

Edge chlorination of hexa-peri-hexabenzocoronene investigated by density functional theory and vibrational spectroscopy

Ali Maghsoumi^a, Akimitsu Narita^b, Renhao Dong^c, Xinliang Feng^c, Chiara Castiglioni^a, Klaus Müllen^b, and Matteo Tommasini^a

^a *Dipartimento di Chimica, Materiali e Ingegneria Chimica – Politecnico di Milano, Piazza Leonardo da Vinci, 32 – 20133 Milano, Italy*

^b *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany*

^c *Center for Advancing Electronics Dresden (CFAED) & Department of Chemistry and Food Chemistry, Dresden University of Technology, Walther-Hempel-Bau Mommsenstrasse 4, 01062 Dresden, Germany*

Electronic Supplementary information (ESI)

Contents

- S1. Description of normal modes of HBC and HBC-Cl relevant for IR and Raman

- S2. Animations of selected vibrational normal modes of HBC and HBC-Cl relevant for IR

S1.1 Description of normal modes of HBC and HBC-Cl relevant for IR

We follow here the notation of the experimental features given in Figure 7 of the main text.

HBC-Cl

- 1 is assigned to a degenerate pair of collective out-of-plane bending modes of the aromatic core; considering a given ring of the core, these modes involve the six carbon atoms with an alternated pattern of up/down displacements.
- 2 is assigned to a doubly degenerate mode involving the out-of-phase C-Cl stretching of the bonds at 1 and 3 (see Figure 2 of the main text) of the chlorinated aryl moieties.
- 3 is assigned to a collective ring-breathing mode of the aromatic core; this occurs with an alternating pattern and mainly involves the six outer Clar rings of HBC-Cl.
- 4 is assigned to a doubly degenerate mode which mainly involves the in-phase C-Cl stretching of the bonds at 1 and 3 (see Figure 2 of the main text) of the chlorinated aryl moieties.
- 5 is assigned to a doubly degenerate mode which mainly involves the CC stretching of the bonds which could be thought to form the edge of a coronene moiety inscribed in HBC-Cl aromatic core (*i.e.*, bonds of kind c and d in Figure 6 of the main text).
- 6 is assigned to two closely located degenerate modes, computed at 1308 cm^{-1} and 1316 cm^{-1} . In both cases the pattern of nuclear displacements is complex and mainly involves the CC bonds of the aromatic core.
- 7 is assigned to the in-phase stretching of the three C-Cl bonds of each chlorinated aryl moiety; the pattern of the mode alternates along HBC-Cl edge (*i.e.*, three aryl moieties have shrinking C-Cl bonds while the other three have stretching C-Cl bonds).
- 8 is assigned to two closely located modes (1463 cm^{-1} , E_u and 1475 cm^{-1} , A_{2u}). The two peaks are not well resolved and appear as a structured feature both in the experimental and simulated spectrum. The E_u normal modes collectively involve CC bonds of the aromatic core; the A_{2u} mode displays a more recognizable pattern, with bonds of kind e (see Figure 6 of the main text) which alternatively stretch in an out-of-phase fashion.
- 9 is assigned to a collective doubly degenerate ring stretching vibration (computed at 1583 cm^{-1}), whose pattern is close to that found in discussing the G line in Raman spectroscopy of PAHs.^[1]

HBC

- 1 is assigned to an alternated out-of-plane bending vibration of the carbon atoms in the aromatic core, coupled with the in-phase out-of-plane bending of the CH bonds at 1,3 (see Figure 2 of the main text).
- 2 is assigned to the collective out-of-plane bending of all CH bonds and correlates with the characteristic TRIO features of PAHs.^[2,3,4]

- 3 is a degenerate doublet involving a collective ring-breathing of the six outer Clar rings of HBC, with half the molecule vibrating out-of-phase with respect to the other half.
- 4,5,6,7,8 are assigned to degenerate modes involving CC stretching of the aromatic core, coupled with in-plane CH bending.
- 9 is assigned to collective doubly degenerate ring stretching vibrations, whose pattern is close to that found in discussing the G line in Raman spectroscopy of PAHs.^[1]

S1.2 Description of the normal modes of HBC and HBC-Cl relevant for Raman

We follow here the notation of the experimental features given in Figure 8 of the main text.

S1.2 Raman B modes

- Peak B₁ is assigned to the ring-breathing mode of the central Clar ring of HBC and HBC-Cl which vibrates out-of-phase with respect to the six outer Clar rings. In HBC-Cl mode B₁ is coupled with the collective C-Cl stretching of the chlorinated aryl moieties. In particular C-Cl stretching at (1, 3) (see Figure 2 of the main text) are both out-of-phase with respect to C-Cl stretching at 2 (see Figure 2 of the main text). Compared to HBC, this mode is remarkably blue-shifted in HBC-Cl (experimentally by 79 cm⁻¹, while according to DFT by 73 cm⁻¹).
- Feature B₂ is only found in the HBC-Cl molecule and it is assigned to a doubly degenerate mode which involves the CC stretching of the outer part of the molecule (mainly bonds of kind *c* and *d*, see Figure 6 of the main text) coupled with the C-Cl stretching of the chlorinated aryl moieties.

S1.2 Raman D and G modes

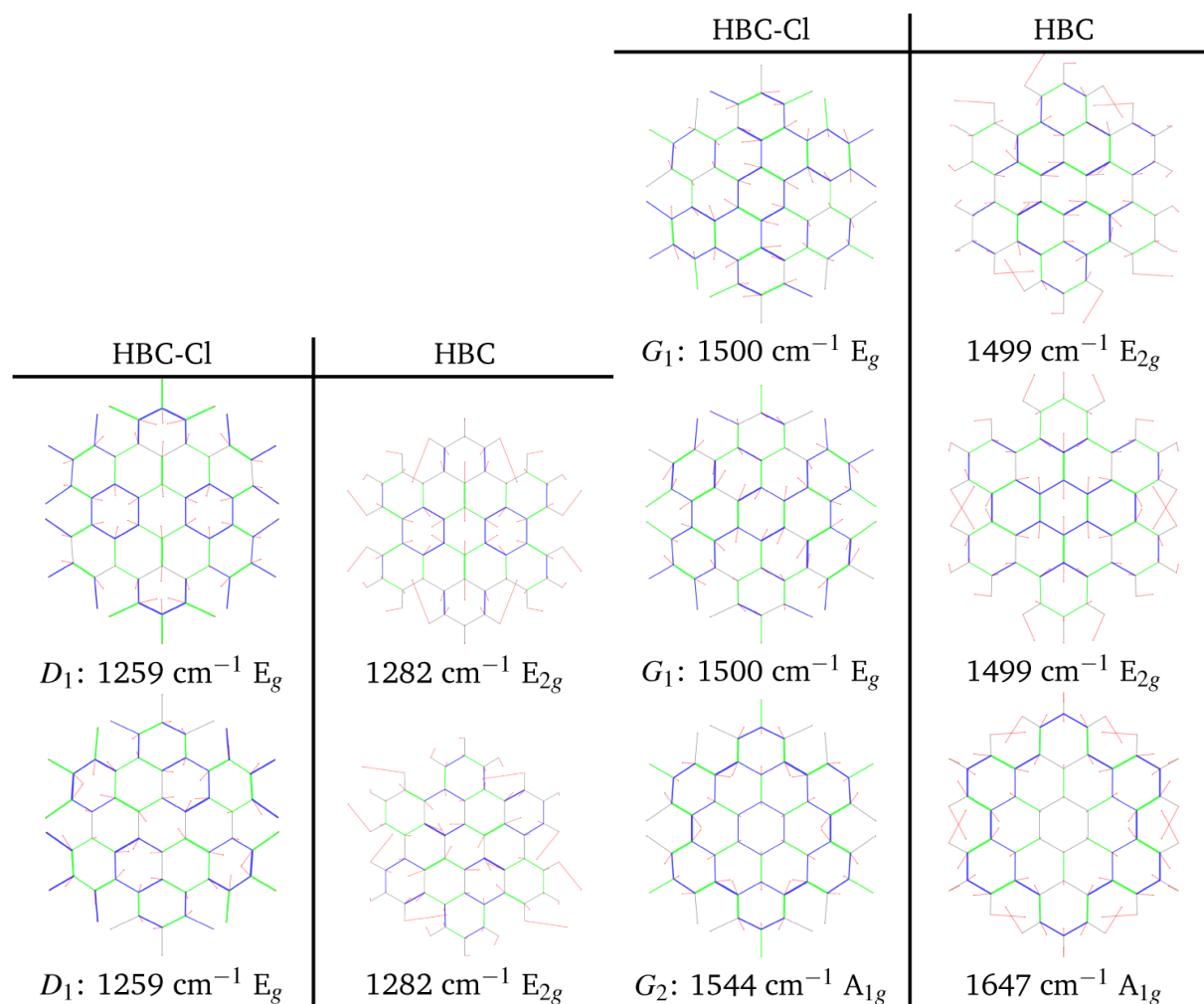


Figure S1.2 nuclear displacements of the D and G modes of HBC and HBC-Cl discussed here.

- The weak Raman active doubly degenerate mode D_1 is assigned to a vibration which involves the breathing of four Clar rings in both HBC and HBC-Cl. In HBC-Cl the D_1 mode is coupled with the in-phase C-Cl stretching of the chlorinated aryl moieties. In HBC the D_1 mode is coupled with the collective in-plane bending of the CH bonds at positions (1,3) (see Figure 2 of the main text).
- The experimental G_1 feature of HBC and HBC-Cl (see Figure 8 of the main text) is assigned to doubly degenerate modes of E species which mainly involve the CC stretching of bonds in the center of the molecule. In HBC the mode G_1 is coupled with collective in-plane CH bending.
- Feature G_2 is assigned to a totally symmetric mode which involves CC stretching (*i.e.*, ring stretching – see above) mainly at the outer rings of the molecule (bonds of kind *b* in Figure 6 of the main text). In HBC the mode G_2 is coupled with collective in-plane CH bending at positions (1,3) (see Figure 2 of the main text). In HBC-Cl the G_2 mode involves the collective C-Cl stretching of bonds at 2 (see Figure 2 of the main text) and it is significantly red-shifted compared to HBC (according to DFT by 103 cm^{-1} ; the experimental determination of the position of G_2 for HBC is not feasible because it is a weak mode overlapped with other stronger G components).

S2. Animations of selected vibrational normal modes of HBC and HBC-Cl relevant for IR

An archive file (7-Zip format [5]) is included in the ESI. It contains a set of animated gif files associated to the modes of HBC and HBC-Cl listed in Tables 3 and 4. These animations have been obtained with the program ChemCraft [6].

References

- [1] C. Castiglioni, M. Tommasini and G. Zerbi, *Philosophical Transactions of the Royal Society of London Series A-Mathematical Physical and Engineering Sciences*, 2004, **362**, 2425–2459.
- [2] M. Tommasini, A. Lucotti, M. Alfè, A. Ciajolo and G. Zerbi, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2016, **152**, 134 – 148.
- [3] A. Centrone, L. Brambilla, T. Renouard, L. Gherghel, C. Mathis, K. Mullen and G. Zerbi, *Carbon*, 2005, **43**, 1593–1609.
- [4] M. Von Zander and B. G. Teubner, *Angewandte Chemie*, 1996, **108**, 2411–2411.
- [5] 7-Zip: see website <http://www.7-zip.org> (accessed 10 Feb 2016).
- [6] ChemCraft: see website <http://www.chemcraftprog.com/index.html> (accessed 10 Feb 2016).