode	(C ₅₉ N) ₂			C ₆₀ ^{a)}	
	ω_i (cm ⁻¹)	$\partial\omega_i/\partial P$ (cm ⁻¹ /GPa)		ω_i (cm ⁻¹)	$\partial\omega_i/\partial P$ (cm ⁻¹ /GPa)
		$P < 5$ GPa	$P > 5$ GPa		$P < 2.4$ GPa
H _g (1)	265	3.3	1.0	272	3.2
ω (1)	344	1.9	1.9	345	2.9
ω (2)	395	0.9	0.9	389	-0.2
H _g (2)	432	1.0	1.0	435	2.4
H _g (3)	707	-0.6	-0.6	710	-0.8
ω (3)	730	2.3	-0.6	729	-2.9
H _g (4)	771	-0.8	-0.8	772	-2.7
		$P < 3$ GPa	$3 < P < 5.5$ GPa		$P > 5.5$ GPa
A _g (1)	491	1.5	8.8	495	4.2

^{a)} Data from [11].

coefficient change in the same pressure region (the pressure slope changes sign). The critical pressure regime, (5.0 ± 0.5) GPa, is in good agreement with the results concerning structural changes obtained by synchrotron X-ray diffraction measurements [4]. These results have shown that the c/a ratio in azafullerene solid increases monotonically with increasing pressure until, at ≈ 6 GPa, it reaches the ideal h.c.p. c/a value, and then remains unchanged up to much higher pressures (20 GPa) [4]. The observed behavior was interpreted by noting that at this pressure (≈ 6 GPa), the interdimer centre-to-centre distance is compressed to ≈ 9.3 to 9.4 Å, essentially identical to the corresponding intradimer distance. So, the Raman data are reflecting these structural “modifications” of (C₅₉N)₂, observed in the same pressure region, with satisfactory sensitivity.

The A_g(1) breathing mode, which is expected to be the most sensitive to the formation of the intramolecular C–C bridge, exhibits two reversible changes with pressure, one at ≈ 3.0 and one at ≈ 5.5 GPa (Fig. 3). In the pressure region $P < 3$ GPa, the breathing mode hardens at a slower rate than that of C₆₀ (Table 1), as the decrease in volume is mainly absorbed by weak van der Waals forces between the dimeric units and has little effect on the intradimer C–C bridge. In the $3 \text{ GPa} < P < 5.5$ GPa region, the A_g(1) mode hardens faster, while in the $P > 5.5$ GPa region, its frequency remains practically unchanged. For pressures above 3 GPa, the change in the intradimer bridge becomes more pronounced leading to the faster hardening of A_g(1) mode in this pressure region. In the end, for pressures higher than 5.5 GPa, where the structure of the material approaches the ideal h.c.p. one, its lower compressibility results in the frequency invariance of this mode. A change at ≈ 3 GPa, due to the difference between the compressibility of the molecular units and that of the bulk solid, has also been observed in the XRD measurements for the (10 $\bar{1}$ 1) reflection [4]. Finally, the modes ω (1), ω (2), H_g(2), H_g(3) and H_g(4) do not show any change in their pressure coefficients in the pressure region under study (Figs. 2 and 3).

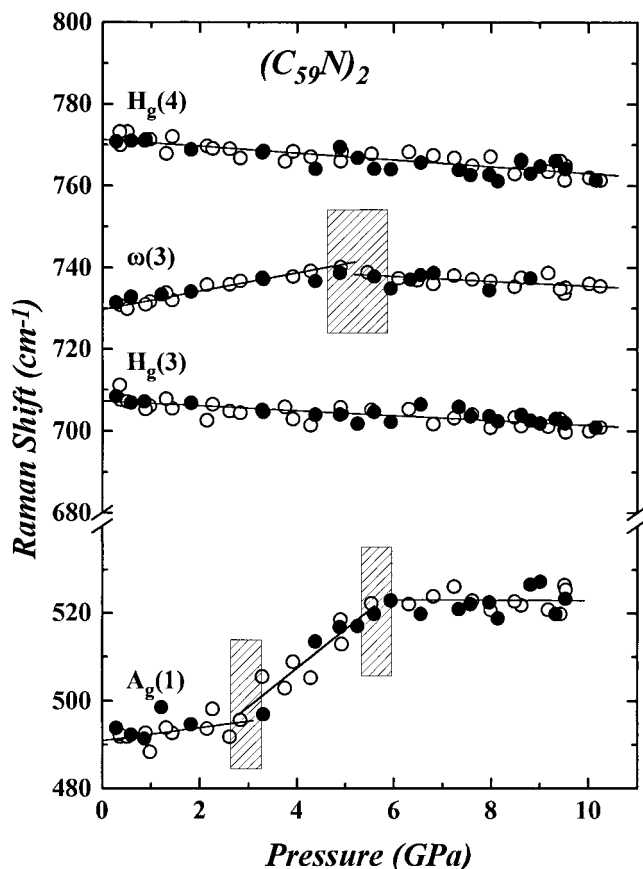


Fig. 3. The pressure dependence of the $A_g(1)$, $H_g(3)$, $\omega(3)$ and $H_g(4)$ intramolecular Raman modes of $(C_{59}N)_2$. The open (solid) circles denote data taken for increasing (decreasing) pressure runs. The shaded areas denote the changes in the slope of the pressure dependence for $A_g(1)$ breathing mode and for $\omega(3)$ mode

4. Conclusions

In conclusion, we can say that the molecular rotations in the case of $(C_{59}N)_2$ are frozen at normal conditions due to the existence of the intradimer bridge. Also, the $\omega(1)$ mode at 344 cm^{-1} may be the Raman signature of this covalent bridge, as in the case of the AC_{60} polymers. Finally, the dimerization results in the separation of the phonon modes into two categories: those, which exhibit pressure coefficient changes, and those, which do not. We propose that the modes showing pressure coefficient changes are those either having their eigenvectors strongly directed along the intradimer bridge (e.g. $A_g(1)$) or having large components in that direction (e.g. $H_g(1)$ and $\omega(3)$).

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