<http://www.diva-portal.org>

Postprint

This is the accepted version of a paper published in *Chemical Physics Letters*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Du, M., Zhou, M., Yao, M., Ge, P., Chen, S. et al. (2017)
High pressure infrared spectroscopy study on C60*CS2 solvates.
Chemical Physics Letters, 669: 49-53
<https://doi.org/10.1016/j.cplett.2016.11.047>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-132131>

High pressure infrared spectroscopy study on C₆₀*CS₂ solvates

Mingrun Du ^a, Miao Zhou ^a, Mingguang Yao ^{a,b,#}, Peng Ge ^a, Shuanglong Chen ^a,
Xigui Yang ^a, Ran Liu ^a, Bo Liu ^a, Tian Cui ^b, Bertil Sundqvist ^{c,a}, Bingbing Liu^{a, #}

^a State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, PR China

^b College of Physics, Jilin University, Changchun 130012, PR China

^c Department of Physics, Umea University, Umea 90187, Sweden

High pressure IR study has been carried out on C₆₀*CS₂ solvates up to 34.8 GPa. It is found that the intercalated CS₂ molecules significantly affect the transformations of C₆₀ molecules under pressure. As a probe, the intercalated CS₂ molecules can well detect the orientational ordering transition and deformation of C₆₀ molecules under pressure. The chemical stability of CS₂ molecules under pressure is also dramatically enhanced due to the spacial shielding effect from C₆₀ molecules around in the solvated crystal. These results provide new insight into the effect of interactions between intercalants and fullerenes on the transformations in fullerene solvates under pressure.

Keywords:

High pressure; IR spectra; Fullerene; C₆₀*CS₂ solvates

Corresponding authors at:

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, PR China.

E-mail addresses: yaomg@jlu.edu.cn (M. Yao), liubb@jlu.edu.cn (B. Liu).

1. Introduction

Fullerene solvates have become a new focus which attracts intensive research interests due to their facile preparation, tunable morphology and outstanding light emission property [1–6]. In general, fullerene solvates are typical molecular crystals, which are sustained by relatively weak van der Waals interactions. Therefore, high pressure technology, as a powerful method to change the distances and the interactions between the molecules, should be a suitable method to be applied in fullerene solvates for producing new novel materials and the investigation on fullerene solvates for basic scientific interest [7].

Recent high pressure studies on the fullerene solvates show that upon compression the fullerene solvates exhibit unusual compression behaviors and can transform to novel phases. It is reported that the fullerene solvates (such as C_{70} **m*-xylene and C_{60} **m*-xylene) can transform to a long-range ordered material containing amorphous carbon clusters as building blocks under pressure, which is hard enough to indent diamond [8,9]. It is striking that the intercalated solvent molecules in fullerene solvates play an important role in tuning the boundary interactions of fullerene units in the high pressure phases, which strongly affect the properties of the final products [10,11]. In view of this, a in-depth understanding of the effects of solvent molecules on the transformations in fullerene solvates under pressure is urgently desirable and of great importance in this field.

Up to now, the high pressure studies have only been carried on several fullerene solvates doped by aromatic solvents [8–11]. Besides the aromatic solvents, carbon disulfide is also widely used as a good solvent for preparing C_{60} solvated crystals. The C_{60} *CS₂ solvated crystals can be produced by evaporating carbon disulfide solution of C_{60} or a solution injection method [1,12,13]. It is known that the neat CS₂ are unstable and reactive under pressure. Above 10 GPa and at 300 K, the neat CS₂ would partially decomposes with the release of sulfur [14]. Black-polymer would be formed in pure CS₂ solid starting from about 8 GPa at room temperature [15]. This is in sharp contrast to the pressure behaviors of aromatic solvents which are more stable under pressure. For example, the critical pressure for the polymerization of benzene is reported to be above 20 GPa [16]. Furthermore, Popov *et al.* report that 3D-polymerized C_{60} can be formed at a low pressure due to the presence of CS₂ molecules in C_{60} powders, which act as catalyzer in the polymerization of C_{60} [17]. Such phenomenon has never been reported in fullerene solvates intercalated by aromatic solvents.

These results suggest that in comparison to aromatic solvents, the CS₂ molecules would play a different role on the transformations in fullerene solvates during the compression process. It is therefore very interesting to carry out high pressure study on C₆₀*CS₂ solvates for discovering new mechanism in solvated fullerenes.

In this work, we studied high pressure IR spectra of C₆₀*CS₂ solvates up to 34.8 GPa. We found that both CS₂ molecules and C₆₀ molecules in C₆₀*CS₂ solvates under pressure behaved differently from their corresponding single-component material due to their interactions. Furthermore, it is found that the intercalated CS₂ molecules could act as a good probe which well reflects the changes in the C₆₀ rotation and the deformation of C₆₀ molecules in the solvated samples upon compression, due to the C₆₀-CS₂ interactions.

2. Experimental methods

C₆₀*CS₂ solvates were synthesized according to the process described in Ref. [1]. In brief, 2.5 ml isopropyl alcohol was dropped into 1 ml C₆₀/CS₂ solution (0.2 mg/ml). After 30 s ultrasonication, brown precipitates were precipitated on the bottom of the bottle. The morphology and structure of the as-grown solvated samples were characterized with transmission electron microscopy (TEM, JEM-2200FS transmission electron microscopy with an acceleration voltage of 200 kV). Raman measurements were carried out using a Raman spectrometer (Renishaw in Via (Renishaw, London, UK)) excited by a 830 nm laser.

High pressure experiments were performed in a Mao-Bell type diamond anvil cell installed with two type-IIa diamonds with 0.2 mm culets at room temperature. KBr was used as pressure transmitting medium. The KBr powder was loaded into a 100-μm diameter hole drilled in the compressed T301 stainless steel gasket with the thickness of 0.04 mm, and then was pressed transparent by the diamond anvils. C₆₀*CS₂ solvates or pristine C₆₀ were loaded onto the transparent KBr plate in the hole for the infrared measurements. In order to obtain high quality IR spectra under pressure, the thickness of the samples in the hole was optimized at ambient conditions by adjusting the sample amount repeatedly, before applying pressure. Small ruby chips were incorporated with the sample for pressure calibration by measuring the shift of the fluorescence line. In situ IR spectra were measured with a Bruker Vertex80 V FTIR spectrometer.

3. Results and discussion

The IR and Raman spectra of C_{60} *CS₂ solvates at ambient conditions are shown in Fig. 1(a) and (b) respectively. The spectra of pristine C_{60} are also shown in the bottom of the figures for comparison. From the figures, we find that the spectra of C_{60} *CS₂ solvates show vibration modes similar to those of pristine C_{60} , suggesting only weak van der Waals interactions between the CS₂ and the C_{60} molecules. The Raman peak located at 650 cm⁻¹ and the IR peak located at 1510 cm⁻¹ are assigned to the symmetric stretching mode and asymmetric stretching mode of CS₂ molecules, respectively. Furthermore, some new peaks (marked with ‘*’) are observed at 300–600 cm⁻¹ in the Raman spectra of the solvated samples. The appearance of similar Raman peaks has also been reported in other fullerene solvates, which are induced by the symmetry reduction of the C_{60} molecular due to the C_{60} -solvent interaction [18]. TEM and the SAED (selected area electron diffraction) images of C_{60} *CS₂ solvates are shown in Fig. 1(c), which are similar to those reported in previous work [1]. The CC₆₀*CS₂ solvates are ultrathin microribbons and the corresponding SAED pattern can be well indexed by a monocline structure. Furthermore, the intensity ratio $I_{CS_2}/I_{F_{1u}(4)}$ (I_{CS_2} and $I_{F_{1u}(4)}$ are the intensities of the asymmetric stretching mode of CS₂ molecule and the $F_{1u}(4)$ mode of C_{60} molecule, respectively) in the IR spectra of the solvated samples (0.88) is close to that of C_{60} *CS₂ solvated crystals (0.85) reported by Bownar et al. [19], which may imply that the concentration of CS₂ in both samples are similar. These results suggest that we have successfully synthesized C_{60} *CS₂ solvates.

Fig. 2(a) shows the recorded IR spectra of C_{60} *CS₂ solvates under pressure. From the recorded spectra up to 34.8 GPa, we can find that the IR peaks of the solvated samples become broad and weak as pressure increases. During the compression process, several new peaks appear, especially at 550–850 cm⁻¹, in the IR spectra. It should be noted that similar new peaks are also observed in the high pressure IR spectra of pristine C_{60} , which may arise from the silent modes of I_h symmetry C_{60} molecule [20]. (Fig. S1) It is known that icosahedral C_{60} has I_h symmetry with only 14 normal modes which are Raman ($2A_g + 8H_g$) or infrared ($4F_{1u}$) active [20–23]. Thus, the appearance of new IR peaks indicates that the C_{60} molecule in solvated samples are deformed to lower symmetry under pressure. Upon compression, the $F_{1u}(2)$ (initially at 575 cm⁻¹) and $F_{1u}(3)$ (initially at 1183 cm⁻¹) modes, which are radial and tangential normal modes of C_{60} molecule [21,22], merge with the background at 7.6–8.7 GPa, indicating the significant deformation of C_{60} molecules in the solvated samples

at this pressure. At 15.2–18 GPa, the $F_{1u}(4)$ mode (initially at 1432 cm^{-1}) become too weak to be observed, and most of other C_{60} peaks have already disappeared. This indicates the significant deformation and amorphization of C_{60} molecules above this pressure. Compared with pristine C_{60} , in which the $F_{1u}(2)$ and $F_{1u}(3)$ modes disappear at ~ 11 GPa, (Fig. S1(a)) and the amorphization of C_{60} molecules is at around 20 GPa [10,24], our samples implies that the presence of CS_2 may promote the deformation and early collapse of C_{60} molecules, decreasing their stability, compared to the case of pristine C_{60} under pressure. This is in sharp contrast to the aromatic solvent (for example, m-xylene), which could enhance the stability of fullerene molecules in their solvates under pressures [9–11].

It is interesting to find that the asymmetric stretching CS_2 mode can be traced even up to 25.5 GPa without any splitting, indicating that part of intercalated CS_2 molecules are still preserved at least to such high pressure. Furthermore, the characteristic IR peaks for the CS_2 polymers (for example, the peaks at 1067 cm^{-1} which is very intense in CS_2 polymers [25]) are not observed in the recorded spectra from the solvated samples even up to 34.8 GPa. Compared to neat CS_2 , in which the CS_2 molecules are partially decomposed and polymerized at 8–10 GPa, our results suggest that the chemical stability of the CS_2 under pressure is significantly enhanced due to the intercalation into $C_{60}*CS_2$ solvates.

Fig. 2(b) shows the IR spectra of $C_{60}*CS_2$ solvates and pristine C_{60} at selected pressures. Furthermore, the $550\text{--}850\text{ cm}^{-1}$ region of the high pressure spectra of the two samples are shown in Fig. S1(c) and (b), respectively. From the figures, we find that there are several differences in the high pressure IR spectra of the two samples. At ambient conditions, the two peaks observed at 711 cm^{-1} and 725 cm^{-1} are distinct for pristine C_{60} but merged with a broad peak centered at 716 cm^{-1} for solvated samples, and the two peaks are separated in the IR spectra of solvated samples under pressure. The intensity of the peak initially located at 669 cm^{-1} dose not increase much with pressure for the solvated samples while it increases dramatically with pressure for pristine C_{60} . A new peak is observed at 589 cm^{-1} for pristine C_{60} at high pressure while such peak is not observed in the IR spectra of the solvated samples. The intensity of the new peak at 753 cm^{-1} increase with pressure for pristine C_{60} . However, for the solvated samples, this peak would disappear with pressure increasing. Furthermore, the intensity of the new peak at 761 cm^{-1} for the solvated samples increases dramatically with pressures, which is not observed in the IR spectra of pristine C_{60} . No splittings are observed in the IR peak initially located at 738 cm^{-1} for the solvated samples under pressure. The modes

from pristine C_{60} at 900–1000 cm^{-1} and 1250–1350 cm^{-1} are absent in the IR spectra of the solvated samples. These spectroscopic differences for the two samples imply that in the solvated samples, the intercalated CS_2 plays an important role on the deformation of C_{60} molecule under pressure. In addition, it should be noted that in comparison to pristine C_{60} , no new peaks in the high pressure IR spectra of the solvated sample are observed, which implies that C_{60} - CS_2 polymers are not formed in the solvated samples at least up to 15.5 GPa.

We further plot the wavenumbers of several selected IR peaks of $C_{60}^*\text{CS}_2$ solvates as functions of pressure, which are shown in Fig. 2(b) and (d). Similar plots for the IR modes of pristine C_{60} are also presented in the figures for comparison. From the figure we find that below 8.2 GPa the plots for the three selected C_{60} modes for the two samples show similar pressure evolutions but slightly different pressure coefficients probably due to the presence of CS_2 in the lattice of the solvated samples. At around 2.6 GPa, we observe slight slope changes in the plotted curves for the three F_{1u} modes from the solvated sample. It is reported that the orientational ordering transition of C_{60} molecules would occur in the $C_{60}^*\text{CS}_2$ solvates at 168 K [13]. Shimomura *et al.* reported a phase transition of $C_{60}^*\text{CS}_2$ solvates related to an orientational ordering transition of C_{60} between 1.1 and 2.2 GPa by X-ray diffraction measurement [26]. We thus suggest that the slope changes observed in our solvates at around 2.6 GPa may indicate the orientational ordering transition of C_{60} molecules in solvated samples. Above 8.2 GPa, the C_{60} modes from solvated samples exhibit quite different pressure evolutions in comparison to those from pristine C_{60} : the $F_{1u}(2)$ and $F_{1u}(3)$ modes disappear, and the slope value of the plot for $F_{1u}(4)$ mode is decreased at 8.2–9 GPa, which suggest a significant deformation of C_{60} molecules in the solvated samples above 8.2 GPa. In contrast, the wavenumbers of $F_{1u}(2)$ and $F_{1u}(3)$ modes from pristine C_{60} blue shift almost linearly with pressure up to ~11 GPa, which is similar to those reported in previous literature [24], and the $F_{1u}(4)$ mode from pristine C_{60} show no slope change at around 8.2–9 GPa. These differences further support that the presence of CS_2 molecules in the lattice of $C_{60}^*\text{CS}_2$ would promote the deformation of C_{60} molecules.

It is striking that we also observe changes in the plot for the asymmetric stretching mode of CS_2 at ~2.4 GPa and ~9 GPa (Fig. 2d). The frequency of the CS_2 mode decrease slightly as pressure increases below 2.4 GPa, which is probably due to the increased CS_2 - CS_2 interactions under pressure [27], and it starts to gradually shift to higher frequencies above 2.4 GPa. The slope value for the plot for the CS_2 mode is significantly decreased at around 9 GPa.

These results imply that the orientational ordering transition and the significant deformation of C_{60} molecules in the solvated samples are related with the C_{60} - CS_2 interactions under pressure. Furthermore, the remarkable slope changes in the plot for the asymmetric stretching mode of CS_2 molecules at 2.4 GPa and ~9 GPa suggest that CS_2 acts as a good probe for detecting the changes of transformation of C_{60} and C_{60} - CS_2 interactions in solvated samples under pressure. This provides us a new way to study fullerene solvates.

IR spectra of the released samples are shown in Fig. 3. The IR spectrum of the as-synthesized C_{60} * CS_2 solvates is also shown in the bottom of the figure for comparison. From the figure, we can see that the asymmetric stretching modes of CS_2 molecules in solvated samples released from 12.4 and 16 GPa are still retained without any splitting and shift, and no traces for the decomposition or polymerization of CS_2 can be observed in the two released samples. Furthermore, the spectroscopic features of the solvated samples and pristine C_{60} released from 16 GPa are quite similar, which implies that no covalent bonds are formed between C_{60} and CS_2 molecules in the released solvated samples. These results indicate that the intercalated CS_2 molecules in the solvates samples are still intact after the compression up to 16 GPa. This is consistent with our in situ high pressure IR spectra results, suggesting the high stability of the intercalated CS_2 molecules under pressure. In the IR spectrum of the solvated samples released from 34.8 GPa, most IR modes disappeared, which indicates the irreversible amorphization of C_{60} molecules at this pressure. In contrast, the asymmetric stretching mode at around 1510 cm^{-1} from CS_2 molecules can still be seen in the collected IR spectrum, indicating that the intercalated CS_2 molecules are preserved after the high pressure compression. It is striking that such high stability of the CS_2 molecules has never been observed in the previous high pressure studies on neat CS_2 . This suggests that the stability of the CS_2 molecules is significantly increased in the lattice of C_{60} * CS_2 solvates. It should be noted that in aromatic solvent doped fullerene solvates, the stability enhancement of fullerene molecules under pressure is due to the separation effect by the intercalated solvent molecules [9]. In the case of compressing C_{60} * CS_2 solvates, we attribute the significant stability enhancement of intercalated CS_2 to the separation by C_{60} molecules under pressure. This may expand the application of some unstable molecules in high pressure research.

In addition, it should also be mentioned that ultrahard 3D polymerized C_{60} , which can ploughed the diamond anvil, can be produced at 6–7 GPa due to the presence of CS_2 [17]. However, we do not find any cracks on the diamond anvil after the compression of the

solvated samples even up to 34.8 GPa. This suggests that the effect of intercalated CS₂ molecules on the deformation of C₆₀ molecules under pressure is strongly dependent on the pressure conditions (hydrostatic or non-hydrostatic pressure).

4. Conclusion

In summary, our high pressure IR study shows that the intercalated CS₂ molecules have significant influence on the pressure evolution of C₆₀ molecules, which promote the deformation of C₆₀ molecules under pressure. The stability of intercalated CS₂ molecules under pressure are dramatically enhanced in comparison to those in neat CS₂ due to the spatial separation effect by C₆₀ molecules. Furthermore, the intercalated CS₂ molecules can act as a good probe which well reflects the changes in the molecular rotation and the deformation of C₆₀ molecules in the crystal upon compression thanks to the C₆₀-CS₂ interactions.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China (11474121, 11634004 and 51320105007), the Cheung Kong Scholars Programme of China.

Appendix A. Supplementary material

Supplementary data associated with this article can be found on the journal home page.

References

- [1] L. Wei, J.N. Yao, H.B. Fu, *ACS Nano* 7 (2013) 7573.
- [2] Moumita Rana, R.R. Bharathanatha, Ujjal K. Gautam, *Carbon* 74 (2014) 44.
- [3] L. Wang, B.B. Liu, D.D. Liu, M.G. Yao, Y.Y. Hou, S.D. Yu, T. Cui, D.M. Li, C.T. Zou, A. Iwasiewicz, B. Sundqvist, *Adv. Mater.* 18 (2006) 1883.
- [4] C. Park, E. Yoon, M. Kawano, T. Joo, H.C. Choi, *Angew. Chem. Int. Ed.* 49 (2010) 9670.
- [5] M.G. Yao, X.H. Fan, D.D. Liu, B.B. Liu, T. Wagberg, *Carbon* 50 (2012) 209.
- [6] M.G. Yao, B.M. Andersson, P. Stenmark, B. Sundqvist, B.B. Liu, T. Wagberg, *Carbon* 47 (2009) 1181.
- [7] L. Wang, *J. Phys. Chem. Solids* 84 (2015) 85.
- [8] L. Wang, B.B. Liu, H. Li, W.G. Yang, Y. Ding, S.V. Sinogeikin, Y. Meng, Z.X. Liu, X. C. Zeng, W.L. Mao, *Science* 337 (2012) 825.
- [9] W. Cui, M.G. Yao, S.J. Liu, F.X. Ma, Q.J. Li, R. Liu, B. Liu, B. Zou, T. Cui, B.B. Liu, *Adv. Mater.* (2014).
- [10] M.G. Yao, W. Cui, J.P. Xiao, S.L. Chen, J.X. Cui, R. Liu, T. Cui, B. Zou, B.B. Liu, B. Sundqvist, *Appl. Phys. Lett.* 103 (2013) 071913.
- [11] M.G. Yao, W. Cui, M.R. Du, J.P. Xiao, X.G. Yang, S.J. Liu, R. Liu, F. Wang, B.B. Liu, B. Sundqvist, *Adv. Mater.* (2015).
- [12] K. Kikuchi, S. Suzuki, K. Saito, H. Shiromaru, I. Ikemoto, Y. Achiba, A. Zakhidov, A. Ugawa, K. Imaeda, H. Inokuchi, K. Yakushi, *Physica C* 415 (1991) 185.
- [13] M.M. Olmstead, F. Jiang, A.L. Balch, *Chem. Commun.* 6 (2000) 483.
- [14] F. Bolduan, H.D. Hochheimer, H.J. Jodl, *J. Chem. Phys.* 84 (1986) 6997.
- [15] S. Agnew, R. Mischke, B. Swanson, *J. Phys. Chem.* 92 (1988) 4201.
- [16] L. Ciabini, M. Santoro, R. Bini, V. Schettino, *Phys. Rev. Lett.* 88 (2002) 085505.
- [17] M. Popov, V. Mordkovich, S. Perfilov, A. Kirichenko, B. Kulnitskiy, I. Perezhogin, V. Blank, *Carbon* 76 (2014) 250.
- [18] A. Talyzin, U. Jansson, *J. Phys. Chem. B* 104 (2000) 5064.
- [19] P. Bowmar, M. Kurmoo, M. Green, F. Pratt, W. Hayes, P. Day, K. Kikuchi, *J. Phys.; Condens. Matter* 5 (1993) 2739.
- [20] A. Graja, A. Lapinski, S. Krol, *J. Mol. Struct.* 404 (1997) 147.
- [21] V. Schettino, M. Pagliai, L. Ciabini, G. Cardini, *J. Phys. Chem. A* 105 (2001) 11192.
- [22] R.E. Stanton, M.D. Newton, *J. Phys. Chem.* 92 (1988) 2141.
- [23] M. Pagliai, G. Cardini, R. Cammi, *J. Phys. Chem. A* 118 (2014) 5098.

- [24] D.D. Klug, J.A. Howard, D.A. Wilkinson, Chem. Phys. Lett. 188 (1992) 168.
- [25] J.J. Colman, W.C. Trogler, J. Am. Chem. Soc. 117 (1995) 11270.
- [26] S. Shimomura, Y. Fujii, S. Nozawa, K. Kikuchi, Y. Achiba, I. Ikemoto, Solid State Commun. 85 (1993) 471.
- [27] K.F. Dziubek, A. Katrusiak, J. Phys. Chem. B 108 (2004) 19089.

Figure Captions:

Fig. 1. IR (a) and Raman (b) spectra of C_{60} *CS₂ solvates (purple) and pristine C₆₀ (blue) (the peaks assigned to CS₂ molecules and the new peaks in the Raman spectrum are marked with ‘#’ and ‘*’ respectively), TEM and SAED images of C_{60} *CS₂ solvates (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. The IR spectra of C_{60} *CS₂ solvates under pressure (a); the IR spectra of C_{60} *CS₂ solvates (color) and pristine C₆₀ (black) at selected pressures (b); the pressure dependence of the three F_{1u} modes of C₆₀ molecules in solvated samples (square) and pristine C₆₀ (circle) (c), the three F_{1u} modes are initially located at 575 cm⁻¹ (F_{1u}(2)), 1183 cm⁻¹ (F_{1u}(3)) and 1432 cm⁻¹ (F_{1u}(4)); pressure dependence of the antisymmetric stretching mode of CS₂ molecules (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. IR spectra of the as-synthesized C_{60} *CS₂ solvates and the released samples from different pressures.

Figure 1

Figure 2

Figure 3