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Quantum phase transition in solid hydrogen at high pressure

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Extensive experimental and theoretical studies have been devoted to determining the high-pressure phase diagram of hydrogen. We present evidence of a phase at a higher pressure than phase III and below the pressure of the recently observed phase of metallic hydrogen (495 GPa). This phase was determined from infrared (IR) spectroscopy of hydrogen samples at static pressures above 360 ± 15 GPa in a diamond anvil cell, and has been observed in three separate experiments. Whereas earlier studies found new high-pressure phases that only occurred at elevated temperatures, this phase transition occurs at the lowest temperatures investigated, ∼5 K, and the steep phase line indicates that it is a quantum phase transition. This phase is characterized by two distinct IR absorption bands (2950 and 3335 cm^{-1} at 365 GPa). Above the transition pressure we observe strong darkening of the sample in the visible spectrum as pressure is increased. Observations are compatible with the *cmca*-12 crystal structure.

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I. INTRODUCTION

Hydrogen is the simplest element in the Periodic Table of Elements, yet in the solid state it has a complex phase diagram as a function of temperature and pressure. Over 80 years ago Wigner and Huntington (WH) [1] predicted that at high pressure the hydrogen molecules of the solid would dissociate to form an atomic metallic solid (WHMH). For many decades there have been extensive studies stimulated by this prediction, revealing a rich pressure-temperature phase diagram. With increasing pressure, several phases have been observed in the molecular solid, while the WH metallic phase was recently observed by Dias and Silvera [2] in a diamond anvil cell (DAC) at a static pressure of 495 GPa. Here we report the observation of an insulating phase above 360 ± 15 GPa, observed at $T = 5\,\mathrm{K}$ and higher temperatures; this phase precedes the WHMH phase and therefore we name it H_2-PRE. At liquid helium temperatures the sample is expected to be pure para-H_2 and the naming is consistent with the phase notation convention (see ahead). We have observed H_2-PRE in three experimental runs at temperatures between ∼5 and 83 K, and higher. The phase line has a steep, almost vertical slope, indicating that it will occur as a quantum phase transition in the limit $T \rightarrow 0\,\mathrm{K}$.

It is useful to review the experimental phase diagram of hydrogen that existed before the observation of the WHMH phase, shown in Fig. 1(a). Hydrogen has two isomers, ortho and para (o-p) corresponding to the symmetric and antisymmetric nuclear spin states. Samples can be prepared in pure or varying o-p concentrations [3]; these classifications are expected to be preserved until the dissociative WH transition [4]. At low pressure the phase diagrams of ortho and para are completely different; pure para remains hexagonal close packed in the limit $T \rightarrow 0\,\mathrm{K}$, while pure ortho-$H_2$ exhibits a phase transition to orientational order at ambient pressures (not shown in Fig. 1). Mixed ortho-para solids have transition temperatures that depend on the concentrations. Thus, in principle there are an infinite number of phase lines if the phases are also indexed by the o-p concentration. At low pressures o-p conversion is very slow, so that (out of equilibrium) phase lines for almost pure ortho- or para-hydrogen have been determined [3]. We note that hydrogen and deuterium have similar phase diagrams, with isotopic shifts of phase lines, while HD has a distinctly different phase behavior [5].

There are two pathways to metallic hydrogen (MH) at the extremes in pressure and temperature [Fig. 1(a)]. In this paper we focus our attention on the low-temperature pathway I. Pathway II is a high-temperature path to a transition in the liquid molecular phase to liquid atomic metallic hydrogen and will not be discussed here. Pathway I is the path where several insulating solid molecular phases have been identified. The first three phases for pure p-H_2 are named LP (low pressure), BSP (the broken symmetry phase, first observed in solid pure o-D_2 at 28 GPa [6]), and the H-A phase [7,8] (notational comment: p-H_2 and o-D_2 are in the same spherically symmetric ground state at low P and T). At lower pressures and temperatures p-H_2 and o-D_2 have similar phase diagrams. In these same P-T ranges, solid phases with mixed concentrations of ortho-para are named I, II, III, respectively, to be distinguished from the pure isomer phases [9]. Phases IV and IV′ were first observed at room temperatures (RT) (but not named) by Eremets and Troyan [10] at pressures of 220 and 270 GPa, respectively, by noting changes in the Raman scattering spectra. Later, Howie *et al.* [11,12] studied these phases and named them IV and IV′. Only phase IV was studied in detail. Phase IV is always a mixed molecular ortho-para phase as it only exists at temperatures above ∼200 K, so there is an equilibrium mixture of the o-p isomers. All of these phases differ by structural changes characterized by orientational order of the molecules in which the solid remains insulating.

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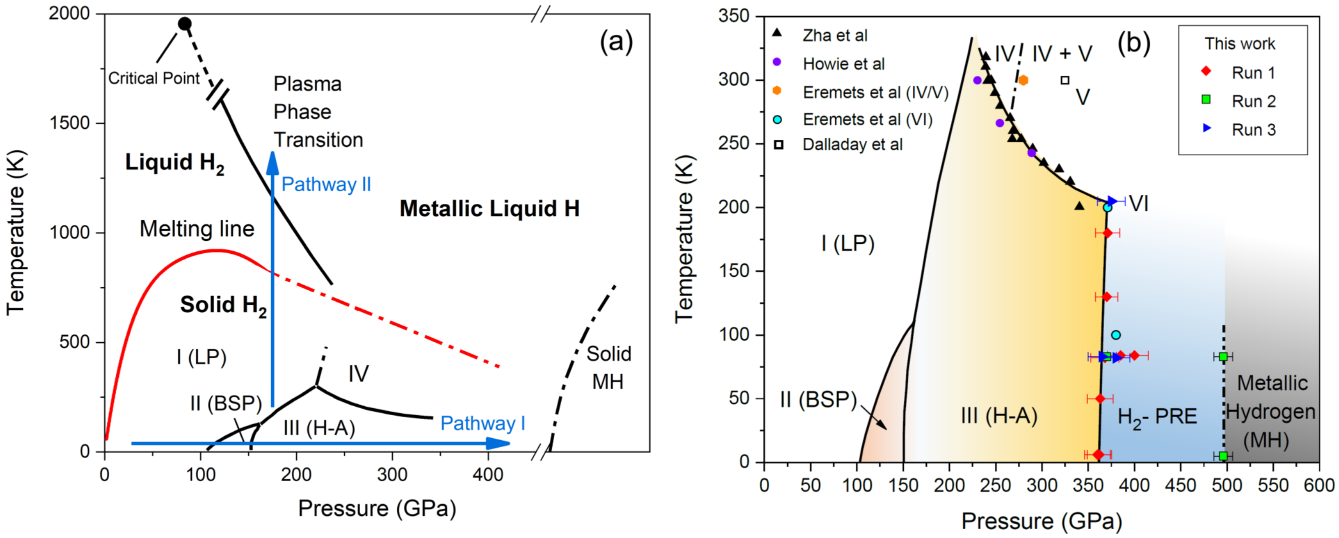

FIG. 1. (a) The *P-T* phase diagram of para-hydrogen showing the two pathways to MH. See text for details. (b) The current experimental phases of H_2 in the pathway I region showing H_2-PRE and the WH phase of MH at lower temperatures. Dalladay-Simpson *et al.* studied the region 270–325 GPa at higher *T* and claimed a new phase at 325 GPa, so with increasing pressure one goes from IV to IV′ to V. Eremets *et al.* did not observe the new phase and suggested that IV′ is a mixed phase region that becomes a single phase at 325 GPa. For consistency of notation we name phase IV′, phase V. See text for further discussion.

Ideally structural phase transitions are determined by x-ray or neutron diffraction techniques. Such methods are very challenging for high-pressure hydrogen studies due to the weak scattering cross sections and the very small sample sizes. Because of these constraints, the main techniques used to study hydrogen are Raman scattering and IR absorption. According to the Landau theory of phase transitions (PTs), based on symmetry of the particle distributions in a lattice, a PT is characterized by an order parameter that is continuous for a second-order PT and usually discontinuous for a first-order PT. Group theoretical arguments show that excitations (vibrons, rotons, phonons, etc.) are allowed or disallowed, depending on the symmetry of the structure. Thus, at a phase transition, lattice modes appear, disappear, or undergo discrete shifts as the symmetry of the lattice changes; these changes are used to map the phase lines in the study of hydrogen.

Recently, Dalladay-Simpson, Howie, and Gregoryanz (DHG) [13] reported a new phase at 325 GPa and RT, based on a single *P-T* point; they named this phase V. Examination of their data shows that there is no basis for the claim of a new phase. Their claim was based to a large extent on line broadening and changes of intensity of Raman modes, neither of which is an accepted signature of a phase transition, while discontinuity of lattice modes is. Their observed Raman modes of hydrogen are continuous through the pressure of 325 GPa. They show (their Fig. 3) that phase IV and IV′ have a large range (270–320 GPa) where they coexist and solid hydrogen becomes single phase (IV′), for higher pressures. Raman studies by Eremets, Troyan, and Drozdov (ETD) [14] did not observe the phase proposed by DHG. Detailed analysis supporting this implied misinterpretation of data by DHG is presented elsewhere [15]. The conclusion is that this *P-T* region *does not* have three phases—IV, IV′, and V—but only two. Due to coexistence of phases, as pressure is increased, phase IV diminishes in favor of IV′. Thus, it appears that IV′ and the "new" phase V (as named by Ref. [13]) are the same phase that begins at ∼270–275 GPa at lower pressure, with a mixture of phase IV and IV′ in the 270–320 GPa pressure region. Henceforth, to simplify the notation we shall drop the name IV′ in favor of V and identify the region 270–320 GPa as IV+V; this is shown in Fig. 1(b), and further delineated in Table I. There are two recent theoretical papers (discussed ahead) in which the solid molecular phases are studied as a function of pressure or density at temperatures of a few hundred K [16,17]. Several structures were examined with a goal to identify phase V′; the energy landscapes of these structures differ by a few mK/atom. Thus, no structure has been conclusively identified. In any case these studies can be applied to the renamed phase V, i.e., the higher-pressure phase first observed by ETD.

II. EXPERIMENTAL RESULTS

The objective of the current experiments was to search for new phases, using optical techniques, by traversing to the highest pressures at temperatures as low as 5 K in a DAC (see the Appendixes). We have observed a unique phase (H_2-PRE) in three experiments (runs 1, 2, and 3). In the first run a maximum pressure of 420 GPa was achieved [18]. We found a phase transition that occurs at a pressure near 360 GPa and liquid helium temperatures, using near-infrared spectroscopy (pressure uncertainties are on the order of ±15 GPa due to the use of the diamond Raman pressure scale). At high densities ortho-para conversion to equilibrium should be very rapid [4] so that this phase should be pure para-hydrogen at low temperature. This phase was again observed in the run that produced metallic hydrogen (at a pressure of 495 GPa, run 2). H_2-PRE was seen for the third time in a run that achieved a maximum pressure of ∼380 GPa and was studied to higher temperatures, up to 220 K. In all three runs the sample changed from transparent to opaque and darkened to black, as pressure was increased above the transition pressure in the

TABLE I. Higher-pressure phases of hydrogen that have been discussed and named in the literature. The original phases IV and IV′ (named by Howie *et al.* [12]) are proposed by Eremets *et al.* [14] to coexist in the region 270–320 GPa, so that above 320 GPa hydrogen becomes pure IV′. Thus, a new phase V claimed by Dalladay-Simpson *et al.* at 325 GPa does not exist. For consistency of notation, we, as well as Eremets *et al.*, propose to drop the name IV′, and replace it with the name V. Phase H_2-PRE is the name for the para-hydrogen phase observed at liquid helium temperatures, also named phase VI by Eremets *et al.* for mixed ortho-para samples at higher temperatures.

	High-pressure phases of hydrogen Pressure range (GPa)					
References	220	270–320	325	360	495	Comment
Eremets *et al.* [10]	(IV)	(V)				Parentheses mean observed but unnamed
Howie *et al.* [11,12]	IV	IV′				Phase lines studied
Dalladay-Simpson *et al.* [13]	IV	IV′	V			The phase at 325 GPa does not exist; rename IV′≡V
Eremets *et al.* [14]	IV	IV+V	V	VI		VI observed for $T \geqslant 200$ K
This work				H_2-PRE		Observed at $T = 5$ K and higher
Dias and Silvera [2]					WHMH	
Consistent naming of phases	IV	IV+V	V	H_2-PRE VI	WHMH	At lower T At higher T

temperature range 5–83 K. We believe that the blackening is due to the closing of the electronic band gap of the molecular hydrogen and the observed phase is semiconducting. After observing H_2-PRE in run 1, an article by ETD [14] appeared on the arXiv; they also observed a phase transition at pressures close to ours and at higher temperatures (∼200 K) and named it phase VI. Their observations were later extended to ∼100 K and overlap our phase line [19]. They suggest that the phase is

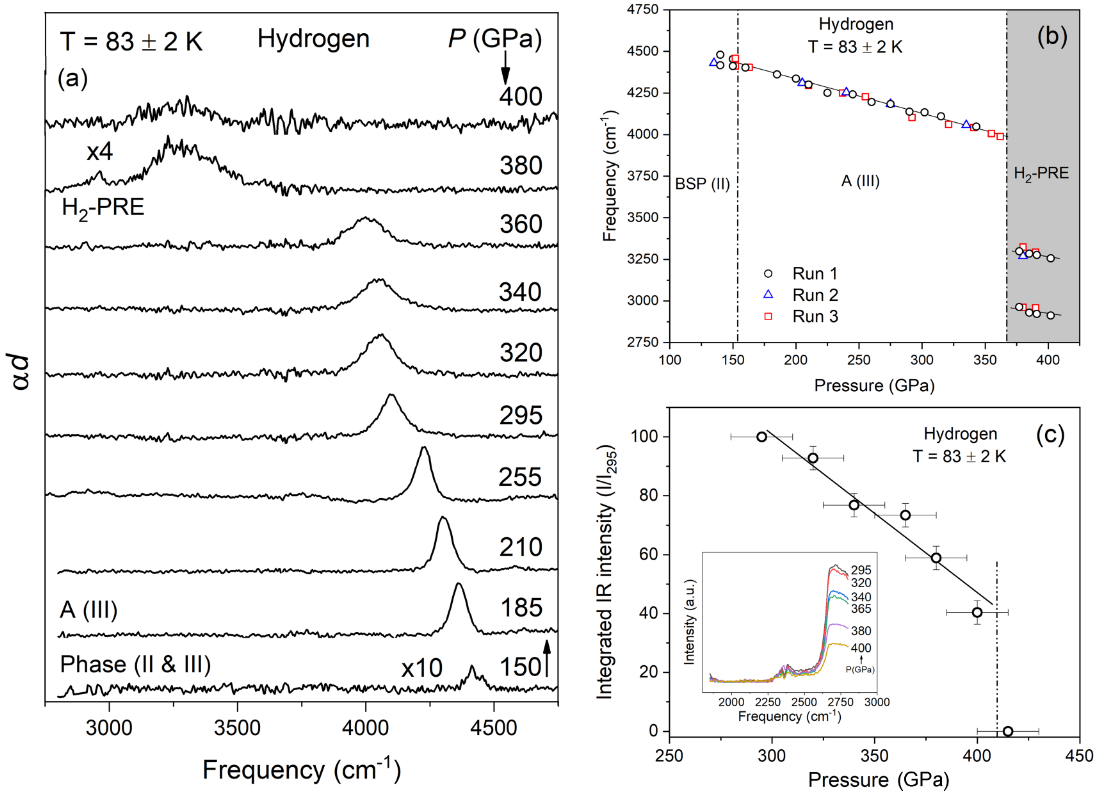

FIG. 2. (a) IR spectra of solid hydrogen in various phases for several pressures at $T = 83$ K. We plot the IR absorption coefficient times the sample thickness vs IR frequency. The spectrum at 150 GPa has two peaks due to coexisting phases. The spectra show disappearance of the characteristic IR peak of phase III above 360 GPa and appearance of a broad peak at around 3335 cm^{-1} and a weak peak around 2950 cm^{-1}, indicating a phase transition. (b) The mode frequencies as a function of pressure at $T = 83$ K, showing the transition from phase III to the alternative phase, H_2-PRE. (c) Integrated transmitted intensity over the IR range (< 2800 cm^{-1}) vs pressure, normalized to a 295-GPa pressure spectrum, indicating that the transmission in the IR region under study goes to zero within the signal-to-noise ratio. The inset shows the raw IR spectrum at different pressures. In this frequency range the sample was opaque to IR above 420 GPa.

semimetallic. More recently, a paper on the condensed matter (CM) arXiv by Loubeyre, Occelli, and Dumas [20] observed hydrogen becoming opaque in the region of 425 GPa and interpret this as band-gap closure and implied metallization (no evidence of the latter was presented). At 427 GPa they plot an abrupt reduction of the intensity of transmission of light to zero. Their data show that the transmission in the IR region goes to zero, not closure of a band gap; their figure implies that the intensity changed discontinuously. This might be the behavior of a metal, but there are other reasons why the intensity can go to zero: for example, a transition to a phase that is absorbing in the IR, but not metallic, that is, a black (absorbing) insulator or semiconductor. A phase with a reststrahlen band could inhibit propagation of light in their IR region. Thus, "zero" transmission is not proof of an insulator-to-metal transition. We observed zero transmission of visible and IR light at 420 GPa [see Fig. 2(c)]. The front illuminated sample was black in reflectance with no evidence of metallization [21].

Figure 2(a) displays the infrared absorption spectra in the region of the hydrogen vibron lines at various pressures and $T = 83\,\mathrm{K}$, while Fig. 2(b) shows the mode frequencies as a function of pressure at $T = 83\,\mathrm{K}$, indicating the abrupt transition from phase III to another phase [see also Fig. 1(b)]. As pressure is increased, the fundamental vibron mode of phase III disappears, and two broad absorption lines appear at $\sim$2950 and $\sim$3335 cm^{-1}. Similar, but sharper spectra were observed at liquid helium temperatures at $\sim$360 GPa and 5 K. During one experimental run we observed a very weak absorption around $\sim$4320 cm^{-1}, but this was not reproducible (see the Appendixes). The modes were further studied at higher temperature in phase H_2-PRE at a pressure of 365 GPa (run 3). The characteristic peaks of the observed phase of hydrogen faded and completely disappeared at 220 K (Fig. 3). These spectra identify a transition to a different phase. In that experiment we did not pursue this phase line, but it appears to be a transition to an extension of the V phase line [Fig. 1(b)], based on the results of Eremets *et al.* [19], addressed in Table I.

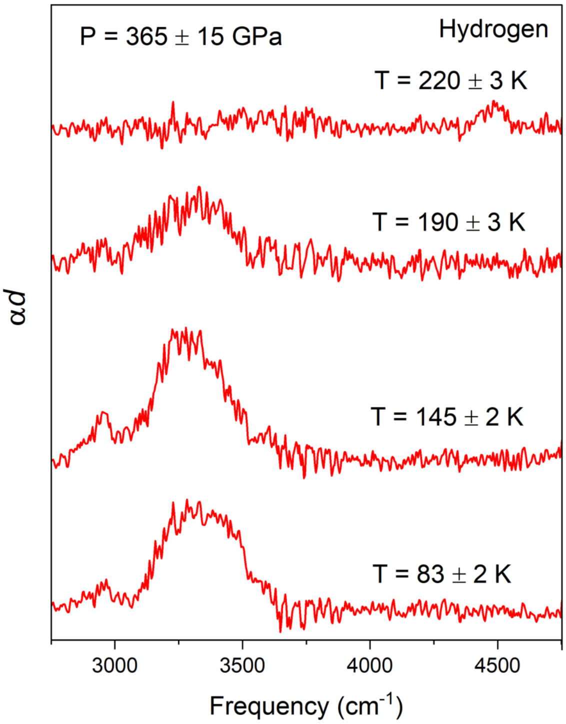

FIG. 3. The H_2-PRE phase mode absorption coefficient times sample thickness vs frequency as a function of temperature for a fixed pressure, $P = 365\,\mathrm{GPa}$, showing the disappearance of the absorption peak at high temperature.

III. THEORETICAL CONSIDERATIONS

Theoretical predictions of the phase diagram of hydrogen have rapidly improved in the past several years. A straightforward application of density functional theory (DFT) gave various and inconsistent predictions [22], leading theorists to focus on more sophisticated, calculation-intensive techniques such as diffusion Monte Carlo (DMC), etc. The predictive powers have made great gains. For example, the phase line for the liquid-liquid phase transition (pathway II) to metallic hydrogen agrees with experiment to within 25 GPa for hydrogen [23]; *P-T* values for phase IV are in reasonable agreement with experiment [22]. Two recent DMC calculations of the high-pressure transition to MH [24,25] predict the WH metallization pressure to be around 400 GPa, with the sample structure transforming from phase III to a molecular *Cmca*-12 to an atomic metallic *I*41/*amd* (the Cs-IV structure), with increasing pressure at low temperature [26]. Rillo *et al.* [17] also find a *Cmca*-12 structure using path integral Monte Carlo and coupled electron-ion Monte Carlo methods. The experimentally observed phase line of H_2-PRE is consistent with the DFT calculation of a transition to a *Cmca*-12 phase [27,28]. Unpublished DFT calculations performed at 350 GPa by Clay and Morales [29] find three IR active modes between 2500 and 4500 cm^{-1}. These modes closely correspond to the proposed molecular *Cmca*-12 structure and are consistent with previous theoretical work of Pickard and Needs [28]. However, these calculations are only indicative, as the mode frequencies are sensitive to the choice of the exchange-correlation functional, as well as anharmonic effects. Thus, we tentatively assign the structure of the observed phase H_2-PRE to *Cmca*-12. In hindsight our prescient naming of this phase as the phase that precedes MH in the phase diagram appears to be correct [18].

IV. DISCUSSION

The lower-pressure phase transitions, I → II and II → III, are quantum phase transitions, appearing in the low-temperature limit as pressure is increased. Many recent experimental studies focused on the earlier largely unexplored region of high pressure around room temperature. Phase IV only appears around RT and the phase line has a relatively weak pressure dependence, as seen in Fig. 1. Theoretical studies have simulated such phases (e.g., IV) and argued that these transitions are entropy driven, so that they only appear at elevated temperatures. For H_2-PRE we observe a phase line rising from low temperature, as was the case for phase lines in a recent paper on HD [5]. We conclude that the ultrahigh-pressure hydrogens exhibit quantum phase transitions or transitions in the limit $T \rightarrow 0$ K with increasing pressure.

There are a number of phases, names of phases, and claims of properties for solid hydrogen that can be confusing; here we hope to clarify the phase diagram with a consistent notation. As a guide to Fig. 1, we summarize these phases in Table I. Phases I, II, and III, discussed above, are well known and established, so they are omitted from this summary. As discussed above, the name IV′ should be dropped in favor of the name V. To be clear and consistent with the naming of phases, H_2-PRE is the name for pure para-hydrogen and continuously evolves into phase VI as temperature is increased and the sample becomes mixed ortho-para. At low pressure there is a large structural distinction between ortho and para phases, whereas at very high pressure, there is little discernible structural difference between the two isomers, only that the nuclear spin states differ. Thus, H_2-PRE and phase VI probably have the same crystal structure and fall on the same phase line.

In conclusion, we observed a quantum phase transition at a pressure above ~360 GPa in the low-temperature limit, consistent with theory. At the highest pressures investigated in phase H_2-PRE, our sample was dark in reflected and transmitted light, but we could still observe faint transmitted light in the visible (see Appendix C, Fig. 7), indicating that it is most likely semiconducting. Our proposed clarification of the naming of the solid phases and pressure regions is summarized in Table I. Pressure uncertainties should not affect any of the conclusions reached here.

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APPENDIX A: METHODS

There are two challenges for studying hydrogen at high pressure, besides the finite strength of the diamond anvils. First, hydrogen is very compressible and the molar volume changes by a factor of ~10–15 when pressurized to the multimegabar region, so that stable, precision alignment of the DAC is required, or the sample blows out of the gasket as pressure is increased. The second challenge arises from hydrogen diffusion and reactivity. Hydrogen is very reactive and can diffuse into the metallic gasket or diamonds. If this happens the diamond anvils can embrittle and fail. Diffusion is an activated process and is suppressed at low temperature but can lead to diamond failure at high P-T, even room temperature, so in this experiment we do not explore the room temperature region.

Three experimental runs were performed. Hydrogen was cryogenically loaded in a DAC and cryostat similar to a design described elsewhere [30]. A rhenium gasket confines the sample. Pressure was determined at lower pressures using the ruby scale of Chijioke *et al.* [31], and from ~150 to 350 GPa using the vibron pressure scale of Zha *et al.* [32] (based on the 2010 diamond Raman scale of Akahama and Kawamura [33]). For higher pressures we measured the diamond Raman line [33]. Pressure uncertainties are on the order of ±15 GPa, due to systematic errors of the diamond Raman scale [34], but we do not think this affects the conclusions reached here. We round our specified pressures to the nearest 0 or 5 GPa. More details are in Appendix C.

APPENDIX B: RAW DATA FITS TO IR MODES AND NORMALIZATION

Normally in IR spectroscopy one solves for the absorption coefficient α in the equation $I/I_0 = \exp(-\alpha d)$. Here, I_0 is the radiation incident on the sample, used for normalization, and I the radiation that passes to the detector through the sample of thickness d. IR spectroscopy in a DAC has special challenges, for it is not possible to take the sample out of the DAC at each pressure to determine I_0. Furthermore, the diamonds are aligned with culets parallel to each other, so that one has Fabry-Perot fringes modulating the spectrum.

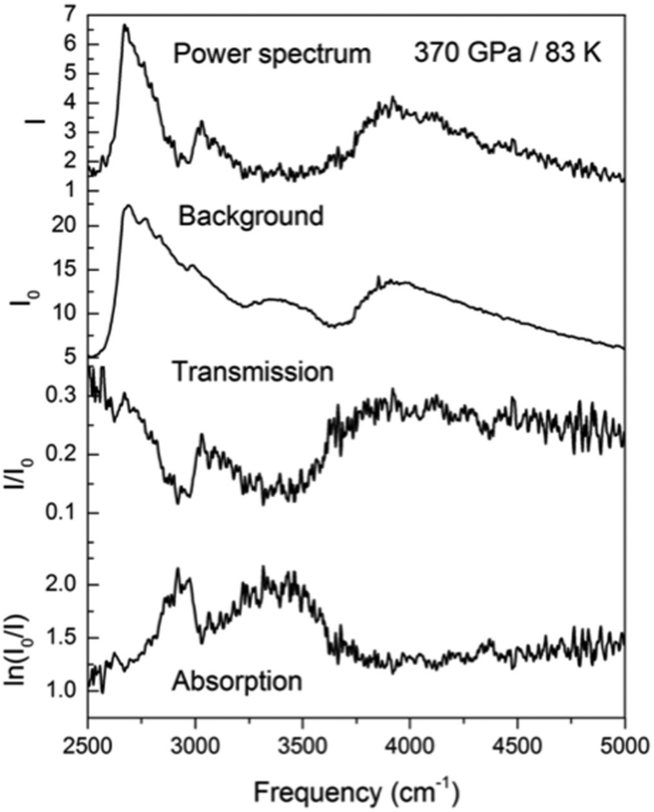

FIG. 4. An example of the normalization procedure. We show the power spectrum of the sample, the background spectrum (in this case a high-temperature spectrum in which the relevant absorption at low temperature is not present), and the transmission and absorption spectra (αd).

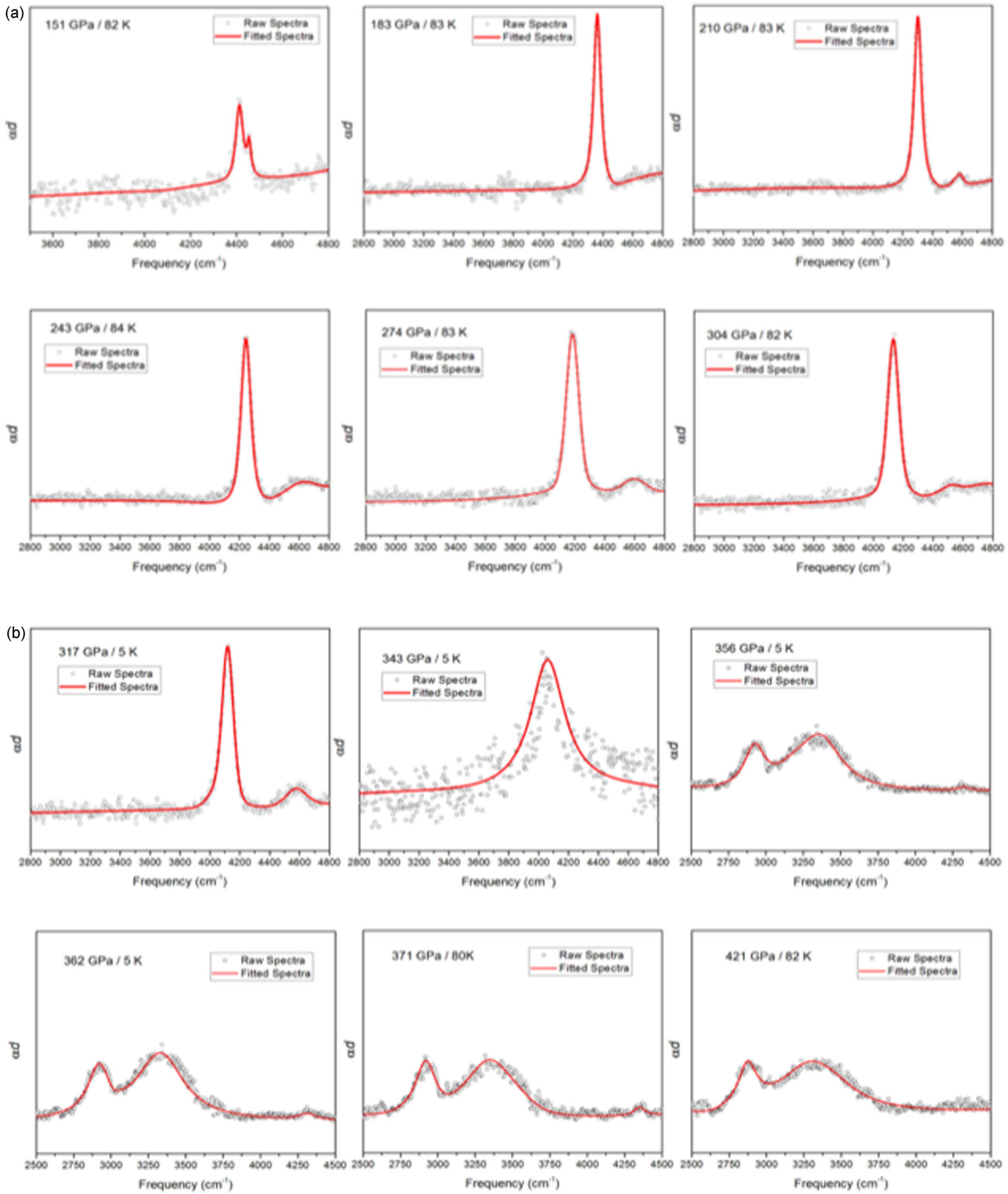

FIG. 5. (a) Examples of normalized IR absorption and the fitted spectra that are used to determine the line shapes and peak positions of the vibron modes. (b) Same as (a), but for higher pressures and lower temperatures.

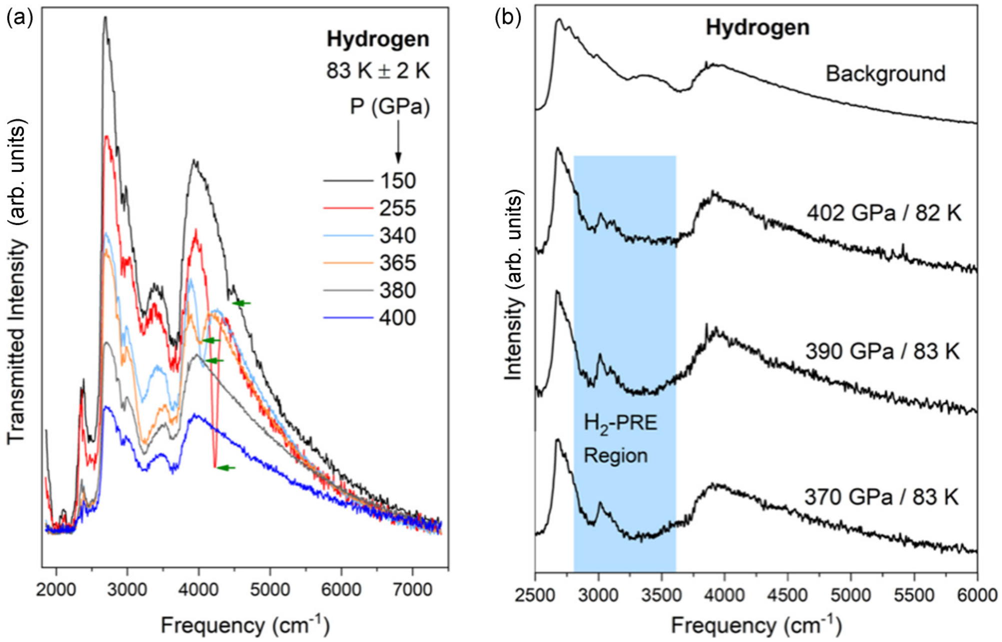

FIG. 6. (a) The raw IR transmission spectra at different pressures. The green arrow indicates the hydrogen vibron. (b) Same as (a), the raw IR transmission spectra above 360 GPa showing the H_2-PRE region.

These fringes change with the density of the sample and the spacing of the anvils as the pressure is changed. Finally, the transmitted signal is proportional to the area of the sample and this changes with pressure because the hole in the gasket containing the sample deforms. To overcome these problems, we Fourier transform the spectrum containing fringes (when needed), edit out the peak due to the fringes, and then back transform. For our normalization procedure below 350 GPa we used empty cell spectra for I_0; above 350 GPa we use high-temperature spectra for I_0 in which the relevant absorption has disappeared (if the sample is in a different phase). This latter procedure produces excellent spectra and can enhance detection of weak absorption peaks [35]. An advantage of this approach is that the two spectra are at the same pressure and DAC samples are isochoric at a fixed load; thus, the density of the sample, as well as the areas, is the same for both I and I_0. Figure 4 shows raw data for such procedures. In Fig. 5 we show raw normalized data and spectral fits to line shapes using a Voigt line-shape function. Figure 6 shows raw IR transmission spectra at different pressures. In Fig. 2, we plot αd vs frequency; we do not measure the thickness d, but estimate it to be 2–4 microns. Because the IR light from the thermal source overfills our sample, the signal is proportional to the area of the sample. To obtain adequate signal-to-noise ratio we integrated the signal for 25–40 min.

APPENDIX C: PRESSURE DETERMINATION

In the region ~150 to 350 GPa we used the pressure dependence of the H_2 IR-vibron measured by Zha *et al.* [32] to determine the pressure of our H_2 sample. For pressures above 350 GPa we used the stress-induced shift of the high-frequency edge of the T_{2g} Raman band of the diamond anvils for pressure determination [33]. An example of a first-order Raman band is shown in Fig. 7. Figure 8 shows photographs of

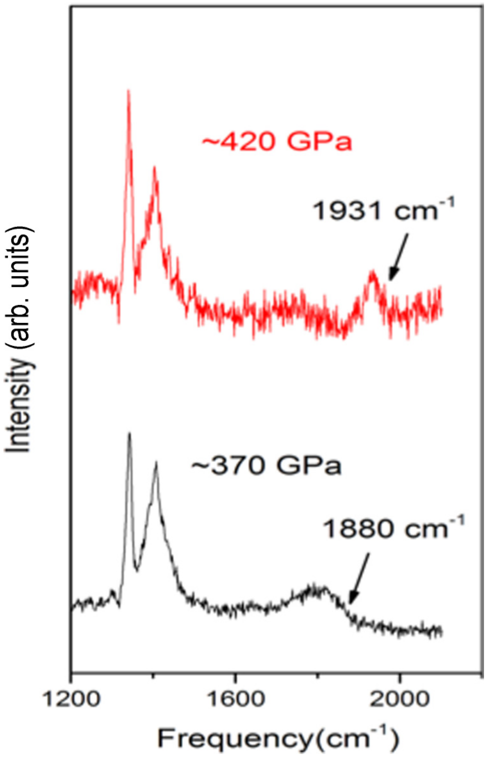

FIG. 7. The diamond phonon Raman signal originating from the stressed diamond at 370 and 420 GPa.

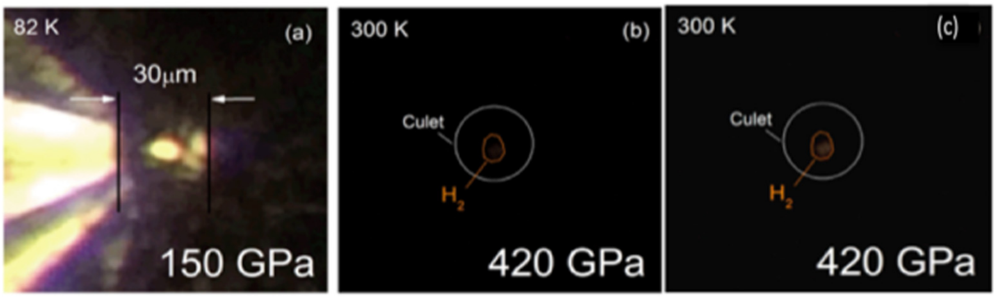

FIG. 8. Photographs of the H_2 sample in a diamond anvil cell at different pressures and temperatures (a) with combined transmitted-reflected light, and (b) with transmitted white light. The arrow indicates the culet diameter of 30 μm. The intensity of the transmitted light was the same for the recording of the photographs. The sample color gradually changes from transmitting to dark with increasing pressure at 82 K, consistent with observations of others. At high pressure the transmitted light is hard to see in the photograph, so we circled the region of the sample, and digitally enhanced it (on the right) and observe weak transmission of light.

the hydrogen sample at various pressures. We note here that in the study of MH [Fig. 1(b)] we measured the diamond phonon Raman shift and extrapolated to a region where it had not been calibrated. There were two recommended extrapolations: the linear and the nonlinear extrapolations. We used the conservative linear extrapolation which yields lower pressures than the nonlinear extrapolation. In the lower-pressure region (150–350 GPa) we use a scale which has been reproduced by a few groups (see Fig. 12 of Ref. [36]). An unpublished calibration by Loubeyre, Occelli, and Dumas (LOD) [37] deviates from all other calibrations to give substantially lower pressures. In a recent comment [21], we point out that LOD's hydrogen samples are probably contaminated with metallic impurities that can shift the vibron frequencies that are the basis of the calibration. Thus, we are confident of the calibration in the region of the H_2-PRE transition. Furthermore there is overlapping agreement with the measurements of Eremets *et al.* [14] for this transition line.

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