![ESRF] **ESRF**	**Experiment title:** Halogen bonding patterns between simple diiodomethane molecules and their role for the formation of polar crystals	**Experiment number**: HS 3837
Beamline: ID27	**Date of experiment**: from 15 may 2009 to 19 may 2009	**Date of report**: 26 february 2010
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Report:

Halogen bonding is a noncovalent interaction, in some ways analogous to hydrogen bonding, occurring between a halogen atom in one molecule and a negative site in another. There are a few theories about electrostatic fundamentals and nature of halogen bond [1-3]. Structural analyses of simple molecular halogen derivatives are very helpful in studying interactions between halogen atoms in crystals.

Diiodomethane (CH_2I_2) is a very simple and convenient model compound for studying halogen···halogen interactions. It is also a very important chemical substrate, solvent, substance commonly used for pharmaceutical and technological applications and it naturally occurs, albeit at low concentrations, in atmosphere and sea water [4]. Therefore it was intensely investigated theoretically, by diffraction [5-9] and spectroscopic methods [10,11]. Diiodomethane crystallizes in three phases at atmospheric pressure: centrosymmetric phases I and III (space group *C*2/*c*) and in polar phase II (space group *Fmm*2) [6]. At high pressure only the structure of phase II is known, which is stable from freezing pressure of 0.1 GPa and has been determined up to 1.56 GPa [7-9]. Far-IR and Raman spectroscopic measurements of diiodomethane at high pressure and ambient temperature revealed a reversible phase transition at 3.1 GPa [11]. Shimizu suggests two transitions at high pressures at 1.7 and

5.5 GPa [10]. Till today there have been no information about structural data of these new phases.

The HS 3837 experiment was directed to the determination of the high-pressure polymorphs of diiodomethane using a membrane diamond-anvil cell available at line ID27 as high-pressure device and 0.27 Å wavelength radiation. It was found that the high intensity short-wavelength X-ray radiation leads to the CH_2I_2 decomposition (Figure 1). Therefore, the intensity was reduced by detuning the undulator gap.
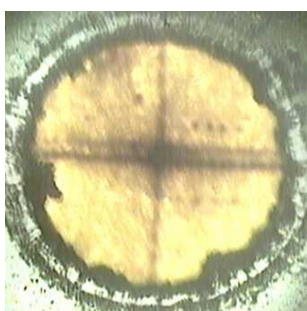

Figure 1. Diiodomethane powder sample damage induced by intense synchrotron radiation. A characteristic dark cross appeared after the beam centring procedure.

A special care was taken to eliminate any uniaxial stress and to perform the experiments in hydrostatic conditions. The pressure transmitting medium for ambient temperature measurements was a mixture of methanol:ethanol 4:1, and a ruby chip was used as pressure indicator. Liquid CH_2I_2:methanol:ethanol mixture was loaded into a high pressure chamber at 295 K. Diiodomethane powder was obtained at 0.1 GPa and diffraction patterns of this sample have been recorded up to 51 GPa (Figure 2). The pressure dependence of the interplanar distances does not provide any evidence of the phase transitions in the pressure range investigated, contrary to the previous findings based on the spectroscopic experiments [10,11]. According to the reflection intensities and the 2θ angles the CH_2I_2 structure is orthorhombic, space group *Fmm*2. This is one of only two polar phases known for all dihalomethane crystals. The remarkable stability of this phase is consistent with the molecular arrangement optimum for deformation of halogen⋯halogen type II interactions [8,9,12,13].

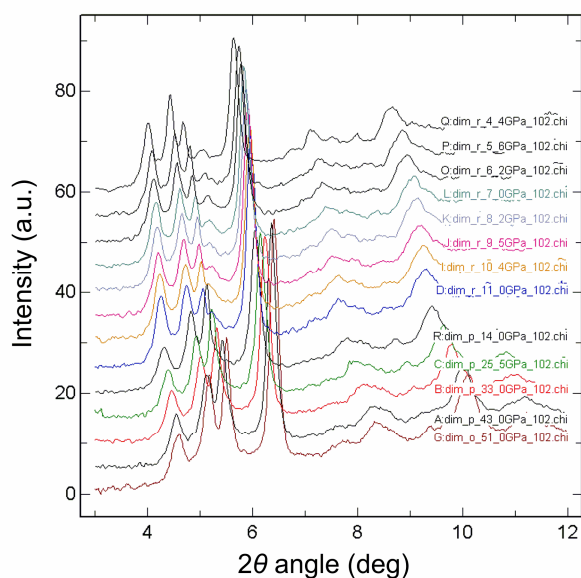**Figure 2.** Pressure evolution of the powder diffraction pattern of diiodomethane recorded at 295 K from 4.4 to 51 GPa.

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