Refractive index measurements of solid parahydrogen

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Solid para-H2 is a promising gain medium for stimulated Raman scattering, due to its high number density and narrow Raman linewidth. In preparation for the design of a cw solid hydrogen Raman laser, we have made the first measurements, to our knowledge, of the index of refraction of a solid para-H2 crystal, in the wavelength range of 430–1100 nm. For a crystal stabilized at 4.4 K, this refractive index is measured to be n_{p-H2} = 1.130 ± 0.001 at 514 nm. A slight, but significant, dependence on the final crystal-growth temperature is observed, with higher n_{p-H2} at higher crystal-growth temperatures. Once a crystal is grown, it can be heated up to 10 K with no change in n_{p-H2}. The refractive index varies only slightly over the observed wavelength range, and no significant birefringence was observed.

Our long-term goal is to develop a cw Raman laser based on solid para-H2. The high Raman gain of the solid should permit such a laser to have a considerably lower finesse cavity than the gaseous H2 lasers, thereby making them easier to align and maintain. The high gain of the solid may also facilitate the extension of the cw Raman H2 laser to longer wavelengths, where the stimulated Raman scattering process is less efficient.

To design such a laser, it is essential to minimize Fresnel losses at interfaces inside the laser cavity, in particular between the solid H2 gain medium and the cell windows (typically sapphire) that contain the H2 crystal. The angles of these interfaces can be chosen to be at or near Brewster’s angle for minimal reflective losses, but this requires knowledge of the refractive index of solid para-H2; to our knowledge, this quantity (which we refer to as n_{p-H2}) has not been previously measured. In this Letter, we describe the procedure used independently in our labs in Illinois and Kyoto to generate a uniform para-H2 crystal and to measure n_{p-H2}. The dependence of n_{p-H2} on wavelength and the polarization angle of light, as well as the temperature of the crystal, is also discussed.

Solid para-H2 crystals were grown in a cell (illustrated in Fig. 1) consisting of a 1.27 cm hole bored in a 5.1 cm stainless steel body. One end of the cell was machined at an angle (ϕ = 10.0° in Illinois; ϕ = 20.2° in Kyoto) to induce a deflection in a laser beam propagating through the crystal; the measurement of this deflection enabled the measurement of n_{p-H2}. The ends of the cell were sealed with sapphire windows using indium gaskets. The cell was mounted to an oxygen-free high-conductivity (OFHC) copper plate machined with a small pin that

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protrudes into the cell body (sealed with an indium gasket), to serve as a nucleation point for crystal growth. The OFHC plate in turn was mounted to the thermally isolated stage of a liquid-helium-cooled cryostat.

The temperature of the cell was controlled by adjusting the thermal contact with the cold head by opening a heat switch, and/or by using a resistive heater on the cell. The temperature gradient within the cell was monitored using a germanium resistance thermometer (GRT) mounted on the bottom of the cell and a silicon diode mounted on the thermally isolated stage where the cell rests. The temperature difference between the two sensors was typically less than 1 K, and because the thermal conductivity of solid para-H$_2$ (1.5 W cm$^{-1}$ K$^{-1}$ at 4 K [11]) is so much higher than that of stainless steel (0.003 W cm$^{-1}$ K$^{-1}$ [12]), the H$_2$ crystal would be expected to be at temperature very close to that of the silicon diode. The cell was filled through narrow stainless steel tubing, which passed along the radiation shield of the cryostat before connecting to the cell body.

The crystal was grown with 99.98% pure para-H$_2$ [13] following the pressurized crystal-growth method [14], which is known to yield a transparent single crystal. Para-H$_2$ gas was condensed into the cell at 15–20 K, while the liquid level was watched. Once the cell was filled, the cryostat’s gas line was connected to a small (150 mL) tank and the cell was heated to 30–45 K to boil off the liquid and pressurize the tank. Fresh para-H$_2$ gas was then condensed into the cell, and, finally, pressurized gas from the small tank (∼200 psi in Illinois, ∼290 psi in Kyoto) was applied to the condensed para-H$_2$ liquid. The temperature was slowly lowered to the final temperature over a 1 h period as the crystal grew. The crystallization was initiated from the coldest point (the copper pin at the top of the cell) and the crystal growth was observed as the liquid–solid boundary (crystallizing surface) slowly moved downward. The same procedure was repeated to create crystals with higher final growth temperatures, which required lower backing pressures [15].

Hydrogen’s ability to yield such a large single crystal stems from the fact that solid para-H$_2$ is a quantum crystal, with a “self-annealing” property, similar to solid helium [16]. We observed a similar liquid–solid boundary during crystal growth as in previous studies [14, Fig. 2], and our observation of a single crystallizing surface is strong evidence that a single crystal was in fact formed. In other trial runs (with different crystal-growth procedures, inadequate backing pressure, or impurities in the sample), a single crystallizing surface was not observed: the resulting samples were not completely transparent; laser beams sent through those samples suffered complex scattering patterns, and cracks would result as the temperature dropped, separating individual crystals. With proper care in the crystal-growth process, however, a transparent single crystal always resulted. Previous work has established that high purity para-H$_2$ crystallizes to form a hexagonal close-packed lattice at low temperature and high pressure [15] and that the $c$ axis follows the largest thermal gradient [4, 17]; in the present case this is the vertical axis.

The optical setup used for measurements of $n_{p-H_2}$ in Illinois consisted of three lasers: an argon ion laser with 476, 496, and 514 nm emission; a He–Ne laser with 632 nm emission; and a tunable diode laser at 945 nm. After the crystal was fully grown, the laser light was passed through the crystal. The angle of the deflected beam ($\theta$) was determined by measuring its distance (labeled $v$) from the horizontal at two positions separated by 1.5 m (labeled $h$), as shown in Fig. 1. The beam position was determined by monitoring the voltage of a photodiode as it was translated vertically. The measured beam positions are accurate to within ±0.013 cm, the precision of the micrometer mount used. In Kyoto, a master oscillator power oscillator laser was used to measure $n_{p-H_2}$ at 15 different wavelengths between 430 nm and 1100 nm. In that measurement, the deflected angle ($\theta$) was measured by locating the laser spot (visually) on a screen 6.5 m from the cryostat.

Snell’s law, $n_{p-H_2} \sin(\phi) = n_{vac} \sin(\theta + \phi)$, was used to infer $n_{p-H_2}$. Here, $\phi$ includes both the tilt of the cryostat stage with respect to the incident laser beam as well as the angle of the intentionally tilted window. The dependence of $n_{p-H_2}$ on the polarization angle of the incident laser was measured by inserting a half-wave plate in the laser path prior to the cryostat and changing its angle in increments of 15°. The results are presented in Fig. 2.

The measurements show only a slight dependence of $n_{p-H_2}$ on wavelength. The 6.0 K data, which have the largest wavelength coverage, show that $n_{p-H_2}$ decreases slightly with increasing wavelength up to ∼650 nm and then levels off, becoming consistent with a constant
value of 1.132±0.001. The 4.4 K and 7.5 K data sets are
each consistent with a constant $n_{p-H_2}$, but these data
have sparser wavelength coverage. The constancy of
$n_{p-H_2}$ with wavelength is expected, since para-H$_2$
has no absorptions between the far-IR and the UV.

The inset of Fig. 2 shows how $n_{p-H_2}$ varies with the po-
larization angle, $\alpha$, of the incoming laser beam (at 945 nm
and 4.4 K). Although there is a hint of an increase of $n_{p-H_2}$
with $\alpha$, the trend is not statistically significant, given our
measurement uncertainties; we adopt an upper limit of
0.002 for the magnitude of birefrigence.

The data indicate that $n_{p-H_2}$ increases with the final
temperature of crystal growth. This is surprising, as
the density of solid para-H$_2$ is known [14,15] to decrease
slightly with increasing temperature in this range. One
might therefore anticipate that $n_{p-H_2}$ would decrease
with decreasing density (as the temperature increases),
but our observations show that $n_{p-H_2}$ instead increases.

To test the sensitivity of $n_{p-H_2}$ to the rate of crystal
growth, we grew a crystal at a faster rate, lowering the
temperature to 4.4 K in only 10 min, rather than
1 h. This crystal had a slightly higher $n_{p-H_2}$ (at 514 nm)
of 1.134 ± 0.001, compared with 1.130 ± 0.001 for the
slowly grown crystal. One might expect the slowly grown
crystal to attain a higher density than the quickly grown
crystal, as the former has more time to rearrange its
lattice. These observations are consistent with the other
measurements, in the sense that in both cases $n_{p-H_2}$ in-
creases with decreasing density (due to either higher
growth temperature or faster growth rate).

After crystal growth is complete, raising the tempera-
ture does not change $n_{p-H_2}$. For a crystal stabilized at
a final growth temperature of 4.4 K, we gradually increased
the temperature up to 10 K (in increments of ~0.5 K) and
observed no change in the deflection of the laser. Once
the crystal is completely grown, the lattice cannot ex-
bend because it is completely confined in the cell, and
the constant density leads to a constant $n_{p-H_2}$.

The observed temperature dependence of $n_{p-H_2}$ is
significantly larger than can be accounted for by the mea-
surement uncertainties. For example, in order for the
measured $n_{p-H_2}$ of the 4.4 K crystal to fall within the un-
certainties of the data at 6.0 K, the measured deflection
angle would have to have been mismeasured by 0.14°,
which corresponds to an error in the vertical beam de-
flexion ($\nu$) of 0.23 cm, or 18 times our precision. We
therefore conclude that the surprising inverse depen-
dence of $n_{p-H_2}$ on density is not due to systematic errors
in the measurements, but we cannot offer a physical
explanation of the effect at this time.

In summary, we have measured the refractive index
of solid para-H$_2$ for the first time, to our knowledge.

Measurements were performed for final crystal-growth
temperatures of 4.4, 6.0, and 7.5 K, over a wavelength
range of 430–1100 nm. The refractive index (at 514 nm)
is $n_{p-H_2} = 1.130 ± 0.001$ for a crystal stabilized at 4.4 K
and increases to 1.140 ± 0.001 at 7.5 K. Our measure-
ments suggest that $n_{p-H_2}$ is dependent on the density
of the crystal, with higher values at lower densities. A small
dependence of $n_{p-H_2}$ on wavelength was observed, but no
significant dependence on polarization was seen. These
measurements can be expected to facilitate the develop-
ment of a cw Raman laser using solid para-H$_2$ as the gain
medium, which may ultimately lead to a new widely
tunable and narrow linewidth laser source in the mid-
IR region.

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