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Note

A remeasurement of the 2.4 μm spectrum of $J = 1$ H$_2$ pairs in a parahydrogen crystal☆

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The solid parahydrogen crystal has proven to be an extraordinary matrix medium. The very weak intermolecular interaction with relatively high-zero-point lattice vibration in combination with the small mass of the molecule lead to a highly quantum system in which hydrogen molecules rapidly tunnel between equivalent sites. This tunnelling process is the basis for a powerful self-annealing behavior of the crystal and the exquisitely homogenous crystal lattice. Its homogeneity, weak intermolecular interactions, and large lattice constant make the parahydrogen crystal a nearly ideal matrix medium for high-resolution spectroscopy. Over the past decade, spectra of a variety of simple impurities have been studied in this material and have demonstrated line widths that can be orders of magnitude narrower than their gas phase counterparts, small vibrational matrix shifts (usually <10 cm^{-1}), and nearly free rotation. Such high-resolution investigations have included hydrogenic species (i.e., various isotopomers [1] and nuclear spin modifications of hydrogen [2]), stable neutral molecules (HCl [3], CH$_4$ [4], H$_2$O [5], C$_{60}$ [6], etc.), free radicals (CH$_3$ [7], CH$_3$CH$_2$ [8], etc.), and recently molecular ion clusters (H$_3^+$(H$_2$)$_n$ and H$^-$(H$_2$)$_n$ [9]).

Another benefit of using parahydrogen crystals as a spectroscopic matrix, that is absent from conventional noble gas matrices, is that the electric field of the impurities induces infrared activity in the matrix itself near the natural vibrational band centers of H$_2$ (the strongest being the $v = 1 \leftarrow 0$ at ∼2.4 μm). These spectral features not only reveal additional information about the dopant but also provide information on the condensed phase microscopic interactions and dynamics—properties that are difficult to obtain by other means. Both broad and sharp induced infrared activity near the $v = 1 \leftarrow 0$ band from hydrogenic ion clusters and several non-hydrogenic neutral species have been reported by FTIR and laser studies [3,9–12], but an understanding of these features is still primitive.

When orthohydrogen (o-H$_2$) concentration in excess of ∼0.05% is present in the parahydrogen (p-H$_2$) crystal, an intricate absorption spectrum is produced. This spectrum, which consists of the strong $v = 1 \leftarrow 0$ transition of lone o-H$_2$ at the center of o-H$_2$ pairs which are split into a few hundred lines due to intermolecular interaction, was analyzed in the work by Zhang et al. [2]. Technical limitations of their spectrometer, however, kept them from recording a continuous spectrum. We have recently made improvements to the spectrometer and detection techniques [13,14] and present the re-recorded pair spectrum for the $v = 1 \leftarrow 0$ band in Fig. 1 of this Note.

The parahydrogen crystal was produced by depositing parahydrogen vapor into a 9 cm long, 2 cm inner diameter cylindrical copper cell which is attached to a liquid helium cryostat. The copper cell was sealed by two sapphire windows with indium gaskets. The flow rate of the gas into the cell was controlled to maintain a cell temperature of 10.8 K. Once grown, the crystal was allowed to cool to the liquid helium temperature of 4.2 K. The final crystal was transparent except near the center axis of the cylindrical cell where the crystal was incompletely formed.

Before crystal production, the parahydrogen gas was prepared by flowing commercial-grade hydrogen into a copper vessel filled with APACHE catalyst which had
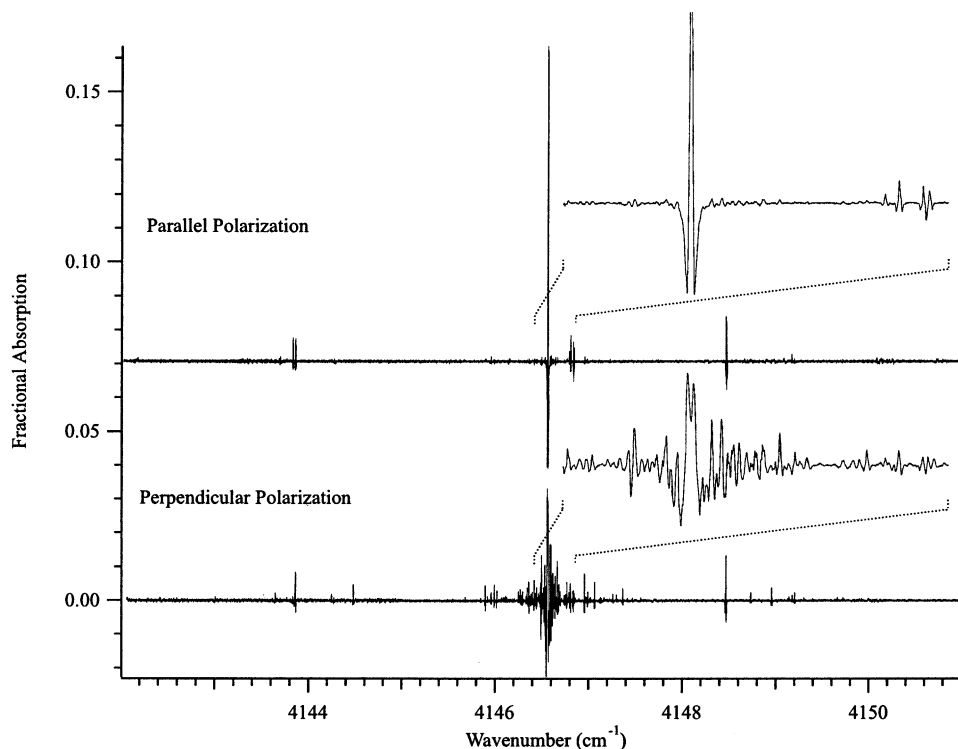

Fig. 1. The absorption spectrum of *ortho*-H_2 pair in a *para*-H_2 crystal with the laser polarization oriented parallel (top) and perpendicular (bottom) to the *c*-axis of the hexagonal close packed (HCP) crystal. The lines were detected with a ∼1 MHz bandwidth color center laser using the tone-burst modulation technique which gives rise to spectral features with a second derivative line shape.

been submerged into liquid helium. After sitting in contact with the catalyst for about an hour at 4.2 K, the copper vessel was raised above the liquid helium level until the vapor pressure of hydrogen above the catalyst was ∼650 Torr. The vapor pressure provides an accurate measure of the converted hydrogen temperature (in this case ∼19.8 K) and allows control of the ortho-to-para-hydrogen ratio. Under our conditions, the sample parahydrogen gas has a 0.2% orthohydrogen fraction [15], with all other impurities being negligible due to condensation within the copper converter. This produces ∼50 ppm of *o*-H_2 pair.

The crystal was probed using a tunable color center laser spectrometer that has recently been automated [13,14]. The laser produces linearly polarized radiation with a bandwidth of ∼1 MHz and about 1 mW of power at 4150 cm^{-1}. For this experiment, the laser was scanned discretely in steps of ∼5 MHz. To increase sensitivity, the tone-burst modulation technique [16] was employed with a tone (sideband) frequency of 105 MHz and a burst frequency of 90 kHz. After the electro-optic phase modulator, the beam was split into two. One of the beams was passed through a half-wave plate and polarizer (for orienting the electric field of the laser relative to the symmetry axis of the crystal) and then through the cell and onto a InSb detector. The other beam was sent directly to a reference de-

tector [11]. The signals from the two detectors were then subtracted in a homemade auto-balancing subtraction circuit [13]. Finally, the subtracted signal was detected in a lock-in amplifier referenced to the burst frequency. The data were recorded with a 1 s time constant, and the fractional noise level (RMS) was better than 2×10^{-4}.

Once we recorded the raw data, the output was frequency calibrated using a combination of two spectrum analyzers and an NO_2 [17] reference spectrum in a manner described elsewhere [13,14]. The calibration accuracy was estimated from the wavenumbers of the NO_2 reference lines to be ∼5×10^{-4} cm^{-1}. A low-frequency baseline drift was present in the absorption signal due to residual amplitude modulation of the electro-optic modulator. This "noise" was easily distinguishable from the sharp spectral features and was subtracted out. The reduced data are plotted in Fig. 1 for the laser's polarization oriented parallel and perpendicular to the hexagonal close packed (HCP) crystal's *c*-axis.

We hope that these data will be helpful as a standard in the continuing study of spectroscopy in parahydrogen, where the orthohydrogen pair spectrum is nearly always present and overlaps with the other impurity induced spectra. While all lines have already been reported in the original work of Zhang et al. [2], the polarization dependence of each of the lines is more pronounced and the

data are cleaner and continuous. The data plotted in the figure are available by contacting the author or from the publisher's website at [www.sciencedirect.com].

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