High-pressure Raman spectroscopy of Ar-H_2 and CH_4-H_2 van der Waals compounds

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We report the results of Raman measurements at pressures up to 40 GPa of molecular compounds $Ar(H_2)_2$ and $CH_4(H_2)_2$ with similar Laves phase structures. We discuss here the rich hydrogen vibron spectra arising from site and vibrational (Davydov) splitting in these materials. The CH_4 compound (in contrast to that containing Ar) reveals substantial site splitting, which we explain by the anisotropic nature of the crystal field produced by methane molecules. We find that the observed number of the vibron sidebands at high pressures are inconsistent with the Laves phase in the case of the CH_4 compound, which is attributed to lowering of its symmetry at 7.2 GPa. The results are compared with synchrotron X-ray and infrared measurements.

1 Introduction

Recent high-pressure studies have revealed numerous new physical and chemical phenomena in highly compressed materials[1]. Investigations of a variety of materials carried out over extended pressure ranges provide crucial tests of condensed-matter theory and have important applications to materials and planetary science. Simple molecular systems are particularly attractive for high-pressure study, in part because of their high compressibility and thus the wide range over which intermolecular distances and interactions can be tuned. Moreover, these studies have revealed the existence of new stoichiometric compounds - so called van der Waals compounds[2] - formed from simple molecular mixtures at high pressure, including binary mixtures[3,4] of H_2, He, Ne, Ar, and CH_4. Raman scattering has been an essential component in characterizing and understanding these new high-pressure materials.

Newly discovered phases in the CH_4–H_2 system are of particular interest[5,6]. This binary system has an extremely rich phase diagram and shows numerous intriguing phenomena at pressures of 7-60 GPa[5,6]. The Laves phase of $CH_4(H_2)_2$ was found to be stable at 5.6-7.2 GPa, with the possible changes in stoichiometry at higher pressures. It has also been

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established that substitution of CH_4 for Ar gives another stable compound $Ar(H_2)_2$, also having the Laves phase structure. X-ray diffraction[7], Raman[7] and infrared[8] measurements show that the compound is stable to very high pressures (>200 GPa). We report here a comparative study of vibrational properties of the $CH_4(H_2)_2$ and $Ar(H_2)_2$ systems to 40 GPa. We find substantial differences in the Raman-active hydrogen vibrons, which are attributed to distinctive features in the nature of the intermolecular interactions in the CH_4–H_2 system.

2 Group Theory

We consider the effects of symmetry on the vibrational modes in the high-symmetry (stoichiometric) structure. For space group D_{6h}^4 (known for Laves phases) with two formulae units [e.g., $Ar(H_2)_2$] per cell, one can predict the following Raman (R) or infrared (IR) active internal modes for hydrogen molecules (vibrons):

  2 H_2 molecules in the argon-rich plane, D_{3d} site symmetry, A_{1g} (R) ;

  6 H_2 molecules in the hydrogen plane, C_{2v} site symmetry, A_{1g} (R)+ E_{2g} (R) + E_{1u} (IR).

3 Experiment

The experiments were carried out using Mao-Bell-type diamond anvil cells with very low-fluoresence type Ia diamonds[4,6]. Mixtures of methane and hydrogen were prepared as outlined previously, and the samples were loaded at room temperature. Raman spectra were excited by various lines of Ar-ion lasers and recorded by a single HR-460 ISA spectrometer with notch filters and Dilor XY triple spectrometer, both equipped with a CCD detector. The pressure was determined using the standard ruby technique. Further details are given in Ref 6.

4 Results and Discussion

The Raman spectra (Fig. 1) clearly show higher frequency sidebands in addition to the main vibrons, as reported in Refs. 6,7. Each of the vibron bands increases in frequency with pressure (Fig. 2), with the splittings between each component also increasing. The methane compound (in contrast to that containing argon) exhibits two main vibron peaks. These observations agree with IR measurements[6], which also show two uncoupled vibron peaks for the methane compound. It should be noted that the spectral positions of the IR bands and Raman sidebands are very close at all pressures[6], while the major Raman band has a substantially lower frequency. Similar observations are generally valid for phases of pure hydrogens and can be understood in terms of Brillouin-zone folding and details of the hydrogen intermolecular interaction potential[9-12]. The frequency differences between the lower and higher frequency vibron components represent the strength of intermolecular interactions (vibrational coupling), which naturally increase when intermolecular distances decreases. The strong lower frequency Raman band essentially corresponds to in-phase hydrogen vibrations, whereas the higher frequency ones (both IR and the weak Raman bands) are associated with out-of-phase motions.
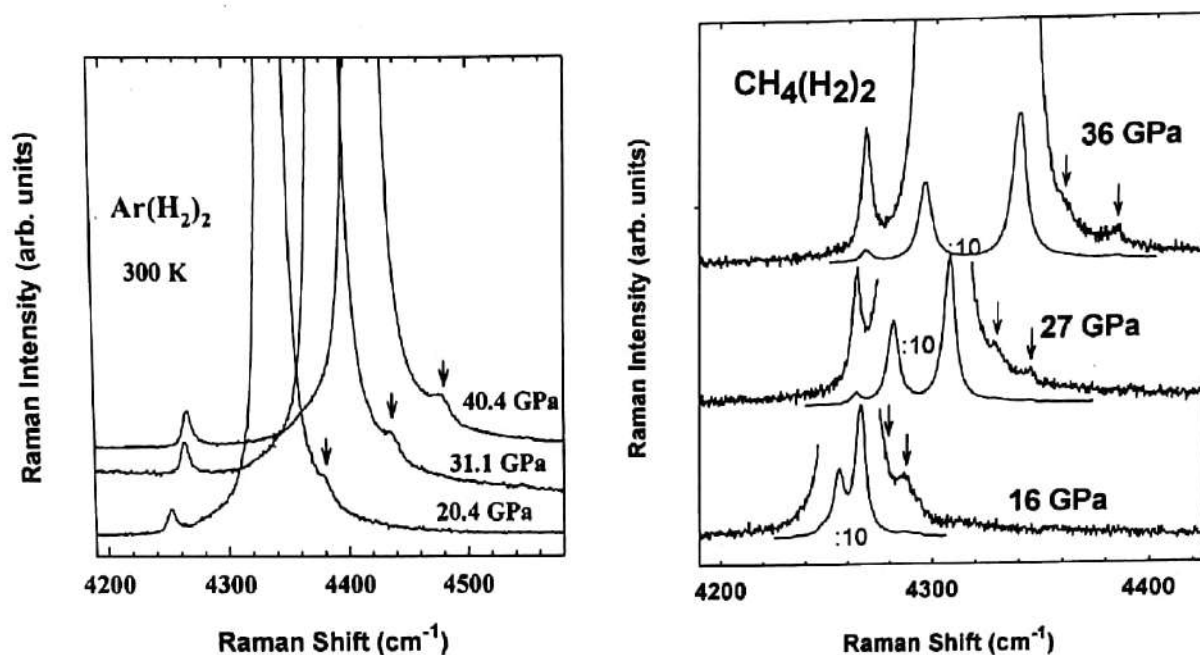
Fig 1: Comparison of the Raman spectra of Ar(H$_2$)$_2$ (left) and CH$_4$(H$_2$)$_2$ (right) at different pressures. Raman peak at 4250 cm^{-1} arises from a small amount of pure hydrogen present in the sample.
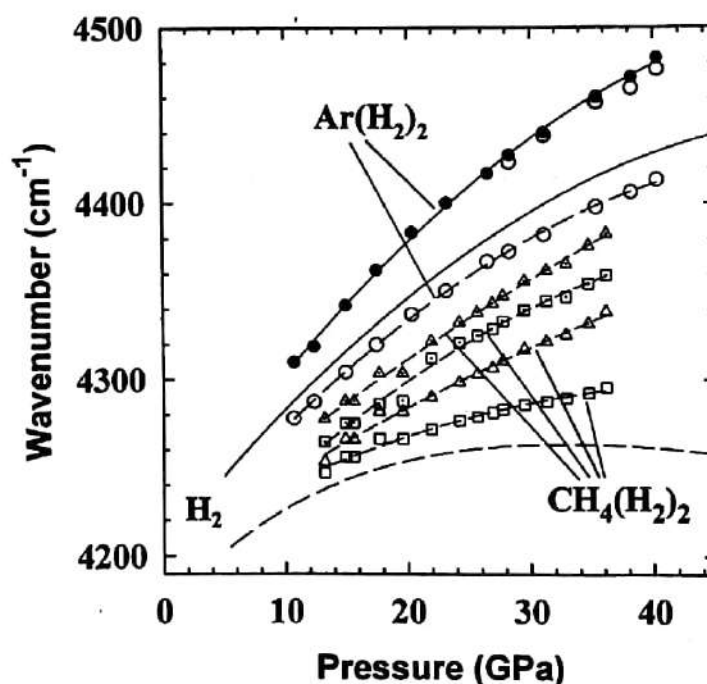

Fig 2: Comparison of pressure dependences of frequencies of the Raman- and IR-active vibron bands in Ar(H$_2$)$_2$ (a) and CH$_4$(H$_2$)$_2$ (b) with those for pure hydrogen[9].

The observation of two strong Raman peaks for the methane compound (Fig 1) is interpreted as arising from the presence of two different crystallographic sites in the Laves phase structure (see above), which also creates two systems of vibron sidebands. From intensity arguments (the main Raman peak of higher frequency is roughly twice that of the

lower frequency one), we deduce that the hydrogen molecules in the hydrogen planes have higher vibron frequencies than those in the methane-rich planes. This conclusion matches the observation that the higher frequency IR vibron is more intense, a fact that becomes very pronounced at high pressure[6]. It should be noted that only one IR vibron and only one Raman sideband, both corresponding to the molecules in the hydrogen planes are formally allowed for the ideal Laves phase. Thus, our observation of forbidden modes of hydrogen in the methane-rich planes may mean lifting of site symmetry for molecules at those crystallographic positions. This may arise from structural distortion or change in stoichiometry, as proposed in Ref 6.

It is interesting to note that although the two compounds start out with virtually identical structures, and the effective diameters of Ar and CH_4 are very close, no sign of a splitting of the main Raman vibron was observed for the Ar compound. Also for the latter, no splitting was evident in Raman measurements[7] carried out to 178 GPa, and only one uncoupled vibron was observed in synchrotron IR measurements[8] to 220 GPa. That the two different crystallographic positions in the methane compound are associated with rather different crystal fields (relative to Ar) may be tied to significant anisotropic intermolecular interactions in CH_4; this should also result in different pressure-induced structural changes for the methane van der Waals compound.

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