Structural Quantum Isotope Effects in Amorphous Beryllium Hydride

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Introduction

Light and heavy liquids or noncrystalline solids fabricated by hydrogen-deuterium substitution chemistry are known to exhibit measurable changes in their thermodynamic properties and structure. The differences in zero point librations and intermolecular binding between isotopically enriched samples are usually reflected in subtle changes in both intermediate range order and local structure. Although these quantum isotope effects are usually small, the extracted information is important for understanding fundamental hydrogen bond interactions and developing realistic interatomic potentials, which include quantum contributions. The magnitude of the quantum component depends on the nuclear masses and the coupling between them. Consequently, there are only a few hydrogenous systems that are likely to show a quantum isotope effect that is larger than that observed for water. Perhaps the most promising candidate is amorphous beryllium hydride (Fig. 1). Its molecular weight increases 18% when it changes from BeH2 to BeD2. The molecular weight of water increases 11% when it changes from light water (H2O) to heavy water (D2O).

Because of their unusually low mass and high hydrogen content, beryllium hydride and its derivatives have historically received much attention for their potential applications in fields such as rocket fuel technology and nuclear materials. Beryllium hydride has also served as a popular test bed for several recent electronic structure calculations that used ab initio methods, and it has been the focus of numerous theoretical studies in both gas and condensed phases. However, very few experimental data are available. An accurate experimental measurement of the Be-H bond length for the linear gas-phase BeH2 molecule has only recently been determined [1]. The standard temperature and pressure phase of BeH2 is an amorphous solid, which can transform into two known crystalline phases at higher temperatures and pressures, both of which are composed of network-forming tetrahedral structures. Early models suggested amorphous BeH2 was composed of edge-shared tetrahedra in a polymeric chain structure, similar to that of beryllium chloride (BeCl2) and dimethyl beryllium [Be(CH3)2]. This has been superseded, however, by more recent modeling of low-resolution neutron diffraction measurements, which suggest that the structure of amorphous BeH2 is composed of corner-sharing tetrahedra, similar to the structure found in the tetragonal crystalline phase (Fig. 2). Consequently, BeH2 is analogous to other classic network-forming glasses such as amorphous H2O, BeF2, SiO2, and GeO2. In comparison, the average intertetrahedral ∠Be-D-Be = 135 ± 1º for BeD2 (calculated from peak positions), whereas ∠Be-F-Be = 139º in BeF3, ∠Si-O-Si = 146º in SiO2, ∠Ge-O-Ge = 132º in GeO2, and ∠O-H-O = 165 in H2O. Consequently, the interesting variation of BeH2 from the other vitreous systems is that it is a hydride, indicating some potential analogy to H2O.

Methods and Materials

Amorphous BeH2 and BeD2 were synthesized by using standard methods. The purity of both samples was determined to be ≥95% by using infrared and Raman spectroscopy as well as elemental analysis. The only difference between the samples was the isotopic enrichment of ≥98% D in the deuteride sample. High-energy x-ray measurements were performed on the weakly scattering BeD2 and BeH2 samples by using a...
Results and Discussion

The observed trend has been interpreted as increased intermediate range ordering of the cation correlations in beryllium deuteride compared to the hydride [3]. This is in good agreement with earlier measurements on other materials. The surprising result here is the magnitude of the measured isotopic structural difference between the light and heavy materials. The marked increase in intermediate range order is probably due to the propensity of amorphous BeD$_2$ to form an extended network compared to BeH$_2$. It may be less likely (but cannot be ruled out) that it is a reflection of the polymorphism that is conjectured in the crystal structures. Nonetheless, the magnitude of the measured effect provides the most rigorous test yet in the development of the quantum part of the interatomic potential in a binary amorphous solid.

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References