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Effect of high hydrostatic pressure on the intramolecular modes of $(C_{59}N)_2$

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The effect of high pressure, up to 10 GPa, on the phonon spectra of azafullerene, $(C_{59}N)_2$, at room temperature has been investigated by Raman spectroscopy. At ambient pressure, the Raman spectrum of $(C_{59}N)_2$ displays eight of the ten molecular modes of C_{60}. Their frequencies are close to those of the corresponding modes of pristine C_{60} solid. The pressure dependence of the $H_g(7)$, $A_g(2)$, and $H_g(8)$ phonon frequencies exhibits reversible changes in their pressure coefficient in the region 6.0 ± 0.5 GPa. In addition, the $A_g(1)$ breathing mode shows two clear changes in the pressure dependence of the pressure coefficient, one at ~3.0 and another at ~6.0 GPa. The results are explained by taking into account the pressure dependence of the structural properties of solid $(C_{59}N)_2$. [S0163-1829(99)14903-8]

I. INTRODUCTION

The introduction of heteroatoms into the fullerene cage leads to significant perturbations of the electronic and geometric character of the fullerene cluster;[1,2] such fullerides (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, nitrogen substitution of a carbon atom on the C_{60} cage leads to the azafullerene radical, $C_{59}N^*$—isoelectronic with the C_{60}^- anion—which has been found to rapidly dimerize, yielding the $(C_{59}N)_2$ dimer.[3] Thus, solid $(C_{59}N)_2$ 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.[2–4] Conductivity measurements have confirmed that the material is an insulator, while the electron paramagnetic resonance (EPR) spectra consist of only one sharp narrow line, attributed to a low concentration of defect spins.[5] Electron energy-loss and photoemission spectroscopy measurements revealed little mixing between the N and C electronic states with strong localization of the excess electron at the N atom.[6]

The samples under investigation had the form of fine dust with a crystalline hexagonal structure (space group $P6_3/mmc$ or one of its subgroups). At room temperature and ambient pressure, the (c/a) ratio is equal to 1.623 ($a=9.97$ Å, $c=16.18$ Å), differing marginally from the ideal ratio of $\sqrt{8/3}$ (~1.633) expected in the case of spheres packed in a hexagonal close-packed (hcp) lattice.[7] Indeed, C_{60} also adopts a hcp structure with $(c/a)=1.633$ ($a=9.98$ Å, $c=16.30$ Å), besides the more stable fcc structure, in which the shortest interball distance is 10.02 Å.[8] The stability of the hcp structure in both C_{60} and $(C_{59}N)_2$ is evidently driven by the presence of residual solvent molecules in the lattice. Finally, azafullerene is a less compressible solid [$\kappa=4.65\times10^{-2}\ \mathrm{GPa}^{-1}$ (Ref. 7)] than C_{60} [$\kappa=5.52\times10^{-2}\ \mathrm{GPa}^{-1}$ (Ref. 9)].

In this work, we present an investigation of the effect of high pressure up to 10 GPa on the phonon spectra of $(C_{59}N)_2$ in order to probe the diversity of the bonding interactions and especially 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}.

II. EXPERIMENTAL DETAILS

The azafullerene sample used in the present study was prepared from a ‘‘holey bucky,’’ [10] as described previously,[3] and was purified by high pressure liquid chromatography (HPLC) on a Cosmosil ''Bucky prep'' column, using toluene as eluent. The 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 ($\sim 10^{-6}$ Torr) at 140 °C for 12 h.[11] Note that if the material is sublimed under the same dynamic vacuum at 500 °C for 12 h, it adopts a monoclinic structure again comprised of dimeric $(C_{59}N)_2$ units.[4]

High pressure was generated using the diamond anvil cell (DAC) of Mao-Bell type.[12] The pressure transmitting media used in the present study included 4:1 methanol-ethanol mixture, distilled water, and 4:1:5 methanol-ethanol-glycerol mixture. The traditional methanol-ethanol 4:1 mixture exhibits Raman scattering in the same frequency region as the sample and because our sample had the form of fine dust, the observed scattering volume contained significant amounts of the mixture, resulting in an interference of the Raman spectra. Distilled water is not a very good hydrostatic medium but gave us the possibility to record the Raman spectrum of the sample without interference from the pressure-transmitting medium. Finally, the methanol-ethanol-glycerol 4:1:5 mixture has better hydrostatic behavior and the results were in excellent agreement with those obtained with the other transmitting media. The ruby fluorescence technique was used for pressure calibration.[13] Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a charge-coupled device (CCD) liquid-nitrogen-cooled detector system. The spectral width of the system was ~ 5 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 softening of the $A_g(2)$ pentagon-pinch (PP) mode observed in C_{60}.[14]

III. RESULTS AND DISCUSSION

The Raman spectra of $(C_{59}N)_2$ in the frequency region 100–1800 cm^{-1} at various pressures and room temperature are illustrated in Fig. 1. At ambient pressure, the Raman spectrum of $(C_{59}N)_2$ is similar to that of C_{60}. It contains eight of the ten principal molecular modes observed in C_{60}, i.e., $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(3)$, $H_g(4)$, $H_g(7)$, $A_g(2)$, and $H_g(8)$. In addition, two more modes, $\omega(1)$ and $\omega(2)$, are observed with frequencies 344 and 395 cm^{-1}, respectively. We note that the $\omega(1)$ and $\omega(2)$ 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.[15] Their presence in $(C_{59}N)_2$ is consistent with the freezing of free rotation caused by dimerization.

The frequencies of the observed phonon modes in the Raman spectra of $(C_{59}N)_2$ are close to the corresponding ones for pristine C_{60}.[15,16] The observed differences do not exceed the spectral resolution of the apparatus (~ 3 cm^{-1}), except for the $H_g(1)$, $A_g(2)$, and $\omega(2)$ modes, where the corresponding differences are slightly larger, in the range of 6–8 cm^{-1}. It is worth pointing out that the frequency of the $A_g(2)$ mode at ambient pressure is ~ 1460 cm^{-1}, exactly the same as for photodimerized C_{60}.[17] Therefore, dimerization results in the softening of the $A_g(2)$ mode in C_{60} and its derivatives. Another interesting observation in the Raman spectrum is the broad (width ~ 40 cm^{-1}) asymmetric feature at 265 cm^{-1}. In photodimerized C_{60}, the $H_g(1)$ intramolecular mode appears to be split into two components with frequencies 258 and 271 cm^{-1}.[17] Thus we assume that this feature in the spectrum of azafullerene is originating from the same molecular vibration in both cases. The above observations, namely: (i) the appearance of the $\omega(1)$ and $\omega(2)$ modes, (ii) the frequency of the $A_g(2)$ mode and, (iii) the appearance of the broad asymmetric peak at the $H_g(1)$ frequency region, are clear manifestations of the dimeric character of azafullerene in its Raman spectra.

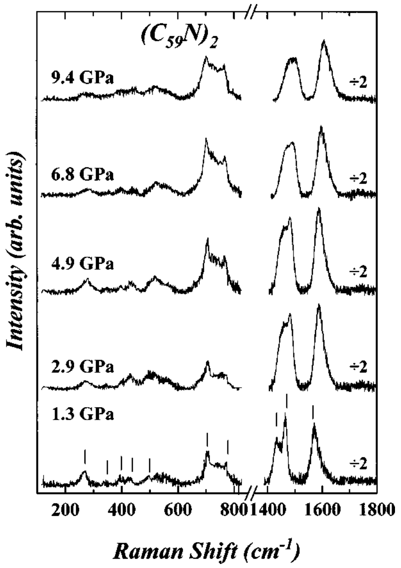

FIG. 1. Raman spectra of $(C_{59}N)_2$ at room temperature and for various pressures up to 10 GPa. The vertical lines indicate the observed phonon peaks.

The pressure dependence of the observed phonon mode frequencies is shown in Figs. 2, 3, and 4 for the high, middle and low frequency regime, respectively. The open (solid) symbols denote data taken for increasing (decreasing) pressure measurement protocols. The peak positions were determined by least-squares fitting of Gaussian line shapes to the experimental data. All modes, except $H_g(3)$ and $H_g(4)$, exhibit a positive response to pressure, in analogy to pristine C_{60}. The shaded areas denote the pressure regions where changes of the pressure coefficients occur. The phonon frequencies as well as their pressure coefficients, as obtained by the least-squares fitting procedure, are tabulated in Table I along with the corresponding data for pristine C_{60}.[15] From Figs. 2, 3, and 4, 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.[18] 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 those also found by x-ray diffraction (XRD) measurements.[6]

The strongest lines of the Raman spectrum of $(C_{59}N)_2$, corresponding to the $H_g(7)$, $A_g(2)$, and $H_g(8)$ intramolecular phonon modes, exhibit a monotonic increase with pressure (see Fig. 2). From Table I, we see that for $P < 6$ GPa the pressure coefficients $(\partial\omega/\partial P)$ of these phonons are system-

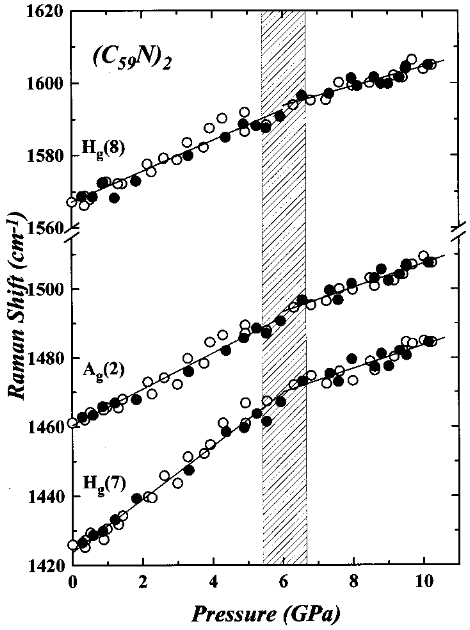

FIG. 2. The pressure dependence of the $H_g(7)$, $A_g(2)$, and $H_g(8)$ intramolecular Raman modes of $(C_{59}N)_2$. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded area near $P=6.0\pm0.5$ GPa denotes the change in the slope of the pressure dependence.

atically smaller than those of the corresponding modes of C_{60}. This can be rationalized by taking into account the lower compressibility of $(C_{59}N)_2$ (Refs. 7 and 9) compared to that of pristine C_{60}. However, when the pressure reaches the region 6.0 ± 0.5 GPa, a reversible change in their pressure response occurs, without any frequency discontinuity or any residual softening after pressure release. Their pressure coefficients above that pressure region are drastically reduced. The effect is most pronounced for the $H_g(7)$ mode, whose pressure coefficient is reduced by more than 50%. The critical pressure regime, 6.0 ± 0.5 GPa, is in excellent agreement with structural results obtained by synchrotron x-ray diffraction measurements. These have shown that the (c/a) ratio in azafullerene solid increases monotonicaly with increasing pressure until, at ~6.5 GPa, it reaches the ideal hcp (c/a) value, and then remains unchanged to much higher pressures (20 GPa).[5,7] The observed behavior was rationalized by noting that at this pressure (~6.5 GPa), the interdimer center-to-center distance is compressed to ~9.3–9.4 Å, essentially identical to the corresponding intradimer distance. So, the

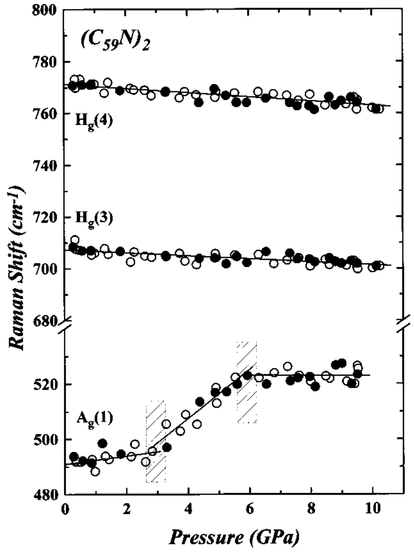

FIG. 3. The pressure dependence of the $A_g(1)$, $H_g(3)$, and $H_g(4)$ intramolecular Raman modes of $(C_{59}N)_2$. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded areas at ~3.0 and ~6.0 GPa denote the changes in the slope of the pressure dependence for $A_g(1)$ breathing mode.

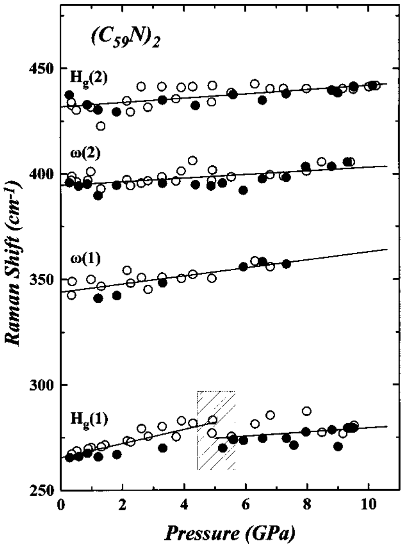

FIG. 4. The pressure dependence of the $H_g(1)$, $\omega(1)$, $\omega(2)$, and $H_g(2)$ intramolecular Raman modes of $(C_{59}N)_2$. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded area at ~5 GPa denotes the change in the slope of the pressure dependence for $H_g(1)$ mode.

TABLE I. The phonon frequencies, assignment and their pressure coefficients for the $(C_{59}N)_2$ Raman active modes. The corresponding values for C_{60} are also included.

	$(C_{59}N)_2$				C_{60}[a]	
Mode	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
		$P<6$ GPa	$P>6$ GPa			
$\omega(1)$	344	1.9	1.9		345	2.9
$\omega(2)$	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
$H_g(4)$	771	−0.8	−0.8		772	−2.7
$H_g(7)$	1424	7.6	3.4		1422	9.8
$A_g(2)$	1460	5.2	3.5		1467	5.5
$H_g(8)$	1567	4.2	2.7		1570	4.8
		$P<3$ GPa	$3<P<6$ GPa	$P>6$ GPa		
$A_g(1)$	491	1.5	8.8	−0.1	495	4.2

[a] Data from Ref. 15.

Raman data are also sensitive to these structural ''modifications'' of $(C_{59}N)_2$ in the same pressure region.

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 ~6.0 GPa (Fig. 3). A change at ~3 GPa has been also observed in the XRD measurements for the $(10\bar{1}1)$ reflection.[7] This behavior was interpreted as reflecting the significant difference between the compressibility of the molecular units and that of the bulk solid. The pressure dependence of the $A_g(1)$ mode supports this interpretation. For pressure $P<3$ GPa, the breathing mode hardens at a slower rate than that of C_{60} (Table I), as the decrease in volume is mainly absorbed by the weak van der Waals forces between the dimeric units and has little effect on the intradimer C-C bridge. For $3<P<6$ GPa, the $A_g(1)$ mode hardens faster, while for $P>6$ GPa, its frequency remains practically unchanged. For pressures above 3 GPa, the change of 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 6 GPa, where the structure of the material approaches the ideal hcp one, its lower compressibility results in the frequency invariance of this mode. The $H_g(3)$ and $H_g(4)$ intramolecular modes of $(C_{59}N)_2$ (Fig. 3) soften with increasing pressure almost linearly in the whole pressure region investigated, as in the case of C_{60} but with smaller pressure coefficients [in particular, the $H_g(4)$ mode]. The $\omega(1)$, $\omega(2)$, and $H_g(2)$ modes have pressure dependence similar to those of C_{60} and do not show any change in their pressure coefficients (Fig. 4). Finally, the pressure dependence of $H_g(1)$ mode exhibits a reversible pressure coefficient change at $P\approx 5$ GPa with smaller slope values at higher pressures (Table I).

IV. CONCLUSION

In conclusion, by comparing the pressure dependence of the modes observed in $(C_{59}N)_2$ to that of the corresponding modes in C_{60}, we find that both materials show the same signs in their frequency shifts $(\partial\omega/\partial P)$. This indicates that the structure of the material does not play a significant role in the pressure response of the intramolecular modes with its role limited to modifying the magnitude of $(\partial\omega/\partial P)$. Dimerization mainly leads to two effects observed in the Raman spectra. First, it induces a red shift to the frequencies of certain modes and second, it separates the modes into two categories: those that exhibit pressure coefficient changes, and those that do not. We suggest that the modes showing pressure coefficient changes are those inducing larger volume changes, e.g., $A_g(1)$, $A_g(2)$, $H_g(1)$, $H_g(7)$, and $H_g(8)$. We note that the H_g modes are quadrupolar which retain an axis of fivefold symmetry and the $A_g(1)$ and $A_g(2)$ modes are the breathing and the pentagon-pinch modes. This is in accordance with the fact that pentagons are more sensitive to volume changes because they contain the weaker single bonds.

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[1] W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. **190**, 159 (1992).

[2] W. Andreoni, A. Curioni, K. Holczer, K. Prassides, M. Keshavarz-K., J. C. Hummelen, and F. Wudl, J. Am. Chem. Soc. **118**, 11 335 (1996).

[3] J. C. Hummelen, B. Knight, J. Pavlovich, R. Gonzalez, and F. Wudl, Science **269**, 1554 (1995).

[4] C. M. Brown, L. Cristofolini, K. Kordatos, K. Prassides, C. Bellavia, R. Gonzalez, M. Keshavarz-K., F. Wudl, A. K. Cheetham, J. P. Zhang, W. Andreoni, A. Curioni, A. N. Fitch, and P. Pattison, Chem. Mater. **8**, 2548 (1996).

[5] K. Prassides, F. Wudl, and W. Andreoni, Fullerene Sci. Technol. **5**, 801 (1997).

[6] T. Pichler, M. Knupfer, M. S. Golden, S. Haffner, R. Friedlein, J. Fink, W. Andreoni, A. Curioni, M. Keshavarz-K., C. Bellavia-Lund, A. Sastre, J. C. Hummelen, and F. Wudl, Phys. Rev. Lett. **78**, 4249 (1997).

[7] C. M. Brown, E. Beer, C. Bellavia, L. Cristofolini, R. Gonzalez, M. Hanfland, D. Hausermann, M. Keshavarz-K., K. Kordatos, K. Prassides, and F. Wudl, J. Am. Chem. Soc. **118**, 8715 (1996).

[8] T. Kitamoto, S. Sasaki, T. Atake, T. Tanaka, H. Kawaji, K. Kikuchi, K. Saito, S. Suzuki, Y. Achiba, and I. Ikemoto, Jpn. J. Appl. Phys., Part 2 **32**, L424 (1993).

[9] S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, Nature (London) **351**, 380 (1991).

[10] J. C. Hummelen, M. Prato, and F. Wudl, J. Am. Chem. Soc. **117**, 7003 (1995).

[11] K. Prassides, M. Keshavarz-K., E. Beer, C. Bellavia, R. Gonzalez, Y. Murata, F. Wudl, A. K. Cheetham, and J. P. Zhang, Chem. Mater. **8**, 2405 (1996).

[12] A. Jayaraman, Rev. Sci. Instrum. **57**, 1013 (1986).

[13] D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).

[14] K. P. Meletov, E. Liarokapis, J. Arvanitidis, K. Papagelis, D. Palles, G. A. Kourouklis, and S. Ves, Chem. Phys. Lett. **290**, 125 (1998).

[15] K. P. Meletov, G. A. Kourouklis, D. Christofilos, and S. Ves, Zh. Eksp. Theor. Fiz. **108**, 1456 (1995) [JETP **81**, 798 (1995)].

[16] D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. S. de Vries, Chem. Phys. Lett. **179**, 181 (1991).

[17] A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P. C. Eklund, D. S. Cornett, W. A. Duncan, and I. J. Amster, Science **259**, 955 (1993).

[18] K. P. Meletov, D. Christofilos, S. Ves, and G. A. Kourouklis, Phys. Rev. B **52**, 10 090 (1995).