

Extended Infrared Studies of High Pressure Hydrogen

Nancy H. Chen, Eran Sterer, and Isaac F. Silvera

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

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We have studied solid molecular hydrogen down to liquid helium temperatures and to a pressure of 191 GPa in a new spectroscopic system, extending the low frequency limit by more than a factor of 3, from 3000 to 1000 cm^{-1} . No evidence for the earlier reported Drude behavior is found within our range of study; a possible explanation of this earlier report is presented. We find a new lattice mode which may be important for determining the structure of the high pressure *A* phase. Observation of an IR active vibron in the *A* phase of parahydrogen sets restrictions on the phase diagram.

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In recent years there have been several reports concerning metallic hydrogen based on optical studies [1–7]. Much of this excitement arose when it was realized that a unique new phase existed at pressures above 150 GPa [8], called the hydrogen-*A* (deuterium-*A*) phase, believed to be the molecular metallic phase of hydrogen. Although the most rigorous method of identifying a metal is to measure the dc electrical conductivity in the limit that temperature goes to zero, such measurements are experimentally challenging and have not yet been carried out on hydrogen. Experimenters have relied on optical properties to identify the conducting state. In particular, experiments have concentrated on measuring the optical response based on a Drude free electron model. In this case for decreasing frequencies below the plasma frequency, reflectivity and absorption of light increase from low values at higher frequencies. A definitive measurement requires a study over a broad range of frequency below the plasma frequency. Since hydrogen is expected to be an indirect band overlap metal with a low carrier density, the plasma frequency should be in the near infrared or lower. Using IR data to a low frequency limit of 4000 cm^{-1} , hydrogen was reported to be metallic by an electronic band overlap mechanism above 150 GPa [4,5]. We have built a new spectroscopic system which extends measurements to 1000 cm^{-1} , more than a factor of 3 lower in frequency, and studied solid parahydrogen down to liquid helium temperatures. We find no evidence of Drude behavior to a pressure of 191 GPa, substantially above the threshold pressure for the *A* phase. If the *A* phase is not metallic, its nature remains mysterious. One of the important observations in both H_2 [9] and D_2 [10,11] is the IR active vibron in the *A* phase, with an unexplained strong intensity, although a charge transfer mechanism has been proposed [12]. Observation of this mode in parahydrogen puts restrictions on the phase diagram, in particular, the existence of a critical point reported earlier [13,14]; a critical point was shown not to exist in orthodeuterium [10]. We have found a second strong mode in hydrogen at lower frequencies. This may be very important for understanding the structure and nature of the *A* phases.

The first reported Drude-type measurements on hydrogen were by Mao, Hemley, and Hanfland [4] who made room temperature measurements of the reflectivity to 177 GPa and $\sim 4000 \text{ cm}^{-1}$ and reported direct evidence of metallic behavior based on a rising reflectivity in the near IR for pressures above 150 GPa. Eggert *et al.* [6] measured absorption and reflectivity to much higher pressures (230 GPa) but observed no evidence of metallization. Even though their lowest frequency did not extend to as low a frequency as that of Mao *et al.*, they showed that the analysis of Mao *et al.* had some fundamental inconsistencies. Hanfland, Hemley, and Mao [5] then reported on IR absorption in the same spectral range, again reporting a Drude edge. They again proposed that hydrogen was metallic, revising their previous Drude parameters; they also suggested other possible mechanisms to explain their observed absorption. Silvera [15] showed that their analysis used physically unacceptable values of the index of refraction of hydrogen at high pressures, again bringing the case for metallization into question. Since these results appeared, efforts have been exerted to develop lower energy IR sources to extend these studies. Hanfland *et al.* [16] developed a powerful synchrotron IR source, but evidently were unable to sort out problems of the Drude behavior [17]. Cui, Chen, and Silvera [7] developed a tunable IR source useful to 3000 cm^{-1} and did not observe Drude behavior in deuterium. In order to extend studies of the Drude behavior of samples in diamond anvil cells (DACs) to very low energies we have built a new bench top spectroscopic system which we describe below.

There are two important limitations for Drude spectroscopy in DACs. First and foremost is that the samples are contained in small holes (diameters $\sim 10\text{--}30 \mu\text{m}$) in metallic gaskets so that for wavelengths greater than those of order $10 \mu\text{m}$ the transmission can be severely attenuated due to diffraction by the gasket hole. Second, in order to definitively establish metallic behavior, measurements must be done in the limit that temperature goes to zero, requiring a cryostat, with windows which can also attenuate the radiation. Our cryostat uses CaF_2 windows

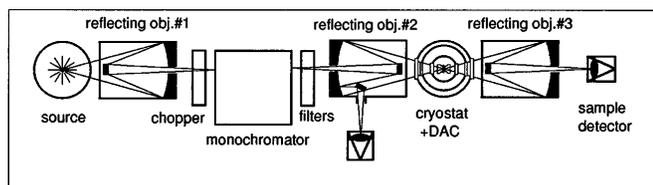


FIG. 1. The optical system for extended IR studies.

which have a long wavelength attenuation cutoff of about $10\ \mu\text{m}$. The spectroscopic system is shown in Fig. 1. The radiation source is a thin walled graphite tube in a 1 atm nitrogen environment, which operates at $\sim 2500\ \text{K}$ (determined from its gray-body spectrum) when heated with a current of about 45 A [18]. This is approximately a factor of 2 hotter than the traditional glowbar sources. The radiation is collected by a large Schwarzschild reflective objective and focused down onto the slits of an ISA HR-320 spectrometer, where it is chopped for detection purposes and filtered to isolate the first order of the grating. A second objective collects this light and focuses it down onto the sample, and a third Schwarzschild collects the transmitted light and images it onto a cooled mercury cadmium telluride detector. A small part of the beam entering the DAC is deflected onto a second reference detector used to normalize out fluctuations of the source. Both detector signals were preamplified and fed into lock-in amplifiers. In order to optimize the Schwarzschild objectives to our system we designed and built them ourselves [19,20]. Since the Drude spectrum does not require high resolution, we used a 50 line/mm grating blazed at $6\ \mu\text{m}$ to enhance our signal, and all spectra shown are low resolution. Although the source has a low intensity per unit frequency as compared to a tunable laser [10], the large bandwidth falling on the detector results in a comparable signal-to-noise ratio. The entire optical system, including the tail of the cryostat, was in a nitrogen atmosphere to eliminate absorption due to water vapor. The spectrometer was computer controlled using a program written in LAB VIEW which sampled spectra at equal intervals in frequency and optimized the signal-to-noise ratio. All data shown are for fixed slit widths.

Three runs were carried out on hydrogen in a DAC at temperatures between 9 and 150 K. The spectra of diamond, shown in Fig. 2, was carefully studied as a function of temperature before loading the samples. Clearly the type II diamonds are superior for long wavelength studies, as the type I have strong impurity absorptions which seriously reduce the transmitted signal in the region of $1000\text{--}1400\ \text{cm}^{-1}$. For frequencies less than $1000\ \text{cm}^{-1}$ the CaF_2 windows do not transmit. Two of the sets of diamonds broke at 128 and 147 GPa and the third at 200 GPa, so that data on the A phase was acquired only with the third set, which was type I. As a result of the low signal-to-noise ratio for the absorption coefficient, we have blanked out data in the $2000\ \text{cm}^{-1}$

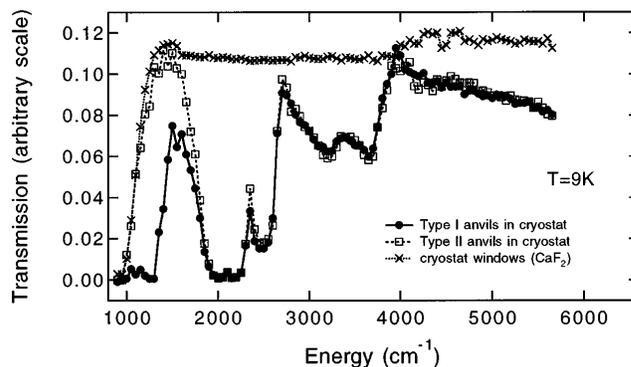


FIG. 2. The transmission spectra of type I and IIa diamonds, as well as CaF_2 cryostat windows.

region, as well as for frequencies less than $1400\ \text{cm}^{-1}$ for the type I diamonds. In the $1400\text{--}1000\ \text{cm}^{-1}$ region there was no systematic increasing absorption in the spectra. All diamonds used had approximately $75\ \mu\text{m}$ diameter central flats, and were double beveled. For the third run, the sample diameter was approximately $30\ \mu\text{m}$. We could only set an upper limit on the sample thickness of less than $8.5\ \mu\text{m}$ at the highest pressure. This was determined from the equation of state of hydrogen and knowledge of the initial thickness. Pressure was determined using the quasihydrostatic ruby scale [21] up to 165 GPa, and the pressure dependence of the IR vibron reported in Ref. [9], thereafter.

Spectra for several pressures, shown in Fig. 3, were normalized to a spectrum at 137 GPa and 9 K, below the A phase pressure. This normalization procedure effectively removes the absorption due to diamond, as described in detail elsewhere [7]. All samples were held at 9 K for a minimum of 24 h before measuring, to ensure that they were completely converted to equilibrium ortho-para concentration, which should be almost 100% para. We observed no Drude edge absorption in our measurements up to 191 GPa. Therefore, our experiment does not support previous conclusions based on optical measurements that hydrogen exhibits metallic behavior in the H-A phase [4,5].

The spectra in Fig. 3 show two strong absorption peaks, one at about $4300\ \text{cm}^{-1}$ and the other at about $1600\ \text{cm}^{-1}$. The pressure dependence of the absorption and the peak frequencies are shown in Fig. 4. The high frequency peak represents absorption due to excitation of a vibron mode. The low frequency peak is somewhat low in frequency to be a vibron and is most likely a phonon. The frequency is consistent with the absorption identified by Hanfland *et al.* [16] as a phonon sideband in hydrogen. Its frequency increases with pressure as might be expected in the quasiharmonic approximation for intermolecular potentials which increase with decreasing lattice constant. An interesting observation [22] is that hydrogen will become atomic metallic when a phonon and vibron of the proper symmetry become degenerate. No evidence of the

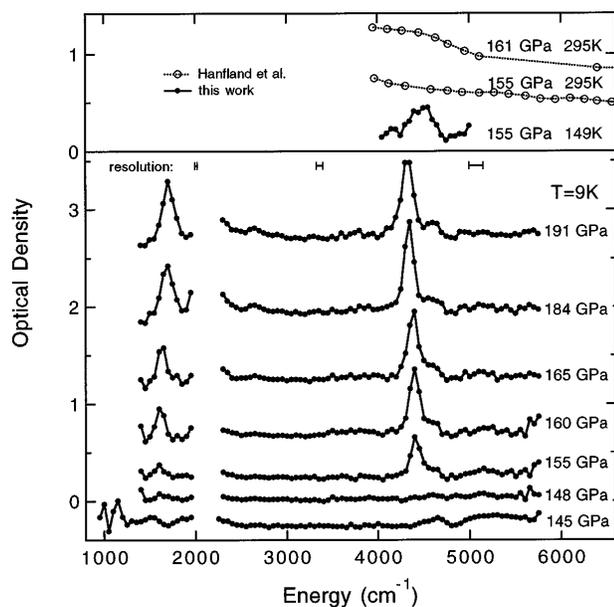


FIG. 3. Spectra of hydrogen at different pressures and temperatures, normalized to a spectrum at 137 GPa. Spectra are vertically displaced for ease of viewing. The lowest curve at 145 GPa is with a type IIa diamond and is normalized to a 100 GPa spectrum. This supports the other data that show there is no low frequency peak below 150 GPa and the new peak must be associated with the hydrogen sample. The curve with open circles is data from Ref. [5].

low frequency peak was found below 150 GPa, so we do not believe that it is associated with hydrogen diffusing into the diamond anvils, resulting in an impurity mode. We note that the integrated intensity for both absorption peaks grows rapidly with pressure. The Raman active phonon (frequency approximately 1000 cm^{-1}) in the A phase observed earlier by Hemley, Mao, and Shu [23] apparently is not affected in intensity or frequency by the transition to the A phase. This observation has been used to argue that the molecular centers remain on an hcp lattice in the A phase. Cui, Chen, and Silvera [11] have shown that from a knowledge of the number of allowed modes, strong statements can be made about the structure of the lattice. This new mode will help in the identification of the structure, but at this time we do not have a structure to propose and are checking on the energy bounds of modes with a dynamical model. We note that recently Tse and Klug [24] have proposed new structures arising from their Car-Parinello molecular dynamics study of hydrogen. They find that at pressures corresponding to the A phase the molecules partition into two types with short bonds and long bonds with a rhombic structure ($Pnma$) having 12 molecules/unit cell. Finally, we note that there appears to be structure on the high frequency side of the 4400 cm^{-1} vibron and possibly another peak in the region of 2700 cm^{-1} . The current run was dedicated mainly to searching for metallic behavior and was carried out at low resolution ($\Delta\nu \geq 50\text{ cm}^{-1}$).

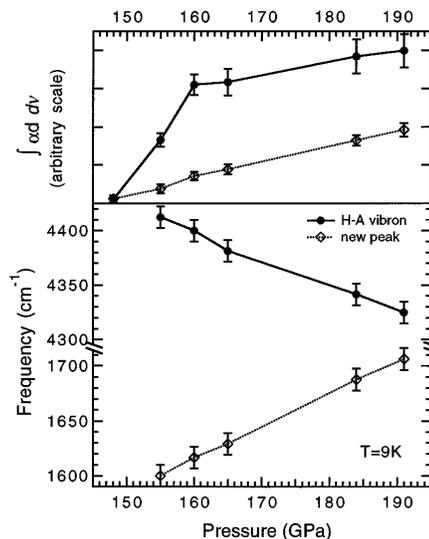


FIG. 4. The pressure dependence of the IR active peak frequencies and integrated intensities. The error bars for the intensity represent 3σ values for the statistical noise. We estimate that the systematic error due to shoulders of the lines could be up to 15%.

We plan to modify our apparatus for higher resolution spectroscopy and study these regions in more detail.

An important result that we have obtained concerns the critical point terminating the hydrogen-A phase line, reported earlier [13,14]. It has been shown that no critical point exists in the D-A phase by Cui *et al.* [10], who suggested that this would also be true for hydrogen. Since an IR active vibron is observed in the H-A phase, it cannot have the hcp structure of the LP phase. Such arguments are only valid for lattices with translational symmetry, so earlier observations of the IR active vibron [9] using mixed (ortho-para) crystals could not be used. We have observed the vibron in pure parahydrogen so that we can now assert that in passing from the LP to the A phase, a phase line must be crossed as the symmetry must change. If only three phases (LP, BSP, and A) exist and meet in a triple point as in deuterium [11] then the H-A line cannot terminate at a critical point.

We made measurements of hydrogen at 155 GPa and temperatures above the transition temperature ($T_t = 104 \pm 8\text{ K}$) of the A phase line (in the LP phase) and still observed the vibron at 4300 cm^{-1} (Fig. 3). If the sample was pure para, then the selection rules forbid this absorption in the LP phase which has the hcp structure. However, this measurement took place several hours after heating up from 77 to 150 K, and the sample converted towards equilibrium (greater than 50% ortho). The explanation for the observed absorption is that the vibron is observed due to an impurity absorption induction mechanism. We suggest that this is responsible for the "Drude" edge reported earlier [4,5] for measurements on hydrogen at room temperature, as the high frequency

edge of the vibron is in the vicinity of the reported Drude behavior. This seems to settle a long standing problem in which other mechanisms were proposed such as the reduction of ruby or the influence of powdered ruby on optical measurements [25,26].

Our conclusion is that there is no experimental evidence that the H-A phase is metallic. Although in the future we can continue these studies to higher pressures, it will be difficult to extend the long wavelength range in search of a Drude edge due to diffraction limits set by gasket hole dimensions. In particular, to achieve higher pressures, smaller holes must be used. Our results are consistent with the A phase of hydrogen being nonmetallic; i.e., the band gap remains open. It may be that with increasing pressure, as the gap narrows, an instability develops. For example, The A phase might be an insulating spin ordered state in which neighboring electron spins are antiferromagnetically coupled. Such instabilities could prevent the formation of metallic molecular hydrogen so that the predicted high pressure atomic lattice would be the only metallic phase. A model such as that of Tse and Klug, or the proposal by Baranowski [27] that the hydrogen lattice forms something similar to LiH, i.e., the hydrogen molecules develop electric dipole moments, should be pursued. The new lattice mode reported here may be useful in understanding the development of the hydrogen lattice at pressures above 150 GPa. Finally, we note that current measurements do not prove that the A phases are not metallic. Such a proof could be made by measuring the static electrical conductivity.

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