

# Inelastic light scattering of hydrogen containing open-cage fullerene ATOCF

P. M. Rafailov<sup>\*1</sup>, C. Thomsen<sup>\*\*1</sup>, A. Bassil<sup>2</sup>, K. Komatsu<sup>3</sup>, and W. Bacsa<sup>2</sup>

<sup>1</sup> Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

<sup>2</sup> Laboratoire Physique des Solides de Toulouse UMR-CNRS 5477, IRSAMC, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France

<sup>3</sup> Institute for Chemical Research (ICR), Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Received 20 July 2005, revised 11 August 2005, accepted 12 August 2005

Published online 18 August 2005

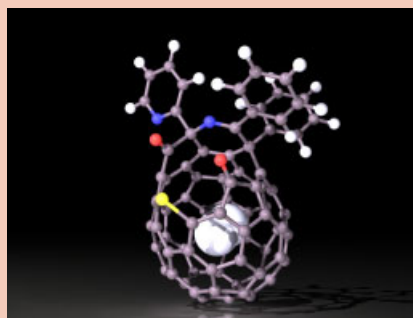
PACS 63.22.+m, 78.30.Na

\* Permanent address: Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Tzarigradsko Chaussee 72, 1784 Sofia, Bulgaria

\*\* Corresponding author: e-mail thomsen@physik.tu-berlin.de, Phone +49-30-23187, Fax +49-30-27705

We report Raman measurements on Aza-Thia Open-Cage Fullerene (ATOCF) containing hydrogen molecules. We analyze the spectral bands of empty and H<sub>2</sub>-filled ATOCF and compare them with Raman spectra of pristine C<sub>60</sub>. We find a large number of additional bands due to the lower symmetry of ATOCF and detect the hydrogen stretching vibration of the caged H<sub>2</sub> molecules. Depending on their environment significant band broadening is observed.

ATOCF molecule containing H<sub>2</sub>.



© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** Endohedral complexes incorporating noble gases and other atomic species have attracted recent scientific interest in fullerene [1] and nanotube research [2]. They offer the possibility of studying quasi-isolated species inside the C<sub>60</sub> cage and, e.g., using them as contrast agent in magnetic resonance imaging.

Transformation of the  $\sigma$  framework of the fullerene cage causing an opening of a sufficiently large orifice by organic synthesis can greatly improve the yields of endohedral fullerenes. The C<sub>60</sub> derivative Aza-Thia Open-Cage Fullerene has a 13-membered-ring orifice [3] on the C<sub>60</sub> cage with dimensions  $5.64 \times 3.75 \text{ \AA}^2$  and is expected to have good hosting properties for small atoms and molecules like H<sub>2</sub> and He. It was shown recently that the encapsulation of an H<sub>2</sub>-molecule in ATOCF creates with very high yield the endohedral complex H<sub>2</sub>@ATOCF [4].

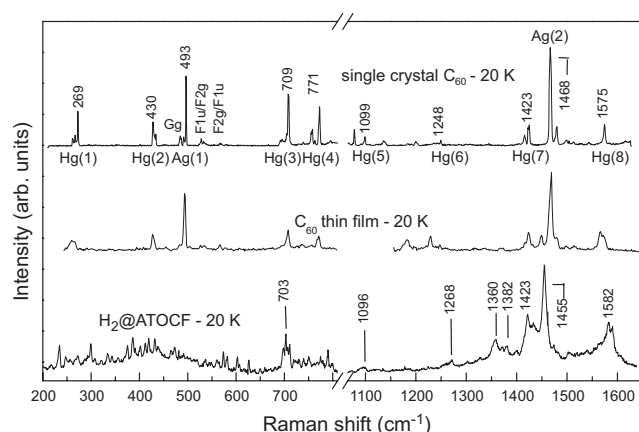
In this work we examine H<sub>2</sub>@ATOCF and the empty ATOCF by means of Raman spectroscopy. We establish significant differences in the Raman response of open-cage

fullerenes (OCF) and pristine C<sub>60</sub> and report the first detection of a signal from the stretching vibration of the H<sub>2</sub> molecule inside the ATOCF.

**2 Experimental** A powder sample of ATOCF was prepared in three steps: (i) thermal reaction of C<sub>60</sub> with a 1,2,4-triazine derivative yielded an OCF with an eight-membered ring orifice; (ii) enlargement of this orifice to a 12-membered ring orifice through a photochemical reaction with O<sub>2</sub>; and (iii) further enlargement to a 13-membered ring orifice through an insertion of a heteroatom into an activated C–C bond. Preparation details are given in Ref. [3]. The ATOCF powder was measured as prepared, as well as after it was dissolved in 1,2-dichlorobenzene and dried on a glass substrate.

The Raman measurements were performed with a Dilor XY 800 triple grating spectrometer with a liquid-N<sub>2</sub> cooled CCD detector. The Ar<sup>+</sup>/Kr<sup>+</sup>-laser line at 488 nm was used as excitation source with spectrometer slits set to

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim



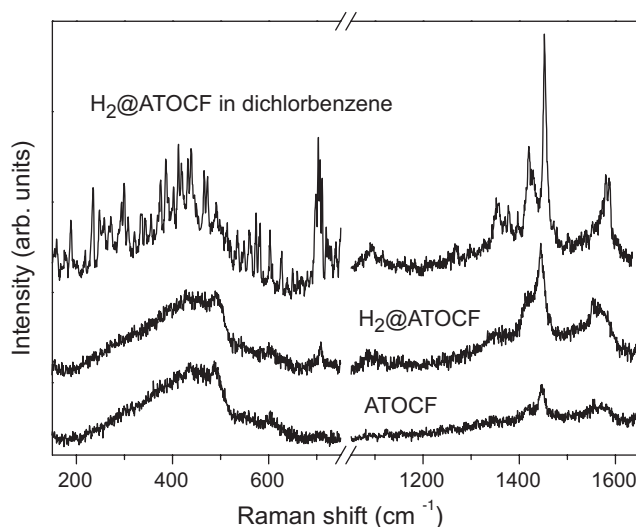
**Figure 1** Raman spectra at 20 K of pristine  $C_{60}$  (upper trace) and 1,2-dichlorobenzene-processed  $H_2@ATOCF$  (lower trace).

$2.5 \text{ cm}^{-1}$  spectral width and absolute accuracy of  $0.5 \text{ cm}^{-1}$ . The laser beam was focused to a spot of diameter  $\approx 2$  micrometer using microscope optics ( $\times 100$ ). The samples were found to be very sensitive to laser irradiation (the Raman spectrum remained stable only a few minutes upon laser power exposure of  $0.5 \text{ mW}$ ). The laser was therefore kept below  $0.1 \text{ mW}$ . Under these conditions no changes in line positions and sample morphology were observed after long laser exposure. The low-temperature measurements were made in vacuum using an Oxford micro-cryostat.

**3 Results and discussion** Comparative Raman spectra of dichlorobenzene-dissolved ATOCF, a thin film of  $C_{60}$  and a  $C_{60}$  single crystal, taken at 20 K are shown in Fig. 1. We find an ATOCF spectrum with no pronounced intense lines but very rich in structure in the energy range of the radial modes ( $200\text{--}800 \text{ cm}^{-1}$ ) of  $C_{60}$ . This is not surprising since the radial symmetry is broken for the ATOCF molecule. While the most intense peak for pure  $C_{60}$  corresponds to the radial breathing mode at  $493 \text{ cm}^{-1}$ , this mode cannot be unambiguously distinguished for ATOCF. We find instead that the  $H_g(3)$ -derived band at  $700\text{--}710 \text{ cm}^{-1}$  dominates the spectrum.

In the energy range of the tangential modes ( $1100\text{--}1600 \text{ cm}^{-1}$ ) we find a couple of pronounced ATOCF bands that can be related to Raman-active  $C_{60}$  modes. The modes  $H_g(6)$ ,  $H_g(7)$  and  $H_g(8)$  are upshifted [ $H_g(7)$  probably mixes with the near lying IR-active  $F_{1u}(4)$  mode at  $1431 \text{ cm}^{-1}$ ]. The  $A_g(2)$  line (the so-called pentagonal pinch mode) is downshifted by  $13 \text{ cm}^{-1}$  to  $1455 \text{ cm}^{-1}$  in the open-cage fullerene, as compared to  $C_{60}$ . There is also an additional intense band with two pronounced peaks at  $1360$  and  $1382 \text{ cm}^{-1}$ . Although the Raman spectrum of pristine  $C_{60}$  does not exhibit any peaks in this frequency range, there are a couple of close-by lying  $C_{60}$   $F_{1g}$ ,  $F_{2g}$ ,  $G_g$ , and  $H_u$  modes between  $1355$  and  $1385 \text{ cm}^{-1}$  [1]. We therefore attribute this band to Raman forbidden  $C_{60}$  eigenmodes activated in the Raman spectrum of ATOCF through the symmetry lowering from  $I_h$  of  $C_{60}$  to  $C_1$ .

The  $A_g(2)$  line of ATOCF is the only phonon band that can be fitted with a symmetric line profile. Its linewidth is

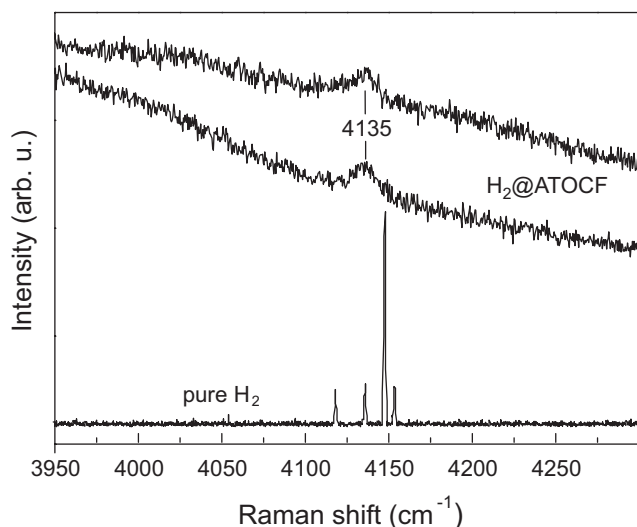


**Figure 2** Comparative Raman spectra at 20 K of 1,2-dichlorobenzene-processed  $H_2@ATOCF$  (upper trace),  $H_2@ATOCF$  powder as obtained (middle trace) and empty ATOCF powder (lower trace).

three times larger than that of pristine  $C_{60}$ . The same broadening factor of 3–4 also applies to the other ATOCF bands. In pristine  $C_{60}$  the downshift of the  $A_g(2)$  line is a sign for a phototransformation to a triplet state that causes a creation of dimers or oligomers via the  $2 + 2$  cycloaddition in the fcc phase [5, 6]. This implies that the charge distribution in ATOCF is different from that in  $C_{60}$  and possibly related to the triplet state of the pristine fullerene.

Figure 2 presents Raman spectra of  $H_2@ATOCF$  dissolved in 1,2-dichlorobenzene and dried (upper trace), a powder of  $H_2@ATOCF$  (middle trace) and empty ATOCF powder (lower trace). In the latter two cases the spectral lines are highly broadened. Our fits revealed that this broadening is accompanied with an amendment to a more Gaussian-like lineshape. This is an indication of an inhomogeneous broadening caused by the random surroundings felt by the ATOCF molecules in the originally obtained powder. The sharpening of the spectral features in the spectra of the dissolved powder implies that processing with 1,2-dichlorobenzene leads to micro-ordering of the ATOCF molecules. We find this related to other fullerene derivatives with self-organizing capabilities in solution, especially the ionic  $C_{60}$  derivative MPFDAC known to form nanorods [7]. The Raman spectra of this compound are similar to those of solution processed ATOCF. The inhomogeneous broadening is also illustrated by comparing the spectra to  $C_{60}$  single crystal and thin films in Fig. 1. In the thin film at 20 K the adjacent  $C_{60}$  molecules are frozen in random orientations and thus experience random surroundings. This leads to a broadening of the sharp  $H_g$  components and the  $H_g$  modes develop into bands.

Motivated by the possible use of ATOCF-incorporated  $H_2$  as a sensitive probe for NMR, we attempted to detect its Raman signal. The range of  $C_{60}$  radial modes overlaps with that of  $H_2$  rotational states. Furthermore, the lower symme-



**Figure 3** Raman spectra of  $H_2@ATOCF$  in the region of the  $H_2$  stretching modes (upper and middle curves) and a sample Raman spectrum of pure  $H_2$  gas phase for reference (lower trace).

try of ATOCF multiplies the modes observed in this energy range. The low frequency spectrum can therefore not be unequivocally interpreted, as the  $H_g$  splitting and the activation of Raman forbidden modes give rise to much of the observed rich structure between 200 and  $800\text{ cm}^{-1}$ . On the other hand, in the energy range of the  $H_2$  stretching mode there are no competing vibrations of other species, and we indeed find a broadened and slightly down-shifted band at  $4135\text{ cm}^{-1}$ , shown in Fig. 3, which we attribute to the  $H_2$  inside ATOCF. We expect that the interaction of the  $H_2$  molecule inside ATOCF leads to broadening and a downshift of the stretching vibrational modes compared to the free  $H_2$  molecule. A Raman spectrum of free  $H_2$  is shown in Fig. 3 for comparison as well. It must, however, be mentioned that this band was detected exceptionally rarely after extensive spot-resolved measurements. Also the spectra of ATOCF vibrations varied strongly in shape

and relative intensity depending on the actual sample spot which is a sign of a variable sample morphology.

**4 Conclusions** The ATOCF Raman spectra exhibit a significantly larger number of modes, as compared to  $C_{60}$ , which we can attribute to the symmetry lowering from  $I_h$  of  $C_{60}$  to  $C_1$ . Some of those modes fall in the energy range of the expected rotational levels of  $H_2$ . ATOCF samples processed with a solvent have richer spectra with sharper and more intense features in them as compared to the original ATOCF powder. This implies that processing with a solvent leads to micro-ordering of the ATOCF molecules. A Raman signal from the ATOCF-incorporated  $H_2$  molecule was detected.

**Acknowledgment** We would like to thank Malcolm Levitt for discussions and motivation of this work and we thank Antoine Zwick for providing the Raman spectra of molecular hydrogen.

## References

- [1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1995).
- [2] S. Reich, C. Thomsen, and J. Maultzsch, *Carbon Nanotubes: Basic Concepts and Physical Properties* (Wiley-VCH, Weinheim, 2004).
- [3] Y. Murata, M. Murata, and K. Komatsu, *Chem. Eur. J.* **9**, 1600 (2003).
- [4] Y. Murata, M. Murata, and K. Komatsu, *J. Am. Chem. Soc.* **125**, 7152 (2003).
- [5] P. Zhou, A. M. Rao, K. Wang, J. D. Robertson, C. Eloi, M. S. Meier, S. L. Ren, X. Bi, P. C. Eklund, M. S. Dresselhaus, *Appl. Phys. Lett.* **60**, 2871 (1992).
- [6] L. Akselrod, H. J. Byrne, C. Thomsen, A. Mittelbach, and S. Roth, *Chem. Phys. Lett.* **212**, 384 (1993).
- [7] M. Mannsberger, A. Kukovecz, V. Georgakilas, J. Rechthaler, G. Allmeier, M. Prato, and H. Kuzmany, in: *Electronic Properties of Novel Materials – Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (AIP, 2003), p. 11.