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Production and characterization of para-hydrogen gas for matrix isolation infrared spectroscopy

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ABSTRACT

Normal hydrogen (n-H_2) has 3:1 ortho/para ratio and the production of enriched para-hydrogen (p-H_2) from normal hydrogen is useful for many applications including matrix isolation experiments. In this paper, we describe the design, development and fabrication of the ortho-para converter that is capable of producing enriched p-H_2. The p-H_2 thus produced was probed using infrared and Raman techniques. Using infrared measurement, the thickness and the purity of the p-H_2 matrix were determined. The purity of p-H_2 was determined to be >99%. Matrix isolation infrared spectra of trimethylphosphate (TMP) and acetylene (C_2H_2) were studied in p-H_2 and n-H_2 matrices and the results were compared with the conventional inert matrices.

1. Introduction

The production of para hydrogen assumes significance (p-H_2) due to its wide variety of uses in several experimental techniques. To name a few, p-H_2 is used in nuclear magnetic resonance (NMR) technique to enhance the signal intensity, in matrix isolation spectroscopy as a matrix material and in the superfluidity studies [1–6]. Matrix isolation technique (MI) is a well known method of isolating the molecules of interest in a rare gas and probe them using a variety of techniques [7]. The use of solid molecular hydrogens (H_2, D_2 and HD) as matrix below 4 K is well known and it is being extensively investigated [8–11]. Solid p-H_2 as a matrix host has several advantages over conventional rare gas solids [12–17]. The ground state of p-H_2 molecule is spherically symmetric with all molecules in the J = 0 rotational state. As a result, the interaction between the guest molecules and host matrix (p-H_2) is greatly minimized and thus the spectra of the guest molecules are unusually sharp in this host. The crystal structure of solid p-H_2 is a pure hexagonal-closed pack (hcp), which makes the optical spectra simple whereas the crystal structures of Ne and Ar matrices consist of both hcp and face-centered cubic (fcc) structures, which results in broadening of the spectra. Furthermore, p-H_2 solid has large amplitude of zero-point lattice vibration, which is characteristic of a quantum crystal. The quantum nature of the solid hydrogen is well suited for matrix isolation spectroscopy as it provides more free space for guest molecules compared to other matrices. Because of the large amplitude of zero-point lattice vibration of the solid p-H_2, multiple trapping sites and crystal defects around the guest molecules are expected to get repaired automatically. This self repairing nature of the solid p-H_2 makes the environment around the guest molecule homogeneous. In addition, the large lattice constant of solid p-H_2 makes the interaction between the guest and the host molecules weak and as a result, the life time of the excited states of the guest molecule in solid p-H_2 becomes longer. This could be the main reason for the relatively sharper spectra of the guest molecules in solid p-H_2 matrix when compared to other solid matrices.

Eventhough there are multitudinous advantages that make p-H_2 as an attractive and promising matrix material, it is a real challenge to prepare pure p-H_2 gas from n-H_2. Normal hydrogen contains 75% o-H_2 and 25% p-H_2. In order to prepare pure p-H_2 > 99%, the o-H_2 is to be converted to p-H_2. There are several methods available for the preparation of pure p-H_2 [10,12,16,18–24]. Tam and Fajardo constructed and operated a catalyst based device, which they used for pre-cooling and equilibrating the o/p composition of a hydrogen gas flow. They used rapid vapor deposition technique (flow rate of ~290 mmol/h) and could get millimeter thick transparent solid p-H_2 with a residual o-H_2 < 0.01% [16]. The enclosed cell method

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developed by Oka condensed the p-H_2 gas prepared along with the guest molecules in an enclosed cell maintained at ~8 K to form transparent crystalline p-H_2 of length 3–12 cm within 2 h [12]. Andrews and Wang showed a simple method for condensing and producing pure p-H_2 by converting the hydrogen gas over a catalyst in a dipstick tube immersed in the liquid helium [4]. Lee et al. used pulse-deposition method using closed-cycle cryostat to prepare p-H_2 matrix [23]. Momose et al. designed and constructed o/p converter, which is capable of producing a wide range of p-H_2 enrichments at a flow rate of up to 0.4 SLM (standard liters per minute). They also discussed the storage of p-H_2 and its back conversion rates and the various techniques involved in quantifying the enrichment [24]. In this work, the design, development and fabrication of the o-p converter (similar to the converter designed by Momose et al.) in our laboratory is described. Raman and Infrared techniques were used to characterize and quantify the p-H_2 enrichment.

Organic phosphates are used as extractants in a number of solvent extraction processes and it also serves as a model system in understanding the biological processes. To understand the extraction chemistry in nuclear industry, it is essential to first understand the conformational preferences of organic phosphates. Earlier, the lower homologue of organic phosphate, trimethyl phosphate (TMP), was studied for its conformations. We have reported earlier that TMP exists in two different conformations, having C_3 ($G^{\pm}G^{\pm}G^{\pm}$) and C_1 ($G^{\pm}G^{\pm}T$) symmetries; with the C_3 conformer being lower in energy relative to the C_1 [25,26]. Reva et al. reported the conformer interconversion of higher energy C_1 conformer to ground state C_3 in xenon matrix [27].

Acetylene and its multimers are important species in interstellar medium and their gas phase spectra are extensively studied [28].

Quantum solid nature of p-H_2 facilitates the rotation of the guest molecules more easily in this matrix than in other inert gas matrices. For example, Lee et al. observed internal rotation of methanol CH_3OH in solid p-H_2 solid but not in solid Ne and Ar [29]. It was thought interesting to study the TMP and C_2H_2 molecules in solid p-H_2 to find out whether these molecules can rotate in the p-H_2 solid and in case of TMP whether internal rotation in p-H_2 matrix leads to conformational interconversion.

2. Experimental

2.1. Design, development and fabrication of ortho/para (o/p) converter

A closed cycle helium cryostat (RDK408D2, Sumitomo Industries) is suitably modified to produce pure p-H_2 gas. Fig. 1 shows the cold head section of the cryostat which holds a copper bobbin. The copper bobbin with a spiral groove was fabricated from a solid piece of oxygen free high conductivity copper (OFHC) block and machined. The total length of the copper bobbin is 105 mm and the depth of the groove is 5.0 mm. Around six loops of ¼" copper tube

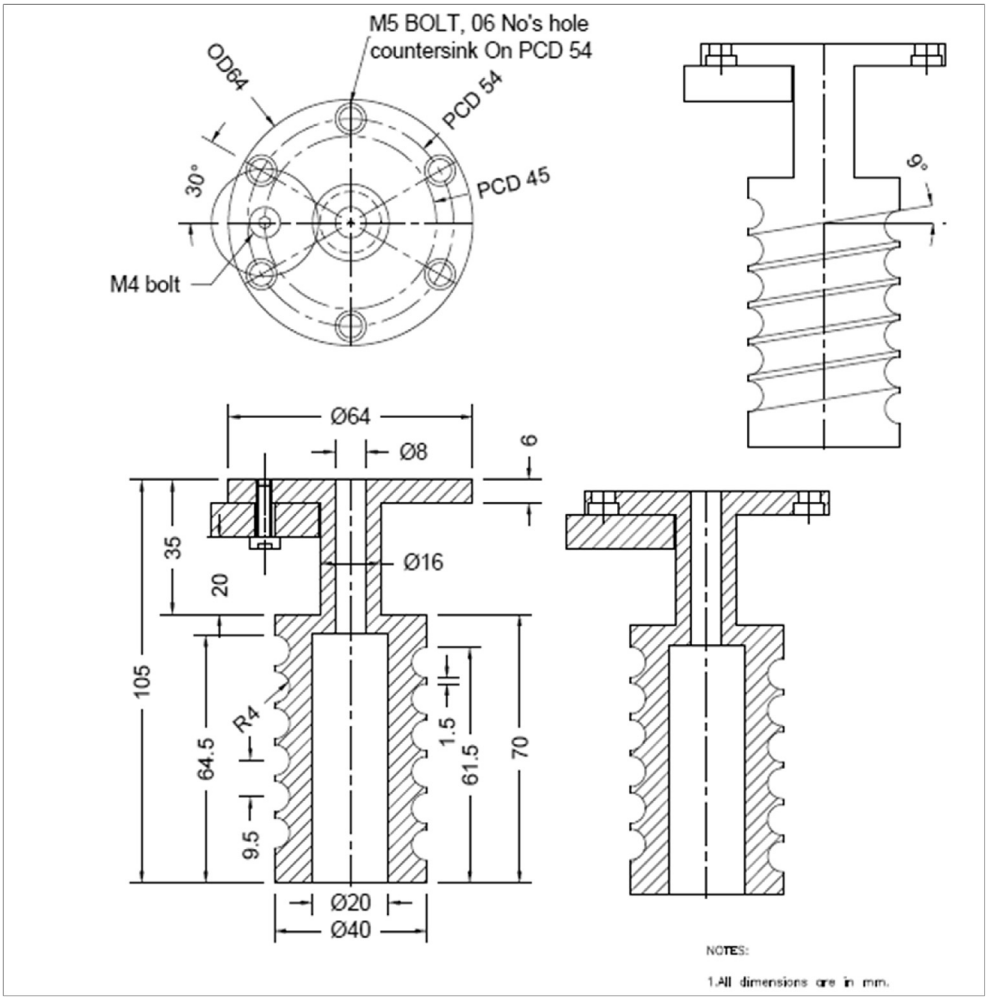

Fig. 1. Design of the copper bobbin.