

## 7-1 The Modulated Structure of Solid Iodine during Molecular Dissociation under High Pressure

Solid iodine is a typical molecular crystal, in which four  $I_2$  molecules are arranged in an orthorhombic unit cell. The application of pressure to solid iodine forces the  $I_2$  molecules in the crystal to approach each other until intermolecular distances become comparable to the bond length of iodine; at this point, the molecules lose their identity and are essentially dissociated. This phenomenon, called pressure-induced molecular dissociation, was first observed in iodine at about 21 GPa in X-ray diffraction experiments [1]. Associated with the molecular dissociation, iodine undergoes successive structural phase transitions under high pressure; phase I (an orthorhombic molecular phase stable at ambient pressure), phase II (a body-centered orthorhombic phase stable above 21 GPa), phase III (a body-centered tetragonal phase stable above 43 GPa) and phase IV (a face-centered cubic phase stable above 55 GPa) [2]. Iodine molecules are dissociated in phases II, III, and IV.

Although X-ray diffraction experiments offer a simple picture of the molecular dissociation, some high-pressure experiments suggest more complicated behavior. Mössbauer [3] and Raman spectroscopy [4] experiments suggest that intermediate molecular phases may exist prior to the molecular dissociation.

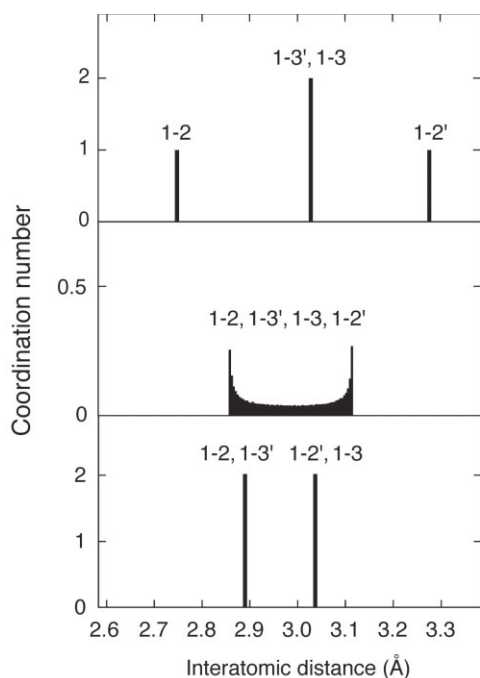


Figure 2  
Distribution of the near interatomic distances for phases I (19.1 GPa), V (24.6 GPa), and II (30.4 GPa).

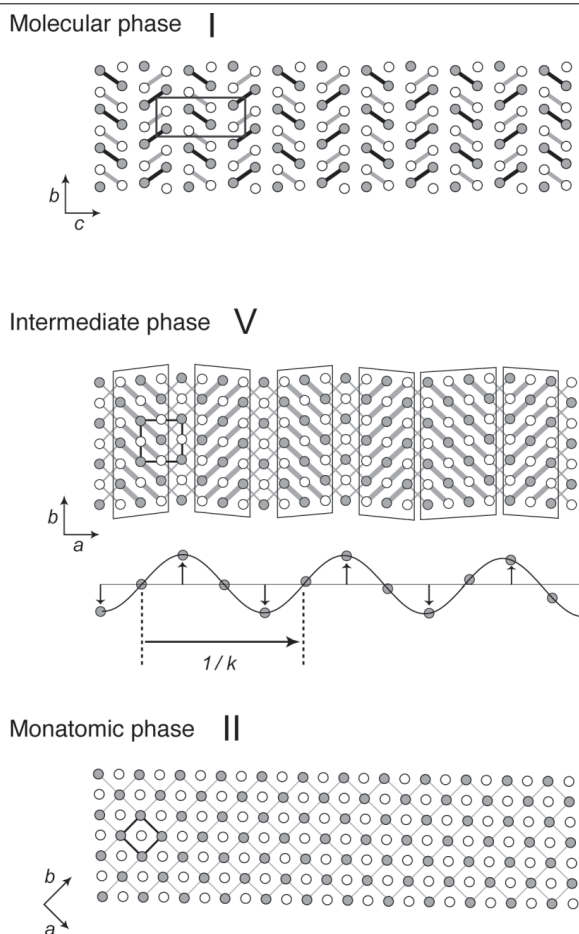
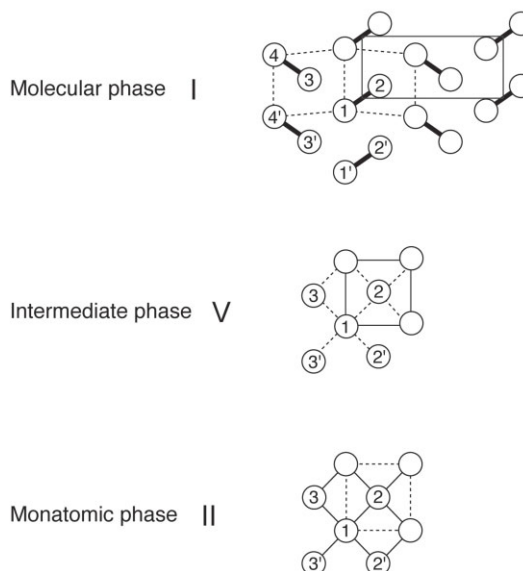


Figure 1  
Crystal structure of iodine for phases I (19.1 GPa), V (24.6 GPa), and II (30.4 GPa).



In order to study the detailed structural change of iodine near the molecular dissociation, we have recorded powder X-ray diffraction patterns with high resolution by using a helium pressure-transmitting medium in a diamond-anvil cell and the intense synchrotron radiation from the multi-pole wiggler (MPW) of BL-13A. The helium medium offers excellent quasi-hydrostatic conditions, thereby reducing pressure inhomogeneity in the sample chamber. It follows that one can specify a narrow pressure range without phase mixture. We found a new intermediate phase (phase V) in the pressure range 24-28 GPa. The crystal structure is incommensurately modulated, a rare case for the elements [5]. Fig. 1 shows the crystal structures for phases I, V and II. The distances between the nearest-neighbor atoms of the intermediate phase are continuously distributed over the range from 2.86 to 3.11 Å (Fig. 2). The shortest of these interatomic distances falls between the bond length of iodine in the molecular crystal (2.75 Å) and the nearest interatomic distance in the fully dissociated monatomic crystal (2.89 Å). This means that the intermediate phase is a transient state during the molecular dissociation.

The origin of the existence of an incommensurate structure near the molecular dissociation is highly interesting. Further experiments at different temperatures are necessary to clarify the stability region of the incommensurate phase. The results may lead to a better understanding of the molecular-level mechanism of the molecular dissociation observed here, and those which can be expected for other molecular crystals like hydrogen, oxygen, and nitrogen.

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### References

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