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Rapid Vapor Deposition of Millimeters Thick Optically Transparent Solid Parahydrogen Samples for Matrix Isolation Spectroscopy

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We report a new method for rapid in-vacuum deposition of millimeters thick solid parahydrogen (pH_2) samples which are remarkable for their excellent optical qualities. Infrared and Raman spectra indicate a very low orthohydrogen content, and a mixed hcp/fcc polycrystalline structure for as-deposited samples. Annealing to 4.5 K converts the samples to polycrystalline hcp. Our approach allows for the efficient trapping and isolation of atomic and molecular dopants by conventional matrix isolation techniques. The increased optical path lengths offer pronounced improvements in the quality of spectroscopic data. We have also observed a variety of novel induced IR absorptions of the pH_2 matrix host itself; transitions induced by the presence of trapped atoms, molecules, and ions.

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The cryogenic solid molecular hydrogens (SMH [1], i.e., H_2 and its isotopomers) are finding increasing acceptance as host materials for matrix isolation spectroscopy (MIS [2]). We recently reviewed the literature on MIS of trapped <u>atomic</u> impurities in SMH [3], as part of our work on condensed phase reactions of energetic species. We have begun to employ spectroscopic characterization of <u>molecular</u> impurities in SMH, a field showing considerable current activity [4-12]. However, certain difficulties in using the SMH as matrix hosts remain to be overcome.

Several advantages of using solid parahydrogen (pH_2 [13]) as a matrix host have been extolled by collaborating groups in Kyoto and Chicago [4,7,8,11,12]. They note the spherical nature of J=0 pH_2, which is preserved in SMH [1]. The absence of permanent electric multipoles contributes to very weak long range intermolecular interactions. This along with the small H_2 mass results in pH_2 being classified as a translational "quantum solid" [1]. Solid pH_2 is seen as an extremely "soft" matrix host, reducing the importance of multiple trapping sites and other inhomogeneities in a guest molecule's environment [11]. Furthermore, weak guest-host interactions and the high symmetry (D_{3h}) of the single substitutional trapping site lead to: quasi-free rotation and vibration of impurities such as D_2 [4] and CH_4 [11], to long impurity excited state lifetimes, and hence to very sharp spectroscopic features. High resolution spectra of the $Q_1(0)$ transition of D_2 in pH_2 show linewidths of less than 10 MHz (0.0003 cm^{-1}) [4]. Thus, pH_2 shows promise as a nearly ideal, almost non-perturbing host for high resolution MIS studies.

However, isolating spectroscopically useful quantities of chemically interesting impurities in solid pH_2 has proven problematic. Thick transparent pH_2 crystals can be prepared by freezing the liquid [14] through the triple point temperature (T_{tp}); however, few impurities (besides Ne [15] and the other hydrogens) are retained at over a few parts-per-million (PPM) levels. On the other extreme, the MIS approach of slow vapor deposition onto a substrate below $\approx$ 0.3 T_{tp} can provide thin film SMH samples containing isolated impurities at and above the 1000 PPM level [3]. Unfortunately, such vapor deposited SMH are notorious for exhibiting strong optical scattering [16] and must be kept fairly thin (below ~ 100 μm) for absorption studies, even in the infrared region [9]. Reverse sublimation of pH_2 gas in an enclosed cell at T $\approx$ 0.5 T_{tp} produces optically transparent solids [4,11,17], but impurity concentrations must be kept well below 100 PPM to avoid aggregation [12,18]. Related techniques for rapidly condensing rare gas and N_2 solids in <u>semi-enclosed</u> cells also produce large
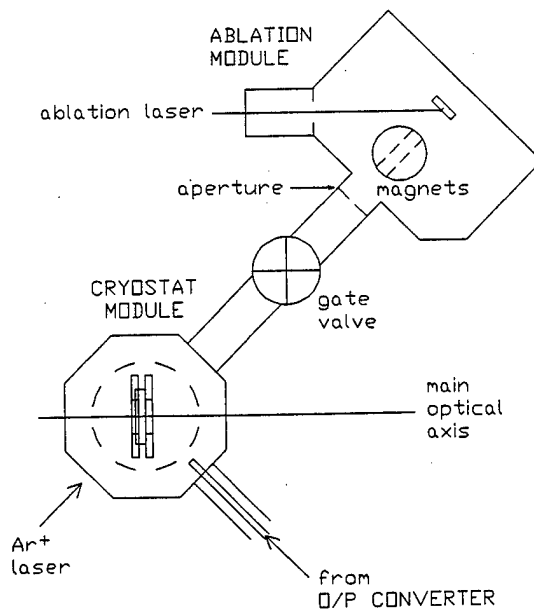

Figure 1. Experimental diagram.

optically transparent samples [19-22]. Impurity isolation in these heavier hosts is easier than in pH$_2$, and dopant concentrations approaching 1000 PPM have been demonstrated [19,21]; however, some guest/host combinations exhibit extensive clustering even at 20 PPM concentrations [20].

In what follows, we describe the production of thick, optically transparent, doped pH$_2$ solids by a modification to the standard MIS substrate-in-vacuum vapor deposition scheme. Our approach offers the compelling advantage of compatibility with most existing impurity doping methods, greatly enhancing its versatility and utility. The resulting large dopant concentrations, millimeters long clear optical paths, and desirable properties of pH$_2$ as a matrix host, lead to a pronounced improvement in the quality of the obtained spectroscopic data. We focus here on the spectroscopic determination of the microscopic structures of our pH$_2$ hosts, and on briefly demonstrating some of the advantages and novel aspects of performing MIS in such samples. Detailed presentations of our techniques and results will appear in future publications.

Figure 1 shows a schematic of our experimental apparatus. Solid pH$_2$ samples are deposited in the cryostat module on a BaF$_2$ substrate cooled by a liquid helium (lHe) bath cryostat. We report the temperature of the flange clamping the BaF$_2$ window to the main substrate holder as the "substrate temperature," T_{sub}, with an estimated uncertainty of $\pm$ 0.2 K. All thermal connections are made with 0.1 mm thick indium foil or conductive epoxy. The sample region in surrounded by a liquid nitrogen cooled aluminum radiation shield which has openings for sample

preparation and optical access. T_{sub} typically bottoms out $\approx$ 0.2 K higher than the cold tip temperature, indicating some minor radiative heating.

Our o/p H$_2$ converter consists of an 1/8 inch OD by 1.5 m long copper tube packed with 1.4 g of APACHI catalyst [1], wound and potted with conductive epoxy onto a copper bobbin which can be cooled to below 10 K by a closed-cycle cryostat. At 15 K, continuous H$_2$ inlet flow rates (Φ_{H2}) can exceed 1 mol/hr, yielding a flow of pre-cooled 99.99% pH$_2$. The cold pH$_2$ is delivered to the substrate through a thin wall brass tube supported near its open end by a room temperature polymer centering ring which makes only loose "knife edge" contact. We do not monitor the temperature of the brass tube, or of the pH$_2$ gas flow.

Solid thickness growth rates (R_{sol}) are limited to < 1 cm/hr by the pumping speed of the small turbomolecular pump which maintains the cryogenic thermal isolation vacuum. The uncondensed H$_2$ results in an additional complication: the deposition of a second solid H$_2$ film on the back side of the BaF$_2$ substrate, amounting to 8.7($\pm$0.5)% of the main front side sample thickness. This front:back thickness ratio, and the total (front + back sides) sample growth efficiency of 64($\pm$5) mm/mol, remain constant over a Φ_{H2} range of 10 to 300 mmol/hr.

Figure 1 also depicts our laser ablation dopant source [23]. The ablation module includes a pair of removable magnets which can eliminate charged species from the ablated beam. For depositions of volatile dopants, such as Xe, CO, N$_2$, and CH$_3$OH, the ablation module is replaced by a copper inlet tube connected to a separate gas handling manifold.

UV and FTIR absorption, and Raman scattering spectra, are obtained along the main optical axis. The $\approx$ 100 mW Ar$^+$ ion laser beam is focused into the pH$_2$ sample at an angle through the BaF$_2$ substrate. Wavelength calibration of the Rayleigh and Raman scattered light is done vs. a Th/Ne lamp. All diagnostics simultaneously probe both front and back side H$_2$ samples. To accommodate the UV and IR diagnostics, the apparatus resides inside a 0.5 m^3 polycarbonate box purged with a constant flow of dry N$_2$ gas.

pH$_2$ matrices deposited at conventional MIS host gas flow rates of ~ 1 mmol/hr ($R_{sol} \approx$ 0.3 μm/min) and T_{sub} = 1.9 K exhibit significant optical scattering (e.g., transmission losses of 20% at λ = 2.0 μm from a 50 μm film [9]). Figure 2 shows the IR absorption spectrum of a 6 mm thick pure pH$_2$ sample deposited at T_{sub} = 2.9 K and Φ_{H2} = 190 mmol/hr ($R_{sol} \approx$ 50 μm/min); the spectrum is presented without any baseline correction. Utilizing $\Phi_{H2} \approx$ 50 mmol/hr ($R_{sol} \approx$ 13 μm/min) and o/p converter temperatures between 28 and 135 K, we have also produced beautifully transparent $\approx$ 1 mm thick solids at T_{sub} = 2.0 to 2.3 K with oH$_2$ concentrations ranging from 2 to 70%. Thus, the use of pure pH$_2$ is not a prerequisite to producing thick solids of exceptional optical clarity.
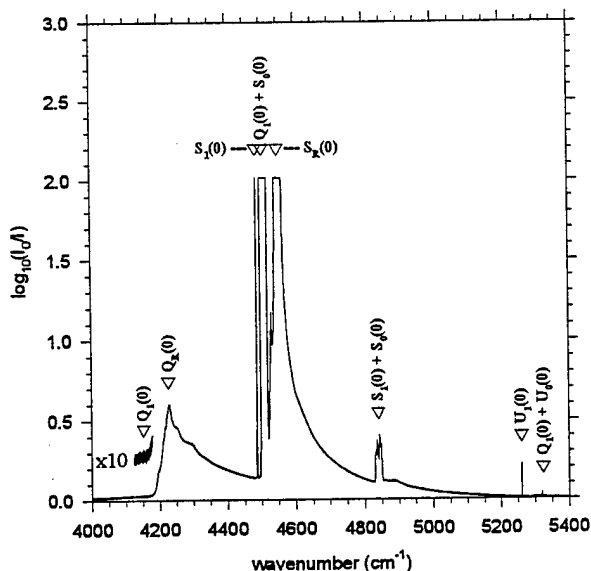

Figure 2. IR absorption spectrum of a 6 mm thick pure pH$_2$ sample. During the deposition T_{sub} rose from 1.9 K to 2.9 K. The spectrum was taken at T_{sub} = 2.2 K, and is presented at 0.15 cm^{-1} FWHM resolution. Non-observation of the Q$_1$(0) transition at 4153 cm^{-1} demonstrates the absence of oH$_2$ impurities, and that the microscopic crystal structure is not amorphous or porous.
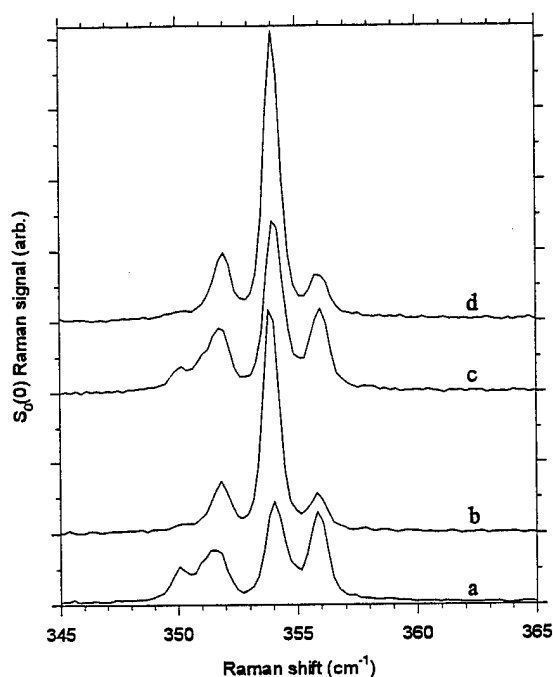
Figure 3. Raman scattering spectra of two pure pH_2 samples. Trace (a) is for a 6 mm thick sample deposited at $\Phi_{H_2} = 200$ mmol/hr ($R_{sol} \approx 50$ μm/min), during which T_{sub} rose from 2.1 K to 3.1 K; the spectrum was taken at $T_{sub} = 2.4$ K. Trace (b) is for the same sample warmed to 4.5 K. Trace (c) is for a 4.5 mm thick sample deposited at $\Phi_{H_2} = 290$ mmol/hr ($R_{sol} \approx 75$ μm/min), during which T_{sub} rose from 2.1 K to 3.3 K; the spectrum was taken at $T_{sub} = 2.4$ K. Trace (d) is for that sample warmed to 4.5 K. The annealed spectra indicate an hcp microscopic structure, while the extra peak at 350 cm^{-1} indicates a mixed hcp/fcc structure.

IR activity in the homonuclear diatomic H_2 molecules in SMH arises from intermolecular interactions in the condensed phase environment [24,25]. In pure solid pH_2, the absorption spectrum depends upon the symmetries of the sites occupied by the pH_2 molecules. More specifically: observation of the $S_1(0)$ absorption near 4485 cm^{-1} demands the absence of inversion symmetry, while non-observation of the $Q_1(0)$ absorption near 4150 cm^{-1} demands that the sum of the vectors connecting each H_2 molecule with all of its nearest neighbors vanishes [24].

Likely structures for our pH_2 samples are close-packed solids, which differ in the stacking sequence of close-packed planes. We consider: hexagonal close-packed (hcp), face-centered cubic (fcc), and random-stacked. Given these choices, figure 2 requires that at least some pH_2 molecules reside in hcp or random-stacked regions. The absence of the $Q_1(0)$ line eliminates amorphous and porous structures, however fcc regions may also be present.

Figure 3 shows Raman scattering spectra of two different as-deposited and annealed pH_2 samples. These spectra are in excellent agreement with those of Collins, Unites, Mapoles, and Bernat [17]. The "triplet" lineshape pattern, obtained by warming our samples to 4.5 K (traces b and d), matches the known Raman spectrum of hcp solid
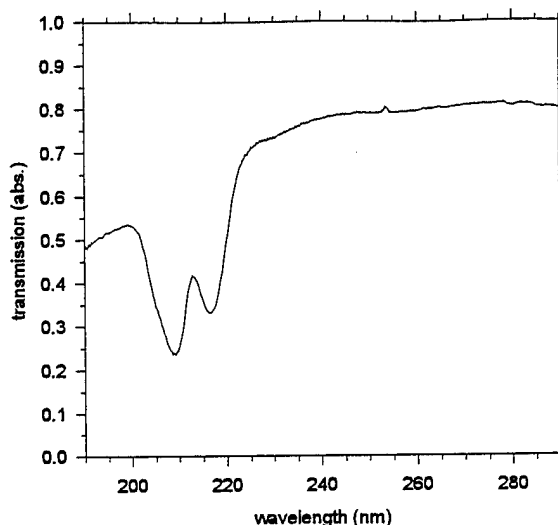

Figure 4. UV transmission spectrum of 1 mm thick B/pH_2 sample. The sample was prepared by laser ablation of solid boron with: $T_{sub} = 2.3$ K, 308 nm ablation laser wavelength, ablation laser intensity = 9x10^7 W/cm^2, 110 mJ/pulse, 10 Hz repetition rate, 60 minute B deposition time, $\Phi_{H_2} \approx 55$ mmol/hr ($R_{sol} \approx 15$ μm/min). The spectrum was acquired at $T_{sub} = 2.1$ K.

pH_2 [17,26]. The quartet pattern observed for the as-deposited samples indicates a mixture of hcp and fcc, with the low-energy shifted peak of the fcc doublet appearing at 350 cm^{-1} [17].

The Raman spectrum of the as-deposited sample produced at the higher H_2 flow rate (trace c) more closely resembles the two annealed spectra than the more slowly deposited sample depicted in trace a. At these high H_2 flow rates, T_{sub} rises by ≈ 1 K during a deposition. We have used temperature reversible changes in the absorption spectrum of CO molecules in pH_2 as a "molecular thermometer" to detect additional bulk pH_2 temperature increases of ≈ 1 K during similar depositions. Thus, we estimate the actual deposition temperature to be ≈ 4 K. We speculate that the higher deposition rates and accompanying higher temperatures allow for "self-annealing" of the accreting surface of the sample during deposition, enhancing the formation of the more stable hcp phase.

We prepare our pH_2 samples by vapor deposition to allow for the incorporation of isolated dopants. Figure 4 shows the UV transmission spectrum of a 1 mm thick pH_2 sample doped by laser ablation of solid boron. We have tentatively assigned the broad absorptions centered at 209 and 217 nm to isolated B atoms [3]. This spectrum too is presented without any corrections for optical scattering losses, and demonstrates the suitability of these pH_2 samples for absorption spectroscopy out to the vacuum UV region. This spectrum shows a vast improvement in signal:noise ratio over our previous efforts [3], of great value to our ongoing effort to prove conclusively the trapping of B atoms in pH_2.

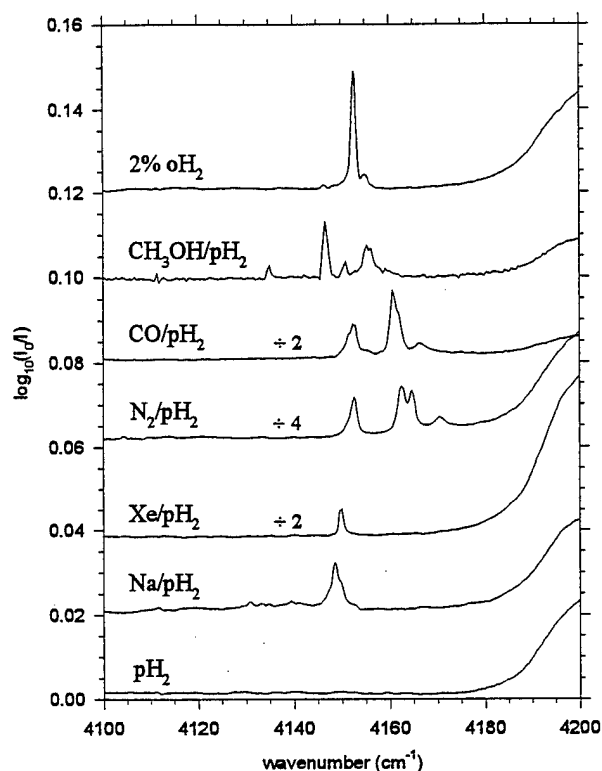In addition to yielding improved spectra of dopant

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Figure 5. Neutral-dopant induced H_2 IR absorptions at T $\approx$ 2 K. All samples are $\approx$ 1 mm thick except for the Xe doped sample which is 3 mm thick. Estimated dopant concentrations range from 100 to 1000 PPM. The Na/pH$_2$ sample was prepared by laser ablation with the ion rejection magnets in place.

species, the increased optical path lengths reveal the weak IR activity induced by the dopant species in the solid pH$_2$ host itself. Perhaps the most familiar example of this dopant-induced IR activity is due to oH$_2$ impurities in pH$_2$ [14], as shown in figure 5. This effect is absent in rare gas matrices, but is a topic of current interest in doped N$_2$ solids [21,22,27]. Figure 5 also shows IR absorptions induced by other neutral dopants. The complexity of the spectral pattern seems to increase as the dopant changes from atomic to diatomic to polyatomic, perhaps reflecting an increase in the number of dissimilar H$_2$ molecular environments around the dopant. We have also observed more strongly red-shifted IR features induced by charged dopants. We believe this induced IR activity provides complementary spectroscopic information to the dopant absorptions, a combination which will be key to the quantitative characterization of microscopic trapping site structures.

We hope that the new possibilities for MIS in pH$_2$ hosts enabled by our new sample preparation technique will encourage its adoption by others. We gratefully acknowledge numerous valuable discussions with our colleagues in the US Air Force High Energy Density Matter program, and the constructive criticisms of our IR data offered by Dr. G.W. Collins and Prof. W.C. Stwalley which prompted our Raman experiments.

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