### REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR PRS (In-House Publication)
FROM: PROI (TI) (STINFO) 11 April 2000

Fajardo, Mario and Tam, Simon, “High Resolution Infrared spectroscopy in Doped Parahydrogen (pH₂) Solids: COpH₂ – a Molecular Thermometer”

Cryocrystals 2000 Conference (Szkolarska Poreba, Poland, 28 Jul – 4 Aug 2000) (Statement A)
(Submission Deadline: 10 May 00)

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APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL Date
Technical Advisor
Propulsion Science and Advanced Concepts Division
High Resolution Infrared Spectroscopy in Doped Parahydrogen (pH$_2$) Solids:
CO/pH$_2$ -- a Molecular Thermometer

Mario E. Fajardo and Simon Tam
U.S. Air Force Research Laboratory, Propulsion Directorate
AFRL/PRSP, Bldg. 8451, Edwards AFB, CA 93524-7680, USA

The phenomenon of high resolution (Δν/ν $\sim 10^{-6}$) infrared (IR) matrix isolation spectroscopy in
cryogenic parahydrogen (pH$_2$) solids was first demonstrated by Oka and co-workers at the U. of
Chicago [1], and subsequently extended to more general dopant species in collaboration with
Momose, Shida and co-workers at Kyoto U. [2]. Both groups prepare doped pH$_2$ solids by
condensing gas mixtures in an enclosed cell at T = 8 K, producing centimeters-thick, beautifully
transparent, hexagonal-close-packed (hcp) polycrystalline solids. To date, concentrations of
chemically interesting dopants isolated by this method have been limited to below $\sim$ 1 PPM.

We have developed an alternative doped solid pH$_2$ preparation technique based on rapid vapor
deposition of precooled pH$_2$ gas onto a substrate-in-vacuum at T = 2 K [3,4]. The resulting
millimeters-thick samples are remarkably transparent, even capable of escaping casual visual
detection; in sharp contrast to previously described “completely opaque brown-black” vapor
deposited hydrogen solids [5]. Our co-deposition geometry enables us to trap dopant species
produced by a wide variety of methods, with excellent isolation efficiencies even at dopant
concentrations exceeding 100 PPM. The excellent optical properties of our samples permit their
spectroscopic interrogation at wavelengths from the vacuum ultraviolet to the mid-IR. The long
useful pathlengths enable the detection of low concentration or weakly absorbing species.

A recent collaborative study comparing the spectroscopy of CH$_4$ doped pH$_2$ solids produced by
the two sample preparation methods demonstrated the suitability of the rapid vapor deposited
solids as hosts for high resolution IR absorption spectroscopy [6], and confirmed our previous
determination of a mixed face-centered-cubic (fcc) and hcp polycrystalline structure for the as-
deposited solids [3]. Annealing of these samples to T = 5 K results in the nearly complete and
irreversible conversion of the fcc regions to hcp. In contrast, spectra of C$_{60}$ doped pH$_2$ solids
indicate that similar temperature cycling of these samples does not eliminate the fcc regions [7].
We conjecture that the multi-substitutional sites occupied by the large C$_{60}$ dopant molecules
intrude into adjacent close-packed planes, precluding their relative slipping motion and thus the
fcc to hcp conversion process.

While we are making steady progress in applying spectroscopic techniques to determine the
microscopic structures of our doped rapid vapor deposited samples, we have only recently begun
our efforts to understand their bulk (e.g. mechanical strength, thermal transport) properties. We
note that our apparatus is configured to facilitate sample production and optical access, as shown
in the Figure. The attendant numerous openings in the liquid nitrogen cooled radiation shield
result in radiative heat loads on the sample which are difficult to quantify. Despite this
limitation, we have performed a series of spectroscopic experiments designed to probe bulk
temperature changes in the pH$_2$ solids during the rapid vapor deposition process.

mario_fajardo@ple.af.mil

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We utilize reversible temperature dependent changes in the IR absorption spectrum of CO molecules isolated in solid pH₂ as a "molecular thermometer." High-resolution spectra are not required for this technique; an instrumental resolution of \(\approx 1 \text{ cm}^{-1}\) FWHM is optimum. The advantage of such a thermometer is that the rotational degrees of freedom of the CO molecules are certain to be in thermal equilibrium with the pH₂ solid; the difficulties come in obtaining an accurate absolute calibration.

The intensity of an isolated absorption feature near 2135 cm\(^{-1}\) shows a monotonic increase with temperature over the 2 to 5 K range. We estimate that the thermally populated initial state of this transition is \(\approx 8\) K above the ground state of CO/pH₂. During the deposition of \(\approx 100\) PPM CO/pH₂ samples, we detect temperature gradients \(\approx 10\) K/cm in \(\approx 0.1\) cm-thick samples subjected to heat loads \(\approx 10\) mW/cm\(^2\). The resulting estimated thermal conductivity is \(2(\pm 1)\) mW/cm-K, averaged over the 2 to 5 K region. This value is about three orders of magnitude lower than the thermal conductivity of single crystal solid pH₂, and more than an order of magnitude lower than previously measured for pH₂ solids doped with 100 PPM concentrations of heavy impurities [8]. We attribute this abnormally low thermal conductivity to the previously determined mixed hcp/fcc structure of the rapid vapor deposited solids.

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**Experimental Schematic**

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