Magnetically Coupled Loading Chamber and Apparatus for In Situ MAS NMR:

Operating Under Either High or Low Pressure

Jian Zhi Hu, Nicholas R. Jaegers, Mary Y. Hu, and Mark R. Townsend

Outline of the Invention Disclosure

1. **Claims:**
2. **Drawings/Figures**
3. **Detailed Description of the invention: Device/Figures:**

1. Claims:

1. A loading device that is capable of operating for both low and high pressure comprises of a holder for statically mounting an in situ rotor therein and a magnetically coupled rotation member that engages and rotates the sealing cap of the NMR rotor, providing sealing or opening of the cap in-situ while the rotor remains statically positioned in said device.

2. The loading and reaction device of claim 1, wherein the rotation member is a magnetically-coupled driver with a cylindrical magnet located inside the sealed chamber that maintains either high or low constant pressure and another set of disconnected magnets placed symmetrically around the circumference outside the sealed chamber. The outside magnet sets, varying between 2 to 12 are at ambient pressure. When the outside magnet sets are manually rotated, the induced magnetic force or toque in the inside chamber cylindrical magnet makes the inside magnet rotate. An engagement mechanism of either a socket or a screw type is solidly attached to the inside cylindrical magnet that facilitates the sealing or opening of the in situ MAS NMR rotor for charging a controlled amount of pressure.

3. Rotor Holder and the said engagement mechanisms are of modular design and adapted to various in situ rotor sizes, i.e., from 1.2 to 9.5 mm.

4. The magnetically coupled loading and reaction device including at least one fluid port operatively coupled for introducing one or more fluids independently into the sample cell within the NMR rotor and monitoring and controlling the internal pressure and temperature.

5. A method for sealing the in situ NMR rotor, comprising the steps of introducing a quantity of sample within the in situ NMR rotor positioned within a low or high-pressure loading and reaction device, and sealing said sample within said in situ NMR rotor and reaction device at said pressure and temperature with a rotor cap operatively coupled to said sample cell by turning same with a magnetically-coupled rotation system, thereby sealing said valve.

6. The method of claim 4, wherein sealing includes a pressure within the in situ NMR rotor less than

ambient pressure, from ambient to 10^{-6} torr, or at significantly elevated pressures, from 1 atm to 1000 atm, and at variable temperatures from liquid N2 to 300 °C.

2. Drawings

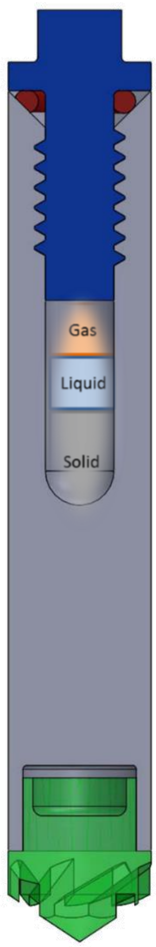

Exhibit A. Diagram of in situ NMR rotor depicting three-phase sample retention.

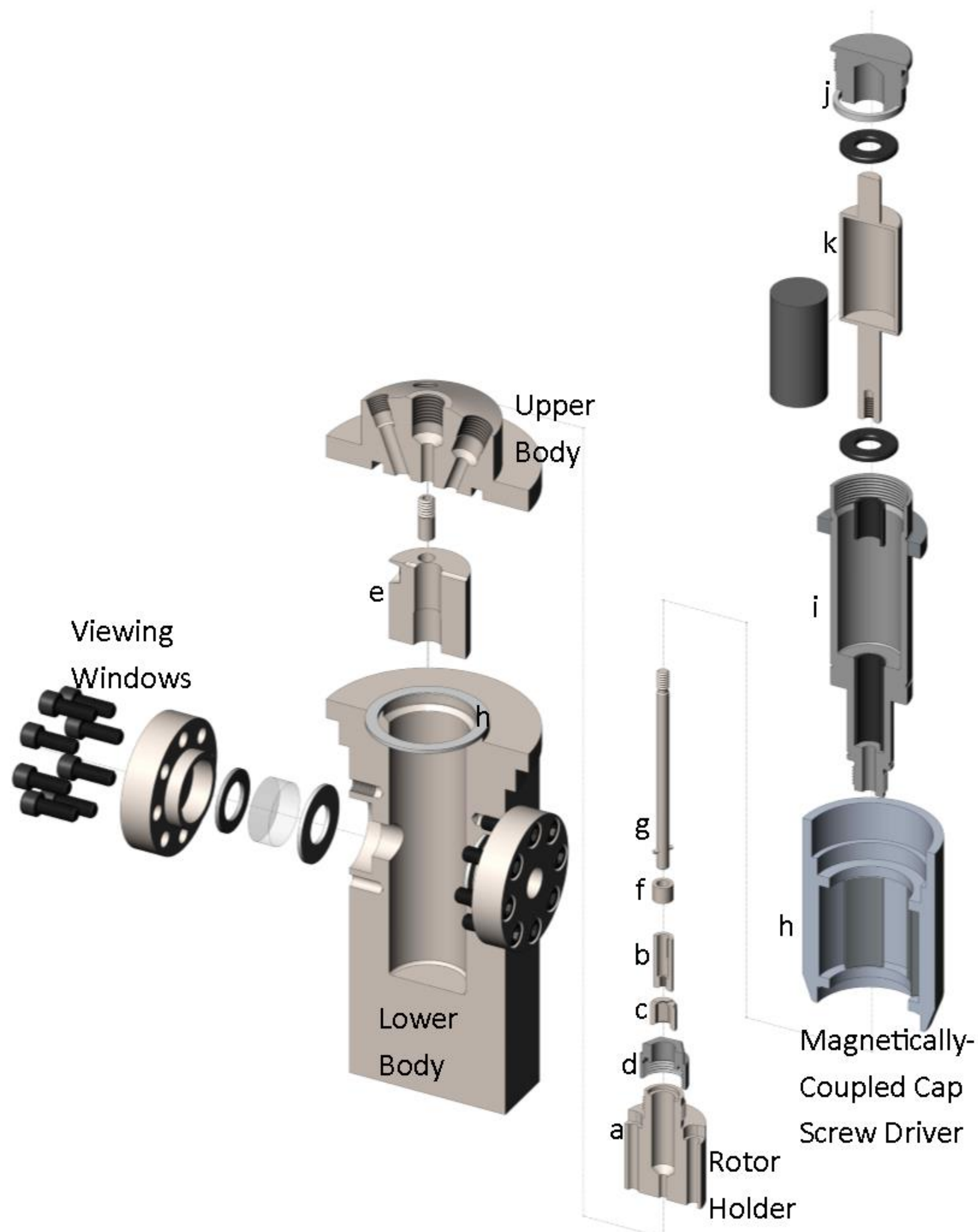

Exhibit B. Schematic of the magnetically-coupled high/low pressure NMR loading vessel.

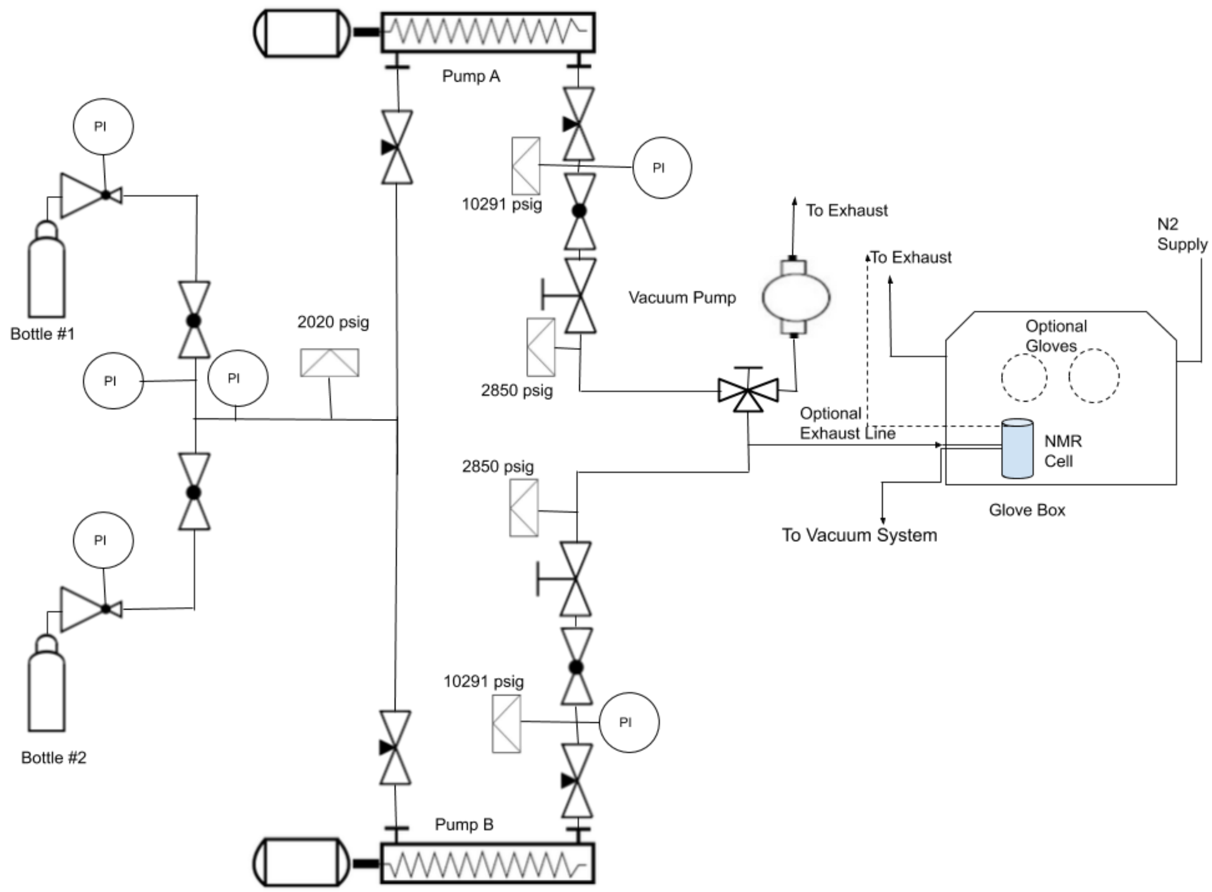

Exhibit C. Schematic of a representative high-pressure delivery aparatus.

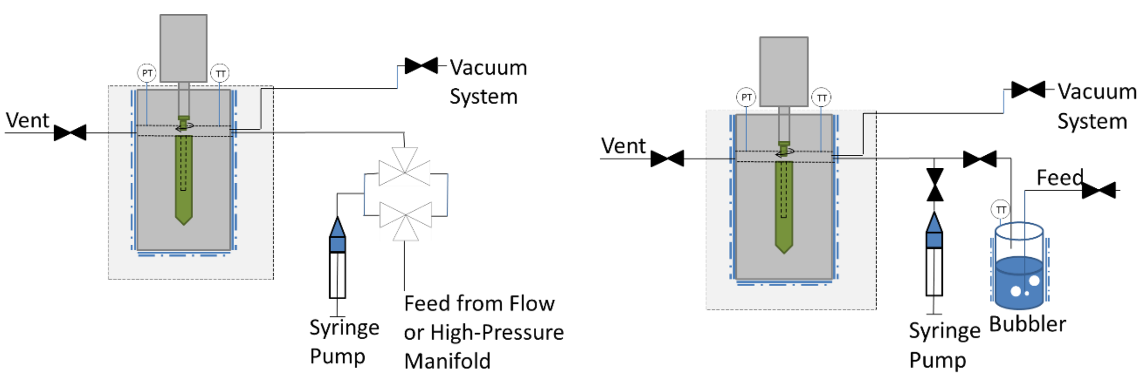

Exhibit D. Representative schematics of gas and vacuum systems coupled with the heated chamber.

3. Detailed Description of the invention: Device/Figures:

Though this device may be suitable for a range of other applications, the contents herein will be centered on its application for magic angle spinning (MAS) NMR sample preparation. The high pressure

MAS NMR loading chamber can be used to carefully control the desired internal chemical composition of in situ NMR rotors (Exhibit A) charged with gases and vapors. The chamber, detailed below and in Exhibit B, is a stainless steel vessel equipped with three (variable quantity) inlets/outlets with needle or similar valves, pressure relief device such as a relief valve or rupture disk, pressure gauge, thermocouple, one or more viewing windows, an internal holder for the NMR rotors, and **a magnetically-coupled cap screw driver that substantially simplifies the loading process over previous designs (detailed below).** The NMR rotor is placed within the holder and the chamber is sealed. After manipulating the gas composition (such as by purging, flowing, vacuum application, or pressurizing; e.g. Exhibit C or Exhibit D), the NMR rotor may be unscrewed within the chamber by the magnetically-coupled cap screw driver to allow the rotor interior to equilibrate with the chamber gas composition. Compositions may include vacuum conditions to high pressures, dictated by the relief device (e.g. 2,000 psig) or the maximum rating for internal pressure of the NMR rotor. **The capability to maintain sealing under vacuum and prepare samples at low pressures is an advancement over complementary technologies** (8,692,548; 9,835,698). The chamber may also be externally heated (e.g. via hot plate and/or heating tape) for enhanced control over the temperature and pressure of sample preparation. The gases can be introduced through any of the three inlets/outlets through a flow-style manifold, high pressure manifold, or vacuum manifold system.

Chamber Lower Body:

The lower body of the chamber houses the rotor holder and void space for the gas atmosphere. It consists of a cylindrical-type stainless steel vessel which is flat on the bottom and rounded about the vertical axis. Two viewing windows are located on opposite sides of the body where the vertical section has been flattened. These quartz windows are sealed with rings on both sides and held in place by a flange with 8 bolts threaded into the body. These windows are vertically positioned to enable the observation of the state of the NMR rotor cap during the screwing process. The top of the chamber body possesses a lip to allow the top and bottom sections to be clamped together as well as a circular protrusion or indentation on the top, flat surface to provide a sealing surface with the upper section of the chamber.

Rotor Holder:

The rotor holder is a small stage that slides into the Lower Chamber Body to hold the NMR rotor in place during cap manipulation and sample treatment. It consists of a cylindrical lower support with a centrally-drilled hold protruding downward from an extruded central cylinder. At the top of the lower surface and along the edge, two small screw holes (a) are present which contain screws with flattened edges and heads that slightly exceed the maximum diameter of the Rotor Holder. These screws are rotated once inside the Lower Chamber Body to secure the Rotor holder in place. A third threaded hole has been cut slightly farther inward on the same surface to allow a threaded rod to lift the Rotor holder up and down into the Lower Chamber Body. The rotor can be inserted into the centrally-located hole on the Rotor Holder by placing it into a stainless steel sleeve (b) of the appropriate size for the rotor (customizable) and placing the sleeve into the centrally-located hole on the Rotor Holder. An o-ring will be placed on the lip at the top of the rotor holder, followed by a compression washer (c). A threaded nut (d) is the placed on top of these and tightened to ensure the rotor is firmly held in place the top of the rotor is visible.

Chamber Upper Body:

The Upper Body of the chamber consists of several components anchored to a circular, Upper Body base. This base contains threaded entry ports that enable gas flow into and out of the chamber by various delivery methods. Five threaded, gasket-sealed and/or Teflon-wrapped entry ports (four depicted) are included that connect external sources to the chamber space: 1) a pressure relief device such as a relief valve or rupture disc set at 2000 psig (pictured in the back), 2) a thermocouple to monitor the internal temperature of the chamber, 3) one port that includes a T-style union to monitor the pressure via pressure gauge and also serve as an inlet/outlet controlled by a needle valve or similar, 4) a splitter union to allow for 2 gas streams to serve as an inlet/outlet, each controlled by a needle valve or similar, and 5) a port which connects to the Magnetically-coupled cap screw driver system. The gas ports are connected to high-pressure, flow, or vacuum manifolds (Exhibit CExhibit D). The gas flow and thermocouple ports merge and are guided down into the Lower Body void space through the protruding cylinder (e) on the bottom of the Upper Body. This cylinder is sized appropriately to 1) allow for viewing of the NMR rotor top, and 2) minimize the void volume in the Lower Body void space. The center of the Upper Body contains the threaded hole for the cap screw driver mechanism. This externally-rotating cylinder that can be easily operated manually is magnetically coupled to an internally-rotating cylinder which protrudes into the chamber void and makes contact with the staged NMR rotor (detailed below). Within this internal cylinder, a bit piece (f) is fit and locked into the drive shaft (g) to couple onto the rotor cap for threading/unthreading of the NMR rotor. This bit piece is removable to accommodate a wide range of driving mechanisms (e.g. extruded hexagonal bit) and may be spring-loaded into the drive shaft with retaining screws or pins to minimize pressure on the NMR rotor. The bottom surface of the supper chamber contains a teflon ring (h) that seats on the Lower Body sealing surface lip and is pressed on to the sealing surface by the Body Clamps.

Chamber Body Clamps:

Two half-circular (arc) Chamber Body Clamps serve the purpose of supplying force to the sealing surfaces of the Lower and Upper Chamber Bodies. The lower lip of the Body Clamps should be positioned below the lip of the Lower Body while the upper section of the Body Clamps should rest atop the Upper Body. The clamps consist of a latch section on each side of the half-circle to securely hold it in place with the other half-circle. The top of each Body Clamp contains three large bolts which thread through the upper section of the clamp and press onto a vertically-moveable plate held onto the clamps by two freely moving bolts running through the top of each Body Clamp. Further threading the large bolts through the Body Clamps will press down on the plates and camp the Upper and Lower Bodies together through force.

Magnetically-coupled cap screw driver:

The magnetically-cap screw driver improves upon previous designs whereby the cap may be threaded and unthreaded with ease, using only the hand for enhanced control and tactile response. Previous thrust/ball bearing models require a wrench to turn which is both less convenient and offers an opportunity to overtighten the rotor cap and break the sample holder. Further, the use of an o-ring to seal along the rotating axis may enable leakages to occur due to the motion of a shaft during high pressure. The magnetically-coupled design mitigates these issues. It consists of three cylindrical components. The outer-most cylindrical component (h) is externally placed and consists of a hallow cylinder with two or more magnetic blades or similar bound to the internal walls. This is the component that is rotated by hand to drive the internal rod (g) to thread the NMR rotor cap. This piece rests along the upper section of the outside of the second cylinder (i) where it is held in place by a lightly magnetic ball-bearing ring (or magnetic cylinders embedded into the cylinder 2) and capped on the top to maintain the second cylinder within (optional, not depicted). The second cylinder (i), also hollow, is threaded into the top center hold of the Chamber Upper Body to seal the chamber and allow entry into the center of this second cylinder. The top of cylinder 2 is threaded to allow a high-pressure cap (j) sealed with a teflon ring to isolate the loading chamber from the atmosphere. Within this second cylinder, the third cylinder (k) rests, suspended in the center with a small clearance space to minimize void. The upper part of this cylinder contains some variation of a magnetic field (blades, solid core, rings, etc.) positioned consistently with the first, outer cylinder to enable magnetic coupling. Below the magnetic section, in the lower section of this third cylinder, the radius is reduced and the lower portion of the second cylinder (i) near the thread connecting to the Chamber Upper Body. The drive shaft (g) passes through this threaded section and connects to the threaded lower part of cylinder 3 (k). The external first (h) and internal third cylinder (k) are magnetically coupled such that a rotation in one will stimulate rotation in the other through the other cylinder. In practice, the outer cylinder (h) will be rotated by hand, which will turn the magnetically-coupled internal cylinder (k), and thus the drive shaft (g) which will manipulate the NMR rotor cap. The rotating cap screw driver is completely contained within the chamber and sealed against leaks. In this way, no moving parts are relied upon as sealing surfaces and the force required to turn the cap is dramatically reduced, enabling fine control over the threading process.

Advances:

This chamber design is a substantial improvement over alternatives due to the following features:

1. The magnetically-coupled cap screw driver improves the operation of the vessel by:
    a. Reducing the force required to rotate the cap screw driver which makes the device easier to work with and more tactilely sensitive, which results in savings of operational time and capital costs associated with overtightening the caps.
    b. The seal of the vessel is no longer dependent upon a rotating surface, which improves system reliability and safety.
2. This preparation vessel enables the employment of finer control over the chemical environment of the samples. In particular, this vessel enables fine control over low-pressure applications and can be connected to a vacuum manifold in addition to high pressure and flow systems