

# 58<sup>th</sup> EHPRG

## MEETING PROGRAMME



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## **Thursday, September 10**

### **TEIDE Room**

#### **Registration (8:30-16:30)**

**Chair: J. A. Sans**

**9:00-9:30 Invited (Audrey Grockowiak) Hot Hydride Superconductivity above 550 H**

**9:30-10:00 Invited (F.J. Manjón) Rare-earth sesquioxides under compression: a review based on recent results on structural and vibrational properties of Tb<sub>2</sub>O<sub>3</sub>.**

#### **10:00-10:30 Coffee Break**

#### **Chemistry at High Pressure (TEIDE room)**

**Chair: J. González-Platas**

**10:30-11.00 Invited (A. Oganov) Discovering high-pressure chemistry by artificial intelligence.**

**11:00-11:15 (V. Garcia Baonza) Structural anomalies in liquid water under high pressures as revealed by 2Dcorrelation Raman Spectroscopy.**

**11:15-11:30 (A.G.V. Terzidou) Pressure response of the lattice modes in the polycyclic aromatic hydrocarbon fluorine.**

**11:30-11:45 (E. Bykova) Thermal Stability of XeF<sub>2</sub> at High Pressures.**

**11:45-12:00 (A. Lobato) Thermodynamics versus Kinetics in Temperature-Driven Transitions of Perovskite-Like Materials .**

**12:00-12:15 (W. Kutcherov) Formation of the hydrocarbon fluid from iron carbide under the thermobaric conditions corresponding to the asthenosphere.**

#### **12:15-14:00 Lunch**

### **TEIDE Room**

**Chair: F.J. Manjón**

**14:00-15:00 EHPRG Prize 2020 (M. Bykov) New high-pressure chemistry of nitrogen**

## Pressure response of the lattice modes in the polycyclic aromatic hydrocarbon fluorene

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Polycyclic aromatic hydrocarbons (PAHs) comprise a large family of molecular crystals, which have attracted significant attention due to their remarkable physical and chemical properties, stemming from the delocalization of the  $\pi$ -electrons along the molecular backbone. Thus, they find a wide range of applications, including medications/drugs, plastics, dyes, liquid crystals and opto-electronic devices [1,2]. Their properties depend on the aromatic rings comprising the molecules and the dihedral angle between them [3,4]. Fluorene,  $C_{13}H_{10}$ , is classified as a three-membered ring PAH but is composed of two aromatic hexagonal rings connected by a pentagon [5]. For commercial purposes, it is obtained from coal tar and to this day it has been used for dyes [6] and for anti-inflammatory drugs [7]. At ambient conditions, fluorene crystallizes in the orthorhombic system (space group:  $Pnma$ ) with four molecules in the unit cell, forming a layered herringbone structure [5]. Most of the properties of organic molecular crystals are mainly determined from those of the corresponding isolated molecules, but in the solid state, intermolecular interactions also play a crucial role for example in charge transport and optical properties [8-10]. The intermolecular interaction strength is not affected only by the distance of the constituent molecules but also by their relative orientation, rendering them by far more sensitive than the intramolecular covalent bonding to external stimuli, like pressure and temperature. In this work, the pressure response of the intermolecular (lattice) modes of crystalline fluorene (Nacalai Tesque Inc.) and its structural stability is examined by means of Raman spectroscopy.

Raman spectra were recorded in the backscattering geometry using a HORIBA LabRAM HR spectrometer. For excitation, the 632.8 nm line of a He-Ne laser was focused on the sample by means of a 50 $\times$  super long working distance (SLWD) objective, while the laser power was kept below 0.4 mW, in order to eliminate any laser-heating effects. Pressure was generated by a Mao-Bell type diamond anvil cell (DAC) using the ruby fluorescence for pressure calibration and Daphne 7474<sup>TM</sup> as pressure transmitting medium.

The Raman spectrum of fluorene at ambient conditions can be divided into two main regions; the intermolecular (external) modes appear in the frequency region below 200  $cm^{-1}$ , while the intramolecular (internal) modes are extended to much higher frequencies (up to 3200  $cm^{-1}$ ) [11]. Raman spectra of crystalline fluorene in the low frequency region recorded at various pressures are illustrated in Figure 1, while the pressure

dependence of the frequencies of the intermolecular Raman modes is presented in Figure 2.

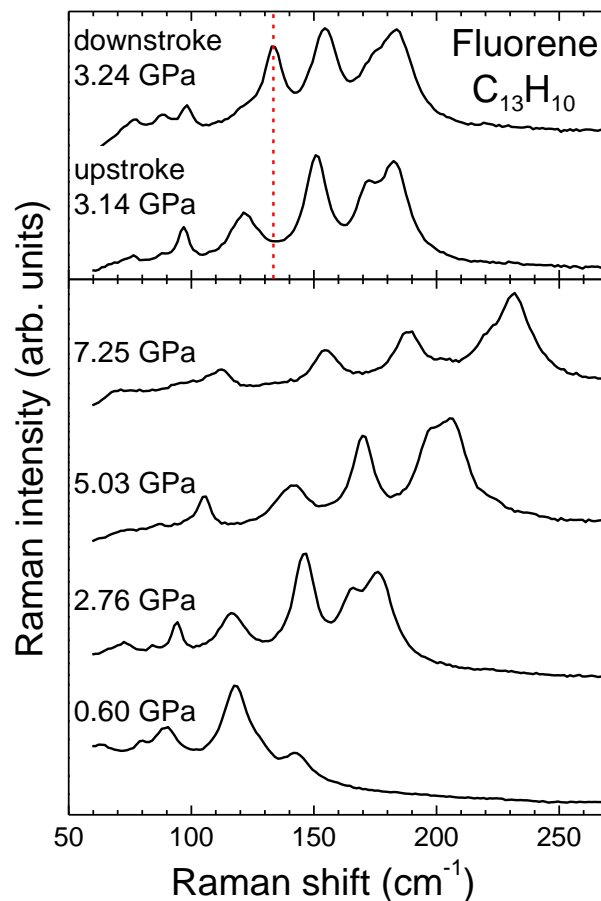


Figure 1. Raman spectra of fluorene at various pressures. **Bottom panel:** spectra recorded upon pressure increase. **Top panel:** spectra recorded at  $\sim 3.2$  GPa during the upstroke and the downstroke cycle. The dashed vertical line indicates a Raman peak of the high-pressure phase of fluorene.

At ambient conditions, three Raman peaks attributed to intermolecular modes are resolved. With increasing pressure, the Raman peaks shift to higher frequencies as expected due to the volume contraction and the concomitant bond hardening. Moreover, under pressure, two additional Raman peaks are resolved due to their different pressure slopes, while two more peaks enter the spectral region from lower frequencies due to their pressure induced frequency upshift. For  $P < 2.5$  GPa, the pressure induced frequency shift of the Raman peaks is rather large and parabolic, as expected for the lattice modes in a molecular crystal, where the intermolecular

van der Waals bonding is initially very weak [12]. However, above 2.5 GPa the pressure slopes of the peak frequencies decrease, signaling a possible phase transition of the studied crystalline PAH. Another pressure slope change of the peak frequencies to even smaller values takes place between 5.5 and 6 GPa, accompanied by the appearance of a new Raman peak at  $\sim 200\text{ cm}^{-1}$ .

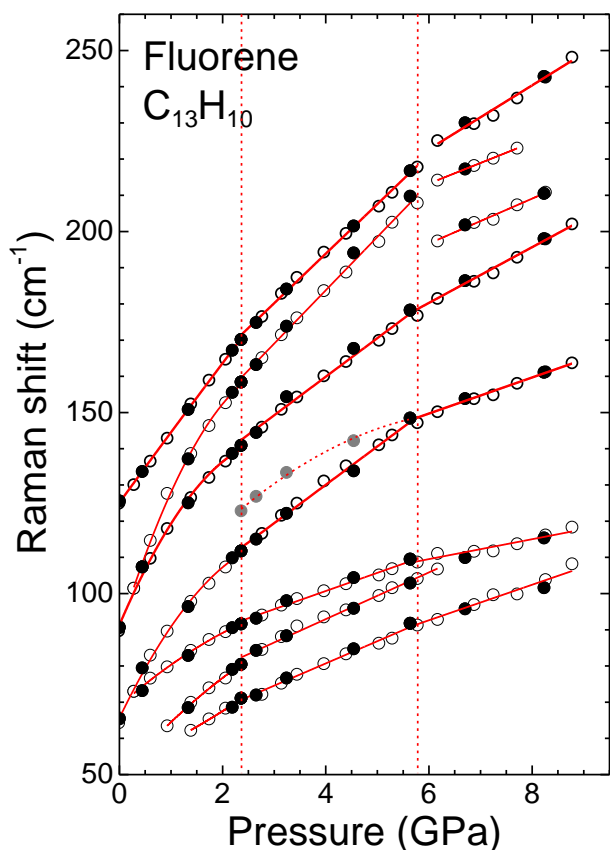


Figure 2. The frequencies of the intermolecular (lattice) Raman peaks of fluorene as a function of pressure. Open (solid) symbols correspond to data obtained upon pressure increase (decrease). Grey circles correspond to a Raman peak of the high-pressure phase of fluorene. Red lines through the experimental data are their least square fits. Dotted vertical lines indicate pressure values, where changes in the pressure evolution of the Raman peak frequencies take place.

According to the high resolution X-ray diffraction (XRD) study of Heimel et al., crystalline fluorene, upon pressure application above 2.5 GPa, undergoes a reversible structural phase transition characterized by abrupt changes in the lattice constants due to a molecular re-arrangement of fluorene from the ambient pressure herringbone pattern towards  $\pi$ -stacking [13]. The low- and the high-pressure phases co-exist up to 5 GPa, where fluorene crystals are completely transformed to the high-pressure phase of smaller compressibility. Our high pressure spectroscopic findings are in good agreement with the XRD results, while the phase co-existence can be also seen in our data upon pressure decrease (top panel in Fig. 1 and grey circles in Fig. 2). In addition, Heimel et al., based on their density functional calculations, have also reported that the molecular

orientation re-arrangement in the high pressure phase affects significantly the electronic properties of crystalline fluorene, causing the reduction of the band gap, the increase of the band widths and the large curvature of the valence bands [13]. These changes could account for the background enhancement in the Raman spectra and the significant intensity redistribution among the Raman peaks at elevated pressures (Fig. 1).

Similar to fluorene, moderate structural transitions at relatively low pressures (below 6 GPa) have been also observed by means of vibrational (Raman and/or infrared) spectroscopy in various PAHs with molecules comprised by 1-4 hexagonal carbon rings (benzene, naphthalene, biphenyl, anthracene, phenanthrene and pyrene) [14-18]. In all cases, the transitions are associated with re-arrangement of the molecular orientations without any considerable distortion of the constituent molecules. These structural transitions appear to be reversible upon pressure decrease as in the case of fluorene studied here (solid symbols in Fig. 2).

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