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Diamond anvil cell techniques have been developed to confine and measure hydrogen samples under static conditions to pressures above 300 GPa from 12 to 300 K using synchrotron infrared and optical absorption techniques. A decreasing absorption threshold in the visible is observed, but the material remains transparent down to 0.1 eV to 360 GPa over a broad temperature range. The persistence of the strong infrared absorption of the vibron characteristic of phase III indicates stability of the paired state of hydrogen. There is no evidence for the predicted metallic state over these conditions, in contrast to recent reports, but electronic properties consistent with semimetallic behavior are observed in phase III.

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Understanding how the hydrogen molecule responds to very high pressures has long been a major problem in the physical sciences. In particular, the behavior of low-temperature solid hydrogen over a broad range of densities has been of central interest in order to identify the thermodynamic ground-state for comparison with fundamental theory. Hydrogen was first predicted to become an alkali-like monatomic metal above 25 GPa [1] and subsequently calculated to exhibit intriguing quantum behavior such as a liquid ground-state and high-temperature superconductivity at higher compressions [2,3]. Theoretical calculations also predicted that solid molecular hydrogen becomes metallic by band overlap, *i.e.,* with the atoms remaining in a paired state [4]. More recently, very high superconducting temperatures and the possibility of more exotic behavior such as combined superconductivity and superfluidity have been predicted above 400 GPa [5].

Information from experiments has relied on spectroscopic techniques, which reveal the existence of three molecular phases (I, II, and III) beginning at megabar (100-GPa) pressures [6]. Of particular focus has been the transition near 150 GPa (relative density ρ/ρ_0 > 12) to phase III [7-11], which is not fully understood. Extensive calculations have been performed on the stability, vibrational dynamics, and electronic properties of candidate structures for phase III (*e.g.,* Refs. [12-14]), though matching all of the observed properties has proved to be a challenge to theory. Notably, an onset in electrical conductivity has been observed in the high-temperature (>2000 K) shock-compressed fluid at these pressures [15,16], but the nature of the transition and connection to the behavior of the solid and possible fluid phases at low temperatures have not been established [17]. Measurements of the vibron, intramolecular stretching mode of H_2, carried out to the 300-GPa range (ρ/ρ_0 > 12) indicate the stability of the molecules but have been limited to <100 K at the highest pressures [18-20]. The observation of the onset of visible absorption as a function of pressure, first reported in 1989 [21] and identified as phase IV [6], has been examined in subsequent optical studies [18-20,22], but the nature of the phase, consistency of the results, and behavior of the system at higher *P-T* conditions remain open questions.

Reaching more extreme static pressures and temperatures on hydrogen and accurately probing the material under these conditions has been a major technical challenge. It has long been known that low temperatures decrease hydrogen embrittlement of diamond anvils and gaskets used in these experiments and extend the pressure range of static compression studies of hydrogen [7,21]. The fluorescence background from the highly stressed diamond anvils can increase dramatically above 200 GPa and complicate spectroscopic measurements of the sample and pressure calibrant [23]. Because of the reactivity of hydrogen with components in the sample chamber (see Refs. [6,24-26]), non-invasive diagnostics are essential for characterizing the material as well as proving there has been no loss of sample. Coatings of the anvils can protect the diamond from attack by hydrogen at the highest pressures, but such coatings can complicate the interpretation of optical measurements. Diamond failure at very high pressures is also readily induced by exposure to visible laser radiation that couples with stress-induced absorption of the anvils. The hydrogen vibron, which has been a key diagnostic of the state of bonding and phase transformations [6], can be probed by IR spectroscopy and is enhanced above 150 GPa in phase III [27]. Moreover, IR spectroscopy at long wavelengths provides a direct determination of optical conductivity, thereby providing essential constraints on the insulator-metal transition and other changes in electronic properties. Here we document the behavior of hydrogen in a newly accessible range of static *P*-*T* conditions up to 360 GPa over a range of temperatures using optical techniques, notably synchrotron infrared spectroscopy. The results provide new measurements of the electronic properties of phase III consistent with a semimetallic ground-state and a wide *P*-*T* stability field of paired states of dense hydrogen.

Experiments were performed using new diamond anvil cells techniques. Improvements in cell stability, sample preparation, and control of pressure have allowed us to reach higher calibrated static pressures than in previous work without the use of coatings or composite sample configurations that can complicate optical measurements [28]. The measurements were carried out at beamline U2A, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Synchrotron radiation provides a high flux, broadband IR source that is essential for measuring transmission at the longest wavelengths allowed by the diffraction limit of the small samples (*e.g.*, <10 μm aperture) at very high pressures. A conventional tungsten-halogen source was used to measure absorption spectra in the visible range (up to the absorption edge of the stressed diamond anvils). Pressure was determined by edge shift of T_{2g} Raman band of the diamond anvils probed with very low-level laser exposure (647 nm and <1 mW) and from previously calibrated IR vibron shifts [28]. Because laser radiation can induce diamond failure at very high pressures, a series of runs was also performed with only broadband IR and visible probes. These runs allowed us to reach the highest pressures. Altogether, 20 experiments were performed to pressures above 200 GPa at a range of temperatures between 12 and 300 K.

Selected IR absorption spectra in the region of the H_2 vibron are shown in Fig. 1. Runs reaching the highest pressures required the samples to be thin ($< 2\ \mu m$), in which case the vibron overlapped the three-phonon diamond band, which shifts to higher frequency with increasing stress. The two bands merge above 330 GPa. For these spectra, the vibron frequencies were determined by varying the reference spectrum and by spectral deconvolution. At the highest pressures, $\nu_{IR} = 4010\ cm^{-1}$, which corresponds to 360 GPa by linear extrapolation of the pressure scale of Ref. [29]. The use of other pressure scales and different fits of the data give pressures above 400 GPa [28]. We choose to use the most conservative pressure scale in our analysis and in the discussion below. The results indicate that the hydrogen molecules remain intact to well above 300 GPa. The values of ν_{IR} shift smoothly as a function of pressure, with no evidence for discontinuities or changes in slope (Fig. 2). A smooth, monotonic splitting between the principal IR and Raman vibron modes was observed well beyond the range of previous measurements [18,27]. In addition, the integrated intensity of the IR vibron, which increases linearly with pressure above the transition to phase III [11], continued to increase to around 250 GPa and then began to decline.

We also successfully carried out temperature excursions in selected runs without failure of the diamond anvils. Because of problems with sample loss due to hydriding of gaskets and hydrogen penetration into the anvils, particularly at higher temperatures [24,26], it was essential to measure clear signatures of the hydrogen contained within the sample chamber. In several runs, the hydrogen was contained to close to room temperature at the maximum pressures, as evidenced by the strong vibron (Fig. 3). Measurements between 250 and 300 K show a systematic rise in IR vibron absorption as a function of pressure associated with the transition to phase III; this extends the previously established I-III boundary beyond the critical point at which the discontinuity in the Raman vibron disappears (Fig. 3) [11]. The results show that hydrogen remains molecular at all temperatures explored. Though the measurements are less clear for the thin samples that reached the highest pressures, our analysis indicates the presence of a vibron at 340 GPa to at least 200 K.

These measurements also provide crucial information about the electronic properties, including whether material has passed over into a metallic state (Fig. 3). The longest wavelength transmission spectra measured to the diffraction limit of the cell, previously limited to 216 GPa and <100 K [8], provide bounds on possible closure of the indirect gap and predicted metallization in this newly accessible P-T range. Transmission is observed down to the limit of the system (800 cm^{-1} or 0.1 eV), a result that rules out a transition to a fully metallic state at these conditions. Drude model fits of the lowest energy portions of the spectra, assuming closure of the gap, indicate that the plasma frequency energy $\hbar\omega_\text{p}$ must be less than 0.2 eV at the highest pressures [28], in contrast to $\hbar\omega_\text{p}$ of several eV for a good metal. No temperature dependence of broad features associated with a possible Drude edge was observed. Measurements in the visible indicate that the absorption edge shifts to lower energies with increasing pressure; at the highest pressures, absorption is observed across the visible spectrum but an edge is still observed, indicating that the direct gap has not closed. Photomicrographs of the samples are consistent with the spectral measurements [28]. The results are consistent with initially semiconducting hydrogen transforming to a semimetal at the transition to, or within, phase III and persisting over the indicated P-T conditions.

During the course of these experiments, Eremets and Troyan [30] reported an important advance in electrical conductivity techniques [10] with observations of a drop in the electrical resistance of hydrogen samples near 240 GPa and room temperature, together with a shift in the absorption edge and strong reflectivity in the visible, which they interpreted as indicating metallization and the transition to an atomic liquid below 300 GPa. Tests of metallization require measurements of electrical conductivity as $\omega \rightarrow 0$ cm^{-1} and $T \rightarrow 0$ K. Our measurements show no evidence for the optical conductivity expected for a metal over the entire range of temperatures to the highest pressures explored, and no signatures of an atomic liquid are observed. The high reflectivity of the samples reported in Ref. [30], which were measured through metal-coated diamonds, is inconsistent with the low values of the conductivity inferred from their resistance measurements, which are well below the minimum metallic conductivity of 2000-4000 $(\Omega\text{-cm})^{-1}$ expected for hydrogen [15]. On the other hand, the maximum carrier density allowed by our results (*i.e.*, $\hbar\omega_\text{p} < 0.2$ eV) is consistent with the resistance values they report (10^7 to 10^4 Ω) [30], though other factors may need to be considered [31]. In another recent study, Howie et al. [32] reported room temperature Raman data indicating the crossing of the I-III phase line at 210 GPa and 300 K, close to that observed here based on IR vibron measurements. They also suggest a transition to a new phase based on a change in the pressure dependence of the Raman vibron frequencies and increasing visible absorption. Our observations of a pronounced IR vibron, together with the lack of major discontinuous changes in frequency or intensity as a function of pressure and temperature, indicate that phase III persists over a broad *P-T* range. However, transitions to similar molecular phases, if accompanied by weak spectral signatures, cannot be ruled out. Additional measurements at 300 K and above are needed to test these proposals as well as possible re-entrant melting [17,25,30,32].

In conclusion, new static compression techniques have opened a window on the behavior of hydrogen at 300-400 GPa over a range of temperatures. The broken-symmetry molecular phase III persists over a broad *P-T* range in a potential charge-ordered state (*e.g.*, Peierls' distortion) [13] that delays or even pre-empts the onset of the originally predicted metallization of the solid. On the other hand, the low-energy IR data provide evidence for changes in electronic properties in phase III with conductivity well below the minimum metallic conductivity. The classical characteristics of hydrogen at these densities [11] combined with the intrinsic quantum character of the system gives rise to an intriguing ground state at these densities. Identification of the ultimate breakdown of the paired ground state on cold compression [13], transitions to a potentially low-temperature fluid [17], the formation of an excitonic insulator or novel quantum phases associated with electron pairing [5], and the possibility of reentrant insulating behavior (analogous to the heavier alkalis Li and Na [33]) require further investigation. This will require continued extension of high-pressure techniques, including refinements in pressure metrology, in this newly accessible *P-T* range for laboratory studies of dense hydrogen.

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Figure Captions

Fig. 1. (Color) Representative synchrotron IR spectra of hydrogen in the region of the vibron (H_2 stretching mode) at selected pressures and 80 K. (a) Spectra from an experiment reaching 300 GPa. (b) Spectra from a higher pressure experiment. Below 150 GPa (in phase I), and at room temperature and at higher pressures (in phase I), the vibron intensity is approximately three orders of magnitude lower than at higher pressures and <100 K (phase III). Thus, single-channel transmission spectra measured under these conditions can be used as a reference (or background) spectrum to obtain clear signatures of the vibron. For (a) the single channel spectrum measured at 140 GPa and 300 K was used as the reference. For the absorption spectra shown in green in (b), a single-channel transmission spectrum measured at 142 GPa and 300 K was used as the reference (see Ref. [28]). In order to ratio out the diamond phonon absorption band at these higher pressures, a series of single-channel transmission spectra measured at corresponding pressures and ≥250 K were also used to obtain the absorption spectra, as shown by the black curves in (b). The absorbance bar refers to the amplitude of these spectra;; the absorbances for spectra in green are scaled by ½ in the plot.. As a cross-check, peak positions were also determined using direct deconvolution of spectra having overlapping bands; the peak positions of the vibrons determined by both approaches were found to be within ±10 cm^{-1}. Further details are provided in Ref. [28].

Fig. 2. (Color) Low-temperature vibron frequencies as a function of pressure, including results from the present study as well as IR data from Refs. [18,27], and Raman data from Refs. [18,19]. Different symbols correspond to different experiments. The red lines are our fits of these combined IR and Raman vibron shift datasets. The blue dashed line is the Raman shift reported in Ref. [20], which follows a trend not found in the other studies.

Fig. 3. (Color) Absorption spectra at selected pressures and temperatures. Synchrotron IR spectra (red lines, offset for clarity) show the persistence of the vibron over the range of conditions studied. The blocked areas at low energy are regions of intrinsic and impurity absorption of the diamond anvils. The initial (160 GPa) sample thickness d for the top three spectra was 3.7 μm (corresponding to Fig. 1a), and for the lower two spectra $d = 2.6$ μm

(Fig. 1b). The blue lines are representative optical conductivities calculated assuming simple Drude model parameters (see Ref. [8]) to provide upper bounds on the possible carrier density: A. $\hbar\omega_p = 2$ eV, $\hbar/\tau = 0.1$ eV; B. $\hbar\omega_p = 1$ eV, $\hbar/\tau = 0.1$ eV; C. $\hbar\omega_p = 0.5$ eV, $\hbar/\tau =$ 0.1 eV. D. $\hbar\omega_p = 0.2$ eV, $\hbar/\tau = 0.1$ eV; E. $\hbar\omega_p = 0.2$ eV, $\hbar/\tau = 0.01$ eV [28]. A nominal sample thickness $d = 2$ μm was assumed. Curves D and E are consistent with the measured data. Sharp features at low energies arise from phonons and hydrogen-diamond interactions and are discussed elsewhere [8,9,28]. *Left Inset:* Phase diagram showing the nominal *P-T* region explored (shaded area). The solid lines are I-II-III phase boundaries [6,11]; the dashed line is the extrapolation of the previously determined I-III phase line [11]. The blue and red dotted lines at higher pressures are nominal melting and plasma phase transition lines, respectively, suggested by experiment or predicted theoretically (see Refs. [17,25]). *Right Inset*: Selected visible absorption spectra. The dashed red lines are from Ref. [19] and are rescaled to fit the plot. The absorption edge appears to have a weak temperature shift under these conditions, but only a limited *P-T* range has been explored [28].

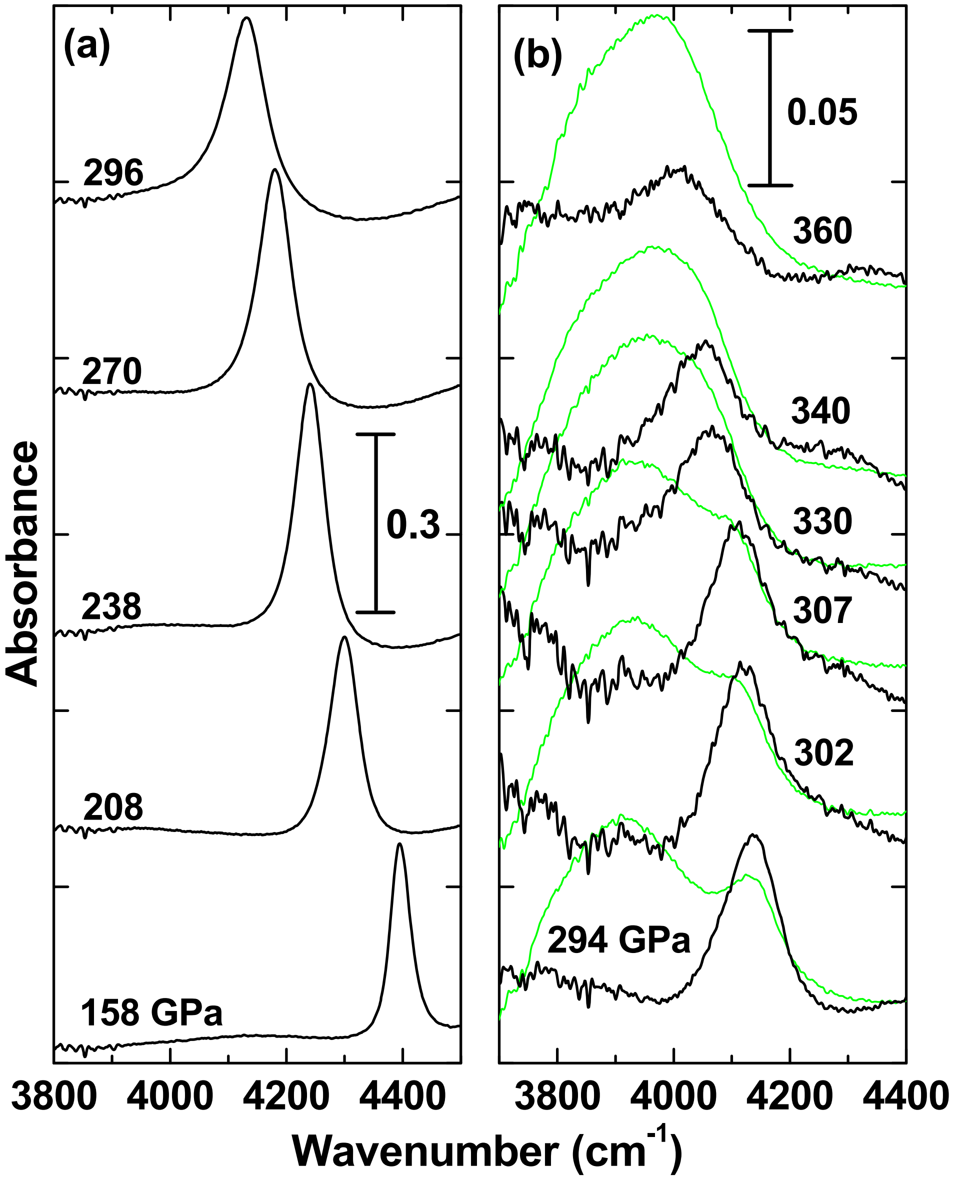

(a)
(b)
Absorbance
296
270
238
208
158 GPa
0.3
0.05
360
340
330
307
302
294 GPa
3800
4000
4200
4400
3800
4000
4200
4400
Wavenumber (cm^{-1})

Fig. 1

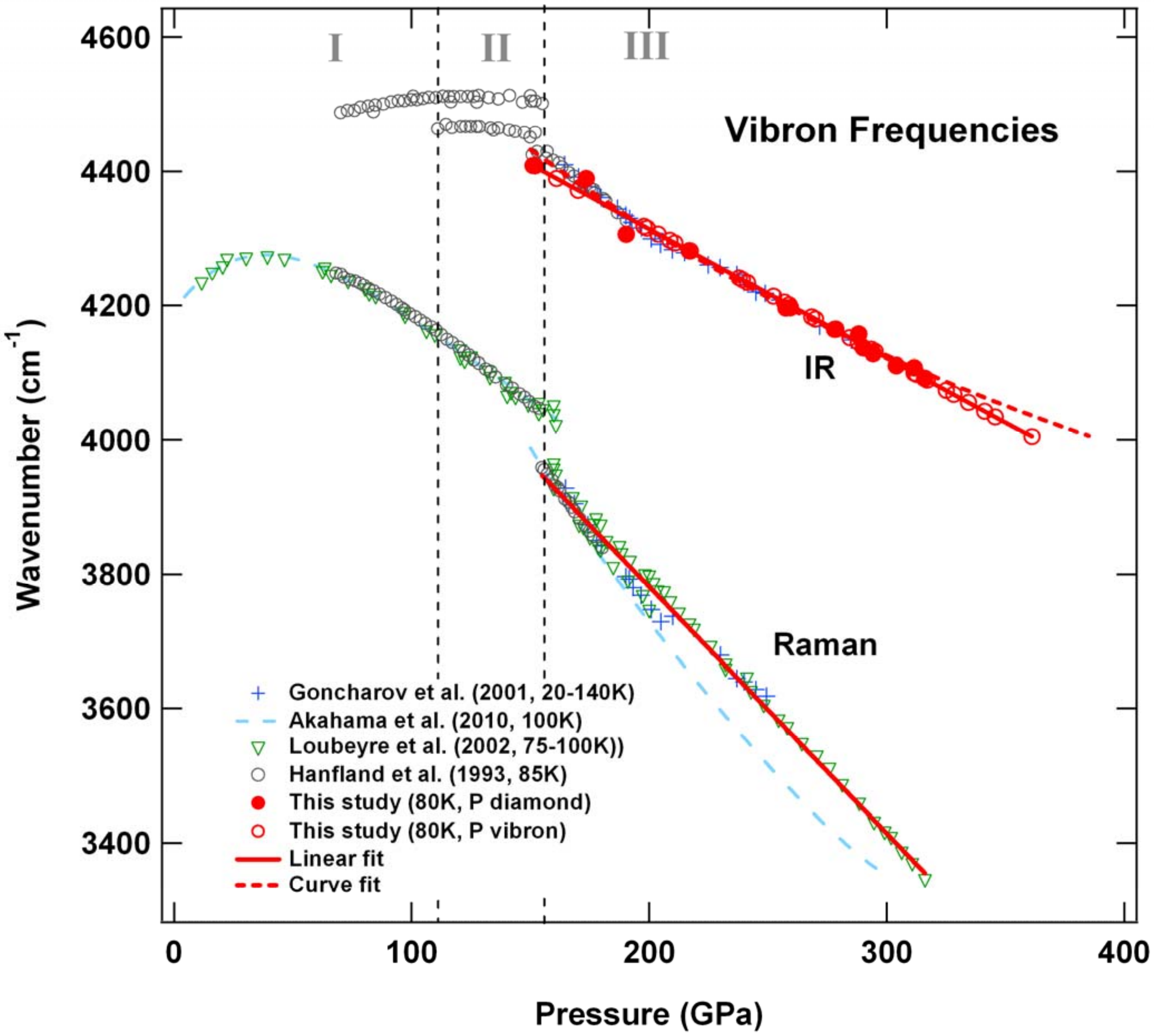
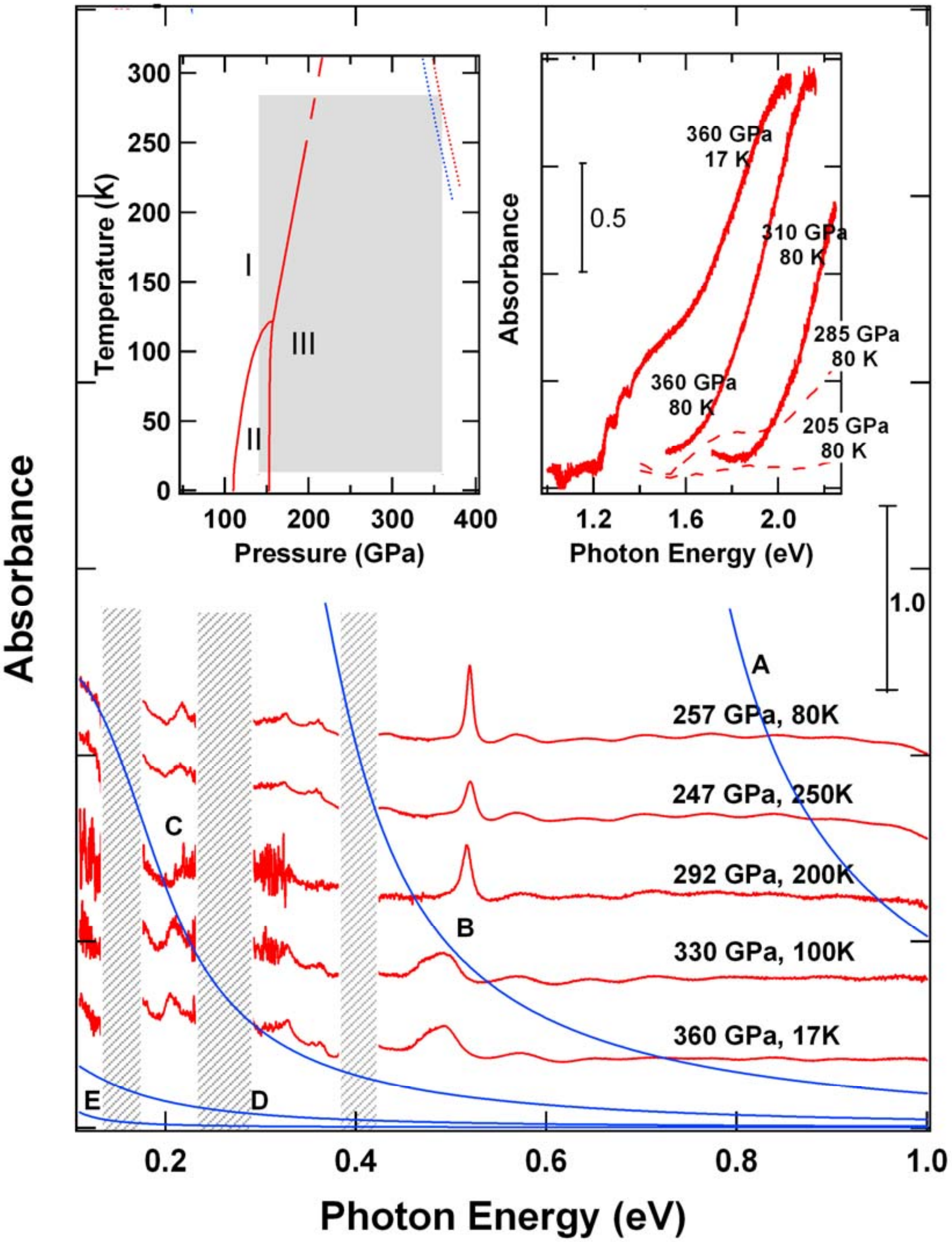

Vibron Frequencies
I
II
III
IR
Raman
Wavenumber (cm^{-1})
Pressure (GPa)
4600
4400
4200
4000
3800
3600
3400
0
100
200
300
400
Goncharov et al. (2001, 20-140K)
Akahama et al. (2010, 100K)
Loubeyre et al. (2002, 75-100K))
Hanfland et al. (1993, 85K)
This study (80K, P diamond)
This study (80K, P vibron)
Linear fit
Curve fit

Fig. 2



Temperature (K)
Pressure (GPa)
I
II
III
Absorbance
0.5
360 GPa 17 K
310 GPa 80 K
285 GPa 80 K
360 GPa 80 K
205 GPa 80 K
Photon Energy (eV)
Absorbance
1.0
A
B
C
D
E
257 GPa, 80K
247 GPa, 250K
292 GPa, 200K
330 GPa, 100K
360 GPa, 17K
Photon Energy (eV)

Fig. 3