

Comparative Raman Study of the $C_{60}H_{36}$ and $C_{60}H_{60}$ Fullerene Hydrides

K. P. Meletov,¹ I. O. Bashkin,¹ V. V. Shestakov,¹ I. I. Tartakovskii,¹
A. A. Maksimov,¹ J. Arvanitidis,^{2,3} D. Christofilos,² and G. A. Kourouklis²

¹Institute of Solid State Physics of RAS, Moscow region, Russia

²Physics Division, School of Technology, Aristotle University of Thessaloniki,
Greece

³Department of Applied Sciences, Technological Educational Institute of
Thessaloniki, Sindos, Greece

Abstract: The hydrogen-induced changes in the phonon spectra of the $C_{60}H_{36}$ and $C_{60}H_{60}$ fullerene hydrides prepared under high hydrogen pressure are studied by Raman spectroscopy. The isotopic substitution by deuterium results in large isotopic shift of the C-H stretching modes.

Keywords: Hydrogenated fullerenes, Isotopic effect, Raman spectra

Predicted theoretically, stable hydrofullerene $C_{60}H_{36}$ has been extensively studied to identify its molecular structure and properties (1–3). The $C_{60}H_{36}$ molecule has a great number of isomers, the presence of which in various samples depends mostly on the material preparation method (2, 4). Unlike $C_{60}H_{36}$, the synthetic routes, the chemical and the physical properties of $C_{60}H_{60}$ are much less studied so far.

The $C_{60}H_{36}$ samples were obtained by 25 hours treatment of C_{60} at a hydrogen pressure of ~ 3 GPa at ~ 620 K, whereas the $C_{60}H_{60}$ samples were synthesized by 16.5 hours treatment of C_{60} at ~ 5 GPa and various temperatures within the 620–770 K range. After annealing at ~ 620 K in vacuum, the C_{60} pellets of 99.99% purity were placed into a copper capsule covered with hydrogen permeable 0.01 mm thick Pd foil. The remaining space was filled with AlH_3 powder, and the capsule was

Address correspondence to K. P. Meletov, Institute of Solid State Physics of RAS, 142432 Chernogolovka, Moscow region, Russia. E-mail: mele@issp.ac.ru

plugged with a Cu lid using Ga as solder. The capsule was maintained at high temperature/high pressure, where AlH_3 decomposes (above 400 K) and the released hydrogen reacts with C_{60} . Hydrogen was always in excess, corresponding to an H/C_{60} ratio of 90–120, whereas the hydrogen impermeable Cu lid and Ga solder prevented any losses. The hydrogen content in the final material was determined by combustion and weighing of the reaction products, H_2O and CO_2 . The mass-spectroscopy performed for $\text{C}_{60}\text{H}_{36}$ shows purity better than 95%, while its X-ray diffraction patterns confirm its *bcc* structure with a lattice parameter of 11.83 Å. Raman spectra were collected from transparent and colorless crystalline specimens using a triple monochromator DILOR XY equipped with liquid nitrogen cooled CCD system. The 647.1 nm and the 676.4 nm lines of a Kr^+ laser with a power of 0.1–0.5 mW on sample were used for excitation.

The Raman spectrum of $\text{C}_{60}\text{H}_{36}$ contains 126 sharp peaks, whereas only 17 broader peaks are observed for $\text{C}_{60}\text{H}_{60}$ (Figure 1). The symmetry lowering of the $\text{C}_{60}\text{H}_{36}$ molecule, resulting in the mode splitting and the lifting of symmetry restrictions, as well as the presence of a number of isomers in the $\text{C}_{60}\text{H}_{36}$ samples, result in the appearance of a huge number of peaks in their Raman spectrum (2, 4). On the contrary, the $\text{C}_{60}\text{H}_{60}$ molecule retains the icosahedral symmetry of the C_{60} fullerene cage and does not seem to have isomeric forms; accordingly, its Raman spectrum is less abundant in peaks (Figure 1). Nevertheless, the detailed analysis of the $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{60}\text{H}_{60}$ Raman spectra shows remarkable coincidence for a number of phonon frequencies. An important Raman feature of

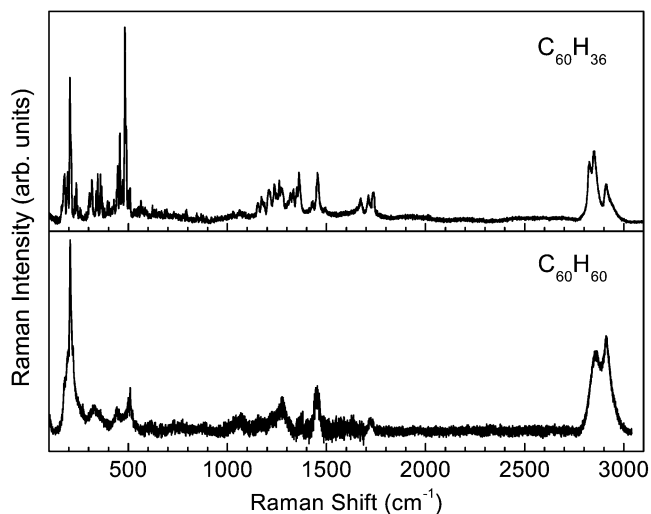


Figure 1. Raman spectra of the $\text{C}_{60}\text{H}_{36}$ and $\text{C}_{60}\text{H}_{60}$ fullerene hydrides measured at ambient conditions.

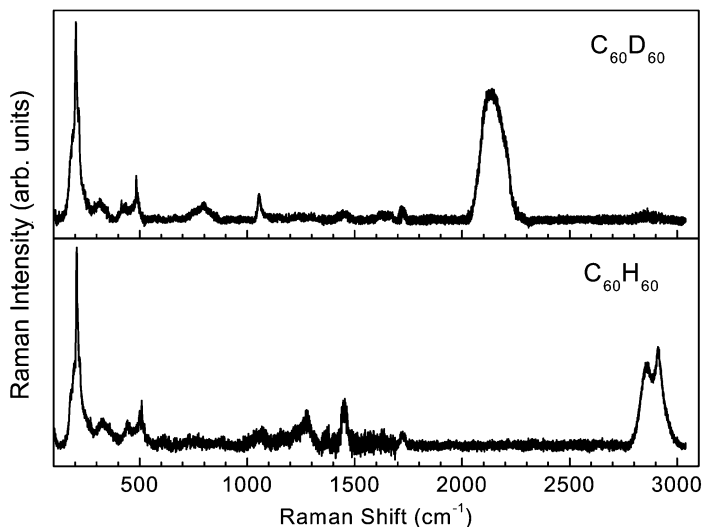


Figure 2. Isotopic shift of phonon bands in the Raman spectra of the hydrogenated $C_{60}H_{60}$ and deuterated $C_{60}D_{60}$.

hydrogenated fullerenes is the appearance of the C-H stretching ($2800\text{--}3000\text{ cm}^{-1}$) and bending ($1150\text{--}1350\text{ cm}^{-1}$) vibrational modes. The frequencies of these modes show a large isotopic shift upon deuterium substitution (Figure 2). The frequency isotopic effect, quantified by the ratio $(\Omega_H/\Omega_D)^2$, is somewhat larger for $C_{60}H_{60}$ than for $C_{60}H_{36}$. It varies from 1.012 to 1.086 for the fullerene cage modes and from 1.78 to 1.839 for the C-H stretching modes. The values for the C-H stretching modes are close to the mass ratio of hydrogen to deuterium ($M_H/M_D=2$). The difference in the isotopic shifts reflects the dominant contribution of the hydrogen atoms to the stretching C-H vibrations, while their contribution to the cage vibrations is very small.

Contrary to the pristine C_{60} , $C_{60}H_{36}$ and $C_{60}H_{60}$ show strong luminescence signal in the visible spectral region. The optical spectra of hydrocarbons demonstrate generally red shifts of this luminescence signal as the number of C-H bonds increases. Accordingly, the luminescence background is more intense for $C_{60}H_{60}$ and in order to reduce the screening of the Raman signal, the 676.4 nm Kr^+ laser line has been used for the excitation of its Raman spectrum.

ACKNOWLEDGMENTS

The support by the Russian Foundation for Basic Research, grant No. 08-02-00890, and the support of the General Secretariat for Research

and Technology (Greece) and Russian Academy of Sciences under the bilateral Greek-Russian collaboration program are greatly acknowledged.

REFERENCES

1. Rathna, A. and Chandrasekhar, J. (1993) Theoretical study of hydrogenated buckminsterfullerene derivatives with benzenoid rings, $C_{60}H_{60-6n}$ ($n = 1-8$). *Chem. Phys. Letters*, 206: 217–224.
2. Bini, R., Ebenhoch, J., Fanti, M., Fowler, P.W., Leach, S., Orlandi, G., Rüchardt, Ch., Sandall, J.P.B., and Zerbetto F. (1998) The vibrational spectroscopy of $C_{60}H_{36}$: an experimental and theoretical study. *Chem. Phys.*, 232: 75–94.
3. Hall, L.E., McKenzie, D.R., Attala, M.I., Vassalo, A.M., Davis, R.L., Dunlop, J.B., and Cokayne, D.J.H. (1993) The structure of $C_{60}H_{36}$. *J. Phys. Chem.*, 97: 5741–5744.
4. Meletov, K.P., Assimopoulos, S., Tsilika, I., Bashkin, I.O., Kulakov, V.I., Khasanov, S.S., and Kourouklis, G.A. (2001) Isotopic and isomeric effects in high-pressure hydrogenated fullerenes studied by Raman spectroscopy. *Chem. Phys.*, 263: 379–388.