

Measuring hydrogen ortho-para composition with a microwave cavity resonator

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The nuclear spin-isomer (*ortho-para*) composition of molecular hydrogen strongly influences the safety and efficiency of cryogenic hydrogen handling, as the energy of *ortho-para* conversion exceeds the enthalpy of vaporization of liquid hydrogen, generating boil-off losses. Accurate *in situ* measurement of spin-isomer composition at cryogenic conditions is therefore essential for liquefaction process design, spin-isomer catalyst characterization, and custody transfer. Here we demonstrate a microwave cavity resonator as a novel sensor for real-time quantification of hydrogen *ortho-para* composition. The method exploits contrast in the dielectric permittivity of the nuclear-spin isomers, enabling precise tracking of natural *ortho-para* conversion dynamics in solid (10.0 K), liquid (16.6–19.9 K), and supercritical (40.4 K) hydrogen. Measurement uncertainties averaged 0.007 mol/mol across all phases. During conversion, the resonant frequencies followed a second-order kinetic model consistent with theoretical predictions and prior studies, with final equilibrium compositions independently validated by Raman spectroscopy. The determined conversion rate constants agree with the empirical correlation of a previous study, while also revealing the potential errors introduced from measuring natural conversion kinetics over a limited concentration range. Furthermore, our results identify significant discrepancies between experimental dielectric data and current predictive models, underscoring the need to refine hydrogen property models at cryogenic conditions. This work establishes microwave cavity resonators as a powerful tool for *ortho-para* hydrogen sensing at cryogenic conditions, with applications spanning industrial liquid hydrogen process monitoring, hydrogen isomer conversion catalyst development, and high-energy physics.

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I. INTRODUCTION

With the ongoing transition toward a clean energy landscape, hydrogen has been increasingly recognized for its versatility as both an energy source and means of energy storage. To overcome the limitations of its low-energy density as a gas, hydrogen is often liquefied and handled at temperatures of around 20 K for storage and transport [1,2]. However, at cryogenic conditions, the quantum properties of hydrogen become an important consideration in liquefaction processes. It is well known that molecular hydrogen exists as a mixture of its two nuclear-spin isomers: *ortho*-hydrogen and *para*-hydrogen [3]. These

isomers differ by their relative nuclear-spin configuration, with *ortho*-hydrogen possessing parallel, and *para*-hydrogen possessing antiparallel spins, thus occupying odd or even rotational quantum numbers (J), respectively [4]. Diagrams of *ortho*- and *para*-hydrogen are depicted in Fig. 1. Hydrogen at standard conditions (298 K) has an equilibrium *ortho*-fraction of 74.9%, approximately the composition of “normal” hydrogen (3 to 1 ratio of *ortho*- to *para*-hydrogen). However, as hydrogen is cooled, attainment of thermodynamic equilibrium requires *ortho*-hydrogen to convert to lower-energy *para*-hydrogen, such that at hydrogen’s normal boiling point (20.3 K) the equilibrium *ortho*-fraction is reduced to 0.2% [5]. The temperature-dependent equilibrium fraction of *ortho*-hydrogen is obtained from the Boltzmann population of rotational states (i.e., from the single-molecule rotational partition function), which determines the relative *ortho-para* composition [5–7]. The resulting curve, calculated using the software package ThermoFAST v2.1 [8], is shown in Fig. 1.

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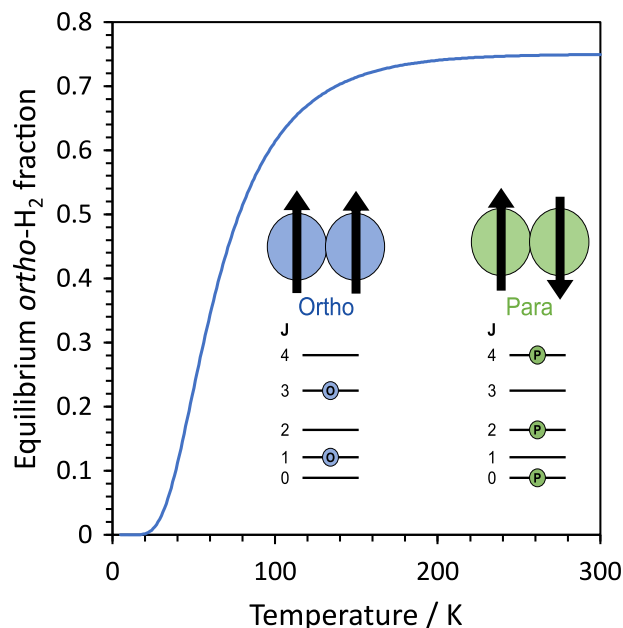


FIG. 1. Equilibrium *ortho*-hydrogen fraction as a function of temperature as calculated from the single-molecule rotational partition function in the software package ThermoFAST v2.1 [8], accompanied with illustrations of the two nuclear-spin isomers of hydrogen (*ortho*- and *para*-) including the allowed rotational energy states they can occupy in terms of total angular momentum (J).

For hydrogen liquefaction, the importance of isomer composition arises from the exothermic nature of *ortho-para* (*o-p*) hydrogen conversion, as the enthalpy of conversion (703 J/g) is greater than hydrogen's enthalpy of vaporization (446 J/g) at its boiling point (20.3 K) [9,10]. Therefore, *o-p* conversion in any metastable mixture of liquid hydrogen can lead to significant liquid boil off [11]. Moreover, *o-p* conversion is an extremely slow process, taking on the order of weeks for hydrogen to reach equilibrium at conventional pressures unless aided by catalyst materials [12]. Hence, real-time measurement of hydrogen *o-p* composition is critical for both research and industrial operations, with applications, including characterizing *o-p* catalyst materials [13]; improving process instrumentation for hydrogen liquefaction, quality assurance and metering [2]; and high-energy physics, where hydrogen is used as a neutron source moderator [14,15].

There are a number of methods and principles for *o-p* composition measurement, each with distinct advantages and limitations. Direct measurement techniques, including nuclear magnetic resonance (NMR) and Raman spectroscopy, probe the spin-isomer state of hydrogen directly. NMR detects the density of *ortho*-hydrogen (nuclear spin $I = 1$) to quantify changes in *o-p* ratio [16]. However, since *para*-hydrogen is “NMR silent” (nuclear spin $I = 0$) [17], measurement of hydrogen with a high *para*-fraction will

have low signal-to-noise ratios, requiring frequent calibration against *ortho*-rich mixtures, like normal hydrogen. Raman spectroscopy has become increasingly prominent in the recent literature [15,17–20] and can discern both *ortho*- and *para*-hydrogen. However, calibration for *o-p* measurement is nontrivial, as peak-area response factors vary with density, temperature, and the instrument used [20,21]. Additionally, as an optical technique, Raman spectroscopy is sensitive to interference, such as fouling, and it can be challenging to acquire and/or integrate the requisite spectra at extreme temperatures and pressures [22].

Indirect measurement methods typically quantify *o-p* composition through a contrast in the thermophysical properties of hydrogen with different *o-p* ratios [13,23–25]. These methods rely on having a robust calibration over the isomer composition range of interest, or a reliable property model to interpret the measured quantity in terms of isomer composition. Furthermore, the sensitivity of these methods is generally temperature dependent, which can make them less effective at cryogenic conditions. For example, the hot-wire thermal conductivity method, applied in most twentieth-century *o-p* hydrogen investigations [12,26–28], is mostly insensitive for hydrogen samples below 50 K (with limited effectiveness below 100 K) due to the convergence of each isomer's thermal conductivity [29]. Thus, the sensor is typically operated at ambient temperature, requiring regassification and warming of cryogenic samples to detect small spin-isomer differences. Recently, speed of sound measurements have gained attention for *o-p* composition determination due to the high accuracy of modern acoustic measurement techniques. Eisenhut and Haberströh [13] developed an apparatus and method for measuring *o-p* composition via the speed of sound across a temperature range of (−19 to 22) °C. While their method achieved one of the lowest reported uncertainties among existing techniques, it suffers from the same limitation as thermal conductivity-based methods in that the speed of sound of each isomer converges at cryogenic temperatures, reducing measurement sensitivity [3].

Figure 2 provides a visual representation of the temperature dependence of measurement sensitivity for thermal conductivity (κ) and speed of sound (w) techniques on a relative scale. Sensitivity is expressed as the difference between normal- and *para*-hydrogen properties, normalized by the best-case resolution reported for each method ($\delta\kappa$ for thermal conductivity and δw for the speed of sound). For this comparison, literature-reported uncertainties are taken to be the sensor resolutions and are assumed to be attainable across the full temperature range. The best-case speed of sound uncertainty reported by Eisenhut and Haberströh [13] (0.11% *p*-H₂ at −19 °C, equivalent to 0.03 m s^{−1}) and the predicted minimum thermal-conductivity uncertainty reported by Bradshaw and Norris [30] (0.35% *p*-H₂ at and above 77 K, equivalent to 1.8 × 10^{−5} W m^{−1} K^{−1}) were adopted. However,

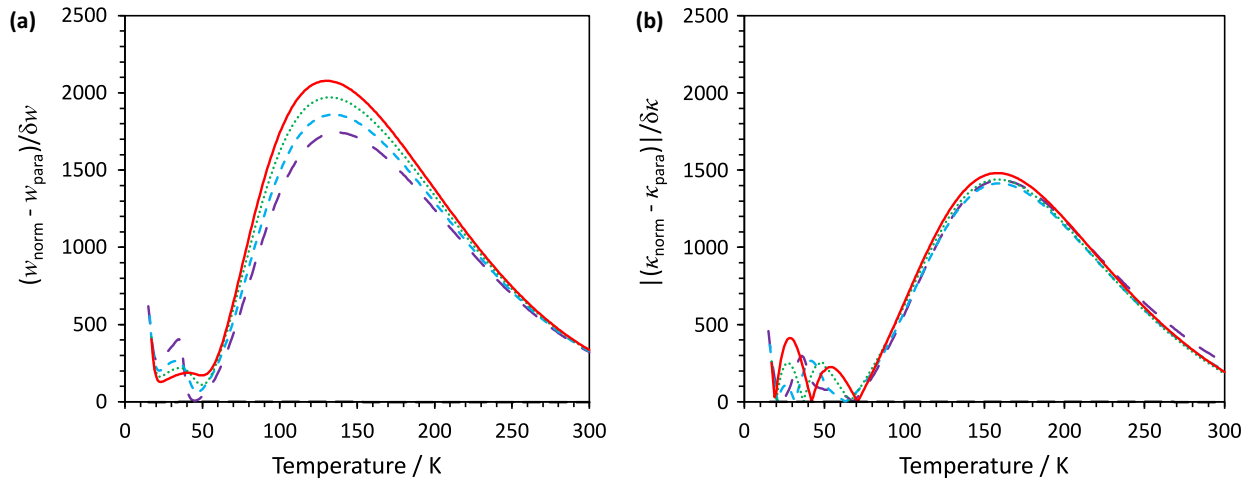


FIG. 2. Relative sensitivity of indirect *ortho-para* hydrogen measurement methods as a function of temperature, expressed as the difference in properties between normal and *para*-hydrogen divided by the best-case measurement resolution (δ), for (a) speed of sound (w) and (b) thermal conductivity (κ). Results are shown at absolute pressures of 2.5 MPa (—), 5.0 MPa (---), 7.5 MPa (···), and 10 MPa (—). Speed of sound data were calculated using the hydrogen equation of state of Leachman *et al.* [3], and thermal conductivity data using the models of Assael *et al.* [29] (taking the absolute value of the difference). The decreasing relative sensitivity at cryogenic temperatures reflects the convergence of thermophysical properties of the two spin isomers.

it should be noted that thermal conductivity uncertainties vary widely across the literature, with some recent studies reporting uncertainties on the order of 5% *p*-H₂ [14]. Accordingly, Fig. 2 represents a best-case comparison intended to highlight the intrinsic thermophysical sensitivity limitations of these methods at cryogenic temperatures.

A new measurement technique that complements the aforementioned methods, especially for cryogenic applications, could help address current issues with sensor operating range and suitability for industrial integration. This work introduces microwave resonant cavities as a tool to measure *o-p* concentration via the difference in polarizations of the two spin isomers. Using a microwave resonator sensitive to the dielectric properties of a fluid contained within the cavity, the technique is demonstrated through cryogenic measurements of natural *o-p* conversion rate (in the absence of a catalyst) for solid, liquid, and supercritical gaseous hydrogen. The experimental data presented are compared against literature models of natural conversion rates and hydrogen's dielectric properties at these conditions.

II. BACKGROUND AND THEORY

A. Microwave resonator approach

For several decades, microwave resonant cavities have been employed to study the thermophysical properties of fluids, including the measurement of relative dielectric permittivity, density, polarizability, and dipole moments [31–35], as well as the characterization of phase behavior [36–39]. Microwave resonant cavities are often small

volume metallic cells that both contain a fluid sample and support a resonant electromagnetic field. They can be designed with internal structures to modify the electromagnetic-field distribution, and thus be sensitive to the dielectric properties of a contained fluid in certain spatial locations [32]. The electromagnetic resonant modes of the cavity are set by the impedance boundaries associated with the cavity's geometry, which give rise to a standing-wave pattern in the electric and magnetic fields influenced by the fluid's properties at those conditions [40]. The resonance frequency (f_n) for a particular mode (n) depends on the dielectric permittivity of the fluid relative to that in vacuum, i.e., the relative dielectric permittivity (ϵ_r). For a system with negligible dielectric losses and a high-quality factor, ϵ_r can be approximated by Eq. (1) as ϵ (the measured effective relative dielectric permittivity, often referred to as the “dielectric constant”), where $f_n^\emptyset$ is the vacuum resonance frequency of mode n :

$$\epsilon \approx \left(\frac{f_n^\emptyset}{f_n} \right)^2. \quad (1)$$

For pure, nonpolar fluids, the dielectric constant (ϵ) is related to polarization (P), and thus to density (ρ) according to the Clausius-Mossotti relation [41] given in Eq. (2), and a virial expression for P as a function of density as shown in Eq. (3) [42]:

$$P = \frac{\epsilon - 1}{\epsilon + 2}, \quad (2)$$

$$P = \rho(A_\epsilon + B_\epsilon \rho + C_\epsilon \rho^2), \quad (3)$$

where A_ϵ , B_ϵ , C , and D are fluid-specific parameters, which can be estimated by regression to experimental data, or in the case for A_ϵ and sometimes B_ϵ , calculated from theory [42,43]. For fluid mixtures, the mixture polarization (and thus the dielectric constant), can be defined by combining pure-fluid polarizations according to the mixing rule proposed by Harvey and Prausnitz [44], which uses scaled volume fractions dependent on critical volumes of the pure components. For hydrogen, the critical volumes of *ortho*- and *para*-hydrogen predicted by the Leachman equation of state (EOS) [3] differ by only 0.6%, and the critical volumes of *ortho*- and normal hydrogen have not been experimentally validated. More elaborate Onsager-type treatments have been attempted in the literature for specifically combining *o-p* dielectric constants [45], but these approaches are highly complex and were reported to yield only marginal differences compared to a simple linear mixing assumption. Consequently, in this work the polarization of *o-p* mixtures will be approximated as a linear combination of the pure *ortho*- and *para*-hydrogen values, with the mixture polarization then converted to the dielectric constant via the inverse of Eq. (2). This approach is rigorous in A_ϵ [the dominant term in the correlation as in Eq. (3)], reduces dependence on the current hydrogen EOS, and avoids additional complexity in the *ortho*-fraction calculations to be presented in Sec. III E.

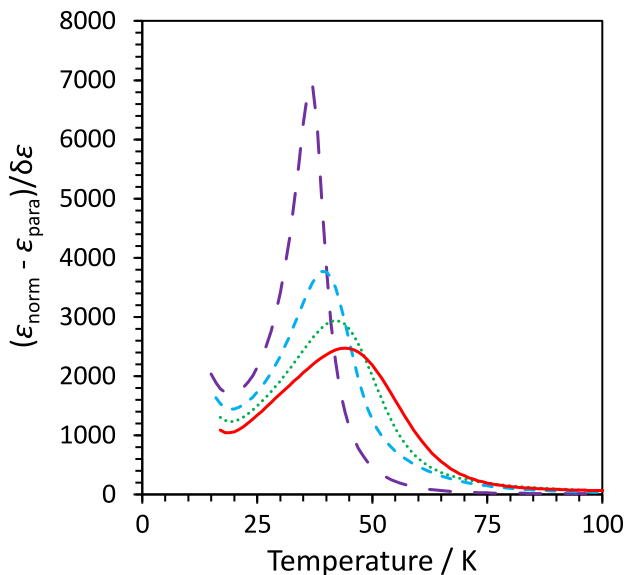


FIG. 3. Relative sensitivity of dielectric constant (ϵ) for an *ortho-para* hydrogen measurement method as a function of temperature, expressed as the difference in ϵ between normal and *para*-hydrogen divided by best-case measurement resolution ($\delta\epsilon$). Results are shown at absolute pressures of 2.5 MPa (—), 5.0 MPa (---), 7.5 MPa (···), and 10 MPa (—). All were calculated with the default models in the software REFPROP 10.0 [24].

The default models for predicting the dielectric constant of *ortho*- and *para*-hydrogen mixtures in the software package REFPROP 10.0 [24] suggest a contrast in this dielectric property between the isomers below 60 K due to their inherent differences in density and polarizability [46]. Figure 3 demonstrates this in a form analogous to Fig. 2, expressing the relative sensitivity as the difference between normal- and *para*-hydrogen dielectric constants normalized by the measurement resolution. In contrast to speed of sound and thermal conductivity methods, the predicted dielectric sensitivity increases substantially at cryogenic temperatures, exceeding even the relative sensitivity of ambient-temperature measurements based on those techniques. As in Fig. 2, a best-case resolution reported in the literature was adopted for this comparison, namely the absolute dielectric-constant uncertainty of 3.4×10^{-7} at 293 K reported by May *et al.* [47].

Some measurements of the dielectric constant for hydrogen with different *o-p* compositions using capacitive techniques have been reported [42,48], and microwave resonant cavities have been used to measure precisely the dielectric constant of both “normal” hydrogen at ambient temperatures [47] and liquid *o-p* hydrogen mixtures at cryogenic conditions [46,49]. However, we are unaware of any previous reports using microwave resonant cavities as a sensor for *o-p* hydrogen composition.

B. Modeling natural *o-p* conversion

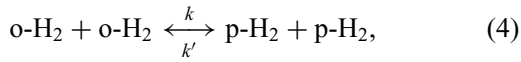
By conservation of angular momentum, an isolated *ortho*-hydrogen molecule is unable to convert to *para*-hydrogen and vice-versa [50]. So-called “natural” *o-p* conversion of hydrogen requires a magnetic dipole interaction between nuclear moments of *ortho*-hydrogen molecules, with the rate of conversion being inversely proportional to the eighth power of separation distance [50]. The natural conversion of low-temperature solid [51–53], liquid [12,54], and gaseous hydrogen [12] has been investigated by various authors such that the mechanisms of conversion are relatively well described.

For solid hydrogen, Driessen *et al.* [53] investigated *o-p* conversion as a function of density, utilizing isochoric measurements and Raman spectroscopy. Their findings demonstrated that the conversion is influenced by the solid’s phonon density of states, which affects the rate at which rotational energy is transferred. Unlike earlier studies by Pedroni *et al.* [55], which suggested a bimodal distribution of conversion rates due to phonon structure, Driessen *et al.* [53] found that the conversion was more consistent with a smooth phonon density distribution. Their model, based on Berlinsky’s theory [52], predicted a second-order reaction rate driven by nuclear-spin interactions between *ortho*-hydrogen molecules, consistent with the expectation that conversion occurs more efficiently

when *ortho*-hydrogen molecules are in close proximity in the solid phase.

In the liquid and gaseous phases, Milenko *et al.* [12] expanded the understanding of natural *o-p* conversion by measuring rates over a broad range of temperatures and pressures. Their work provided experimental data for conversion rates in liquid hydrogen at temperatures between (17 and 32) K and in gaseous and supercritical hydrogen up to 120 K. Milenko's model, which also describes the conversion as a second-order reaction rate, emphasized the role of molecular collisions and the importance of collision velocities in determining the probability of conversion in the gas phase. This velocity dependence improved upon classical Wigner theory [50] and matched experimental results more closely. Milenko *et al.* [12] also proposed an interpolation formula that connects conversion rates to both density and temperature, allowing for a unified description of the conversion behavior across fluid states.

Hence, for hydrogen in all states, it is expected that the natural *o-p* conversion of hydrogen [as depicted in Eq. (4)] occurs as a second-order reaction, that is, dependent on the square of the *ortho*-hydrogen concentration. The rate equation is shown in Eq. (5) [12].



$$\frac{dx_o}{dt} = -kx_o^2 + k'x_o(1 - x_o), \quad (5)$$

$$k' = \frac{kx_o^{\text{eq}}}{1 - x_o^{\text{eq}}}, \quad (6)$$

where x_o is the mole fraction of *ortho*-hydrogen, k is the rate constant for the forward conversion, and k' is the rate constant for the reverse reaction. The rate constants k' and k are related by Eq. (6) [12], where x_o^{eq} is the equilibrium fraction of *ortho*-hydrogen at the experimental temperature (as in Fig. 1). Integrating Eq. (5) with respect to time achieves the following discrete and linearized expressions for x_o with time (t) for natural conversion with a single rate constant k in units h^{-1} :

$$x_o = -\frac{x_o^i x_o^{\text{eq}} e^{(kx_o^{\text{eq}}/(1-x_o^{\text{eq}}))t}}{x_o^i - x_o^{\text{eq}} - x_o^i e^{(kx_o^{\text{eq}}/(1-x_o^{\text{eq}}))t}}, \quad (7)$$

$$\ln\left(\frac{x_o}{x_o - x_o^{\text{eq}}}\right) = \frac{kx_o^{\text{eq}}}{1 - x_o^{\text{eq}}}t + \ln\left(\frac{x_o^i}{x_o^i - x_o^{\text{eq}}}\right), \quad (8)$$

where x_o^i is the initial *ortho*-fraction at $t = 0$. For this work, values of x_o^{eq} were calculated at the experimental temperature from statistical mechanics predictions, implemented in the software package ThermoFAST v2.1 [8] (see Fig. 1).

III. METHODS

A. Modeling natural *o-p* conversion

The dielectric properties of the hydrogen samples were monitored using a microwave cavity resonator identical in geometry to the one described by Hopkins *et al.* [38], as pictured in Fig. 4. In this work, the cavity was made from Aluminum 6061 to reduce any magnetic-field influence on the hydrogen conversion rate (the cavity used in Ref. [38] was made of 316 Stainless Steel, which exhibits weak magnetic properties [56,57]). There still remains the possibility of minor promotion of the spin-transition rate through adsorption to and interaction with the metal surface, which has been reported for other nonmagnetic materials, such as silver and copper [58,59], with the suggestion that a virtual transference of a metal electron to the antibonding orbital of the hydrogen molecule induced spin transition. However, as this effect cannot be reliably quantified and is expected to be negligible relative to the overall uncertainty, it was disregarded in the data analysis for this work.

The microwave cavity was cooled using two different commercial cryocooler apparatus. For solid and liquid measurements at (10.0 to 19.9 K), the microwave cavity resonator was integrated into a modified commercial dual-stage pulse tube cryocooler (CryoMech PT407RM). The resonator was affixed to an extension of the 4-K cold plate, as depicted in Fig. 5. The cavity and surfaces of the cryocooler were lined with cryogenic insulation to minimize radiative heat transfer. Thermal impedances added to the extension broadened the operating temperature range of the cavity, which, along with panel mount resistors, allowed for temperature control over a range from (5 to 35) K with a typical long-term temperature stability of 6 mK. All wires, including microwave and temperature cabling, were thermally grounded on both cryocooler stages, while the 1/16" fluid feedthrough was only grounded to the first stage to avoid solids forming in the fluid line. A LakeShore model 340 temperature controller was used to monitor two Cernox 1050 type AA temperature sensors in the cooler stage and resonator, with standard uncertainties of 10 mK. Fluid pressure was monitored outside the cryogenic environment with a Digiquartz® pressure transducer (1621-001), with a standard uncertainty of 2.7 kPa. The first resonant mode of the sensor was monitored in transmission using a Keysight N9917A vector network analyzer (VNA) with an internal reference frequency stability of 0.4 ppm. The complex S_{21} coefficients were acquired across 3201 stimulus frequencies spanning a range of 30 MHz centered on the resonant peak. The measured complex S_{21} data was fit to a "Q circle" [60] to determine the resonance frequency and bandwidth (quality factor Q). The total time required for each measurement and fit is dominated by the data-acquisition rate, which is limited by the VNA noise-filtering setting (in

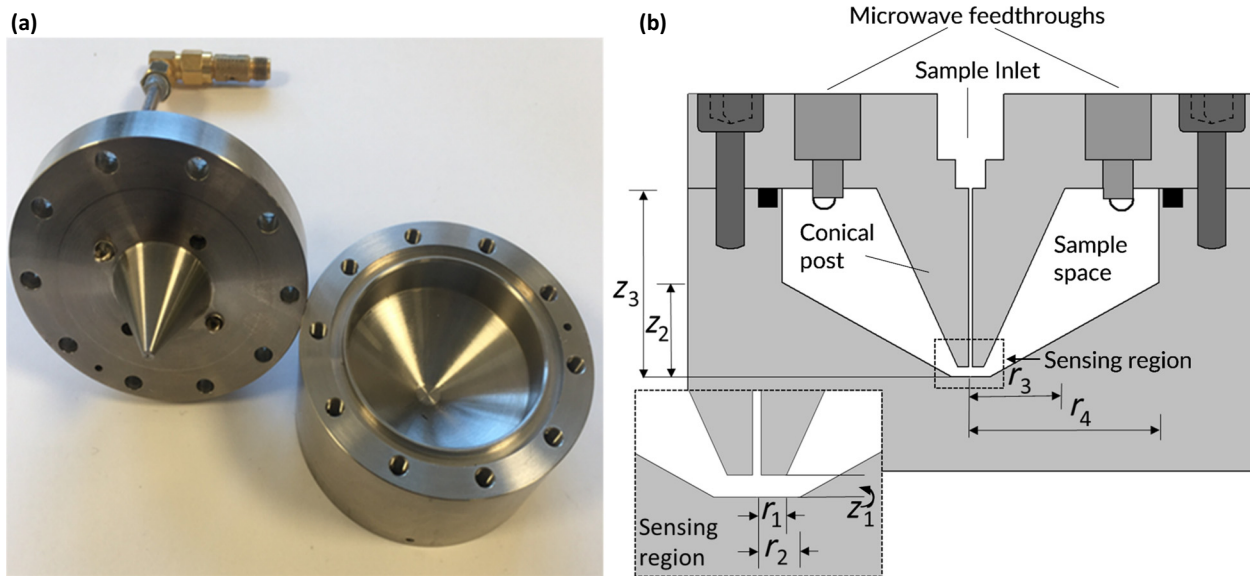


FIG. 4. (a) Photo of the microwave cavity resonator from [38] separated into its two pieces. (b) Schematic of the microwave sensor in cross section with key components highlighted and dimensions $r_1=1$ mm, $r_2=2$ mm, $r_3=10$ mm, $r_4=20$ mm, $z_1=0.2$ mm, $z_2=10$ mm, and $z_3=20$ mm. The cavity's total sample volume is 14.9 cm^3 and its outer radius is 30 mm.

this work, the intermediate-frequency bandwidth filter was set to 300 Hz) and the number of points. This equates to approximately 10 s for this measurement. In contrast, the Q -circle fit is processed within 0.1 s. For applications monitoring conversion process systems, the read-out system can be significantly optimized; for example, a narrow frequency span with 201 pts would allow composition measurement rates greater than 1 Hz, and faster rates could be achieved by replacing the VNA with a high-bandwidth frequency locking scheme.

For gaseous measurements (40.4 K), a single-stage pulse-tube cryocooler (CryoMech PT60) was used with the cavity resonator affixed to the copper heat-exchanger plate to which all wires and tubes were thermally grounded, as shown in Fig. 6. Similar to the dual-stage cryocooler, resistance heaters were used to control temperature range from (35 to 80) K with a typical long-term stability of 10 mK. A LakeShore model 218 temperature controller was used to monitor a Cernox 1010 type AA and a Cernox 1080 type AA temperature sensor in the heat-exchanger plate and resonator base, with standard uncertainties of 16 and 10 mK, respectively. Fluid pressure was monitored outside the cryogenic environment with an Additel ADT685 pressure transducer possessing a standard uncertainty of 2 kPa. The first resonant mode of the sensor was monitored and tracked by measuring the transmission response using a Keysight P9374B VNA with an internal reference frequency stability of 7 ppm. This measured the complex S_{21} transmission coefficients across 401 stimulus frequencies spanning a range of 20 MHz centered on the resonant peak, where the resonance frequency and Q were determined in the same manner as described above for the dual-stage

apparatus. To enable almost immediate, independent measurement of both the initial and final concentration of the *o-p* mixture in the microwave resonator, a Raman spectrometer (Renishaw Virsa, 532 nm 50 mW source, 2400 lpm grating) was positioned downstream of the measurement sensor. The generated Raman spectra allowed the rotational [$S_0(J)$] excitations of the hydrogen molecule to be analyzed (350–1045 cm^{-1}) where the associated *ortho*- and *para*- H_2 peaks (up to $J = 3$) were integrated to determine the *o-p* ratio, and thus *ortho*-fraction. The raw integrated areas and total *o-p* ratio were scaled in accordance with the *o-p* Raman calibration method outlined in Luther *et al.* [20], where calibration constants were determined through measurement of approximately normal hydrogen (0.749 mol/mol *ortho*- H_2) at a known temperature and the final ratio was corrected to account for the molecules at higher-energy states (above $J = 3$) that could not be resolved by the spectrometer.

B. Materials

Compressed pure hydrogen (BOC, UHP 5.0) was used with supply composition and impurities as detailed in Table I. For the solid and liquid experiments, no further purification was performed as most of the listed impurities were expected to freeze in the fluid lines prior to reaching the sensor. For the lower-density supercritical gas experiment (40.4 K), further purification was necessary to minimize the risk of solid freezeout in the sensor during the experiment, which could have a significant influence on resonant frequency measurements even at the part-per-million (ppm) concentration levels [38,61]. As

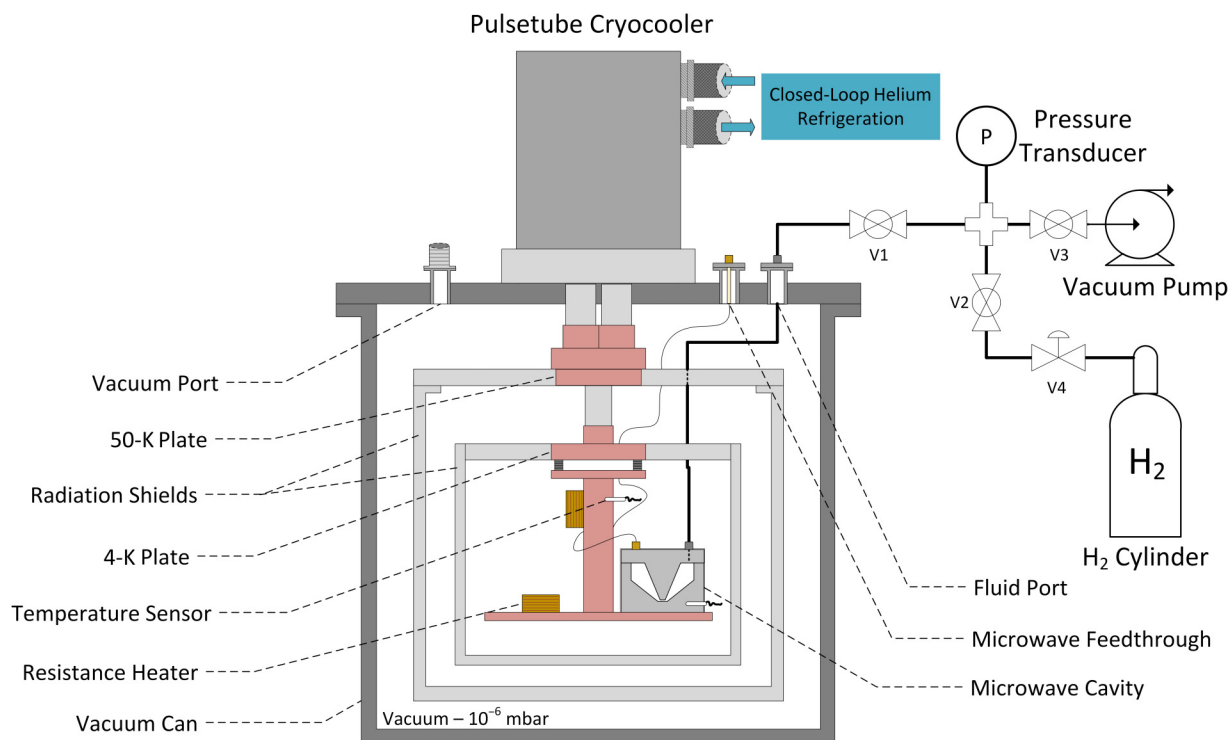


FIG. 5. Schematic of the two-stage pulse-tube cryogenic thermal control system capable of controlling temperatures between (5 and 35) K. The microwave resonator is mounted to the second stage. Hydrogen is introduced from room temperature through a stainless-steel tube. The vacuum in the experimental chamber is maintained by a turbomolecular pump.

such, prior to entering the cryocooler, the hydrogen was purified via a carbon-based adsorbent cold trap immersed in liquid nitrogen (77 K). The efficacy of the cold trap was independently verified by moisture analysis (Ametek 3050), showing that the purified hydrogen stream consistently contained a moisture level below the detection limit of the analyzer (<0.1 ppm) at 295 K. Upon exiting the cold trap, the hydrogen was then flowed via an *o-p* catalyst (Ionex®, Molecular Products Inc.) filled “normalization cell” at ambient temperature, designed to return any converted hydrogen to equilibrium ambient hydrogen (approximately 0.749 mol/mol *ortho*-H₂) before entering the measurement system.

C. Measurement of hydrogen’s triple point

The microwave cavity sensor and apparatus were tested by measuring the triple point of hydrogen with the dual-stage cryocooler arrangement (Fig. 5). Ambient temperature hydrogen (1 MPa) was loaded into the cavity at 35 K as a gas and the sample was then isolated in the apparatus by closing V1. An isochoric path was followed by subsequently cooling, stepwise, in 0.2-K increments with 90-minute hold times. Following the phase diagram in Fig. 7, this constant density pathway reached and then followed the vapor pressure curve through the triple point and onto the sublimation line until the minimum temperature

of 10 K was reached. A phase transition was detected near the triple point during cooling. However, cooling experiments cannot be relied upon for accurate thermodynamic triple-point measurements due to the stochasticity of solid formation [62]. Consequently, after the system was held at 10 K to solidify the remaining liquid, the system was heated in controlled 0.2-K increments through the triple point.

Onset of a liquid phase at the triple point is indicated by a change in the dielectric properties. This is observed as a transient change in resonant frequency of the sensor as the solid-vapor equilibrium enters a state of solid-liquid-vapor equilibrium, changing the dielectric permittivity of the sample present in the region of high electric field. Figure 8 shows the frequency response with warming of the system both over temperature and time. Onset of melting is first observed at 13.80 K, indicated by a decrease in frequency, which is attributed to partial melting and filling of any pore space present in the solid, thereby increasing the effective permittivity in the sensing region. Between (13.8 and 14.0) K, an increase and stabilization of frequency indicates that melting is complete. Therefore, the average of the two temperature steps is taken as the melting condition (where the step size is accounted for in the measurement uncertainty). Hence, the measured triple-point temperature is taken as 13.9 ± 0.28 K at a corresponding measured pressure of 8.85 ± 2.68 kPa (the

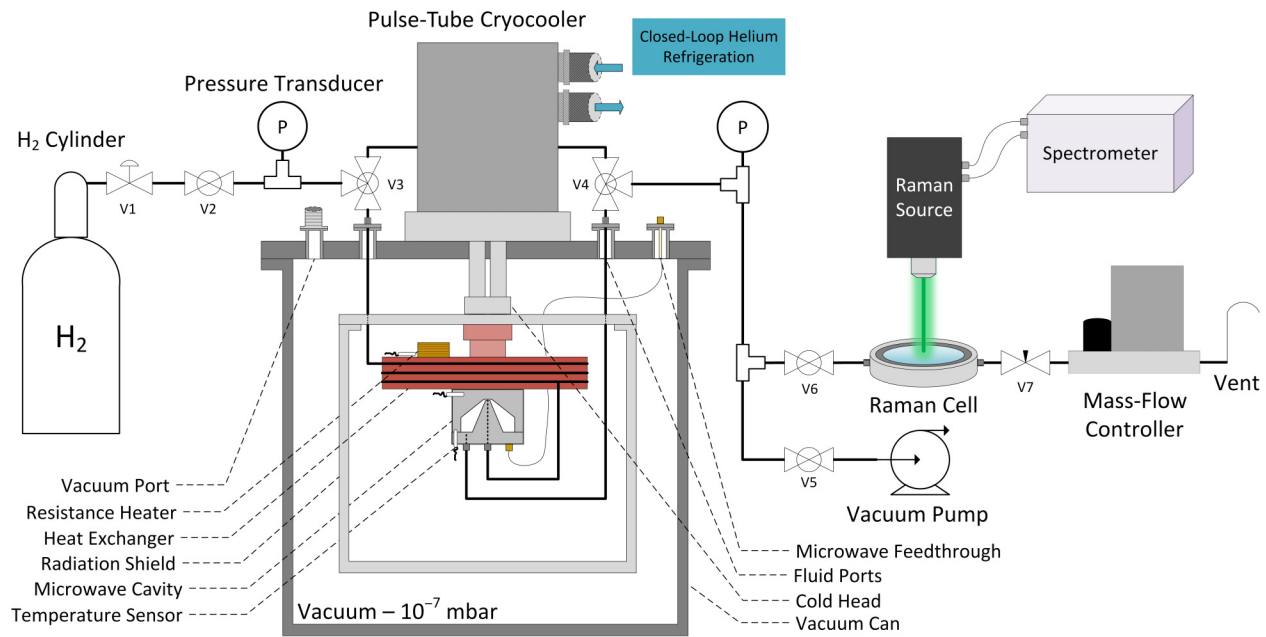


FIG. 6. Schematic of the single-stage pulse-tube cryogenic thermal control system capable of controlling temperatures between (35 and 80) K. The vacuum in the experimental chamber is maintained by a turbomolecular pump. A Raman spectrometer is present downstream of the microwave cavity sensor (at room temperature) for independent *o-p* compositional measurements.

relatively large uncertainty in pressure is due to the large operating range of the transducer). For comparison, the reference triple-point condition for normal hydrogen is also depicted in Fig. 8(a) [63]. Given the length of the experiment, it is expected that some natural *o-p* conversion may have occurred. For comparison, the reference triple-point temperature for equilibrium hydrogen (99.79% *para*-hydrogen) is 13.8033 K [64] and the predicted triple-point pressure of *para*-hydrogen is 7.04 kPa [3]. The measured triple-point temperature is between the values for normal and equilibrium hydrogen, consistent with conversion occurring, although both values are within the experimental uncertainty so no quantitative inferences can be drawn.

D. Experimental method

The natural *o-p* conversion of hydrogen was measured at five different combinations of temperature and pressure

TABLE I. Manufacturer certified analysis for hydrogen specification as supplied (BOC, 240, Grade 5.0) used in all measurements.

Component	Composition
Hydrogen (H ₂)	99.999 mol%
Moisture (H ₂ O)	<4 ppm
Nitrogen (N ₂)	<4 ppm
Oxygen (O ₂)	<1 ppm
Hydrocarbons (in form of methane) (CH ₄)	<1 ppm

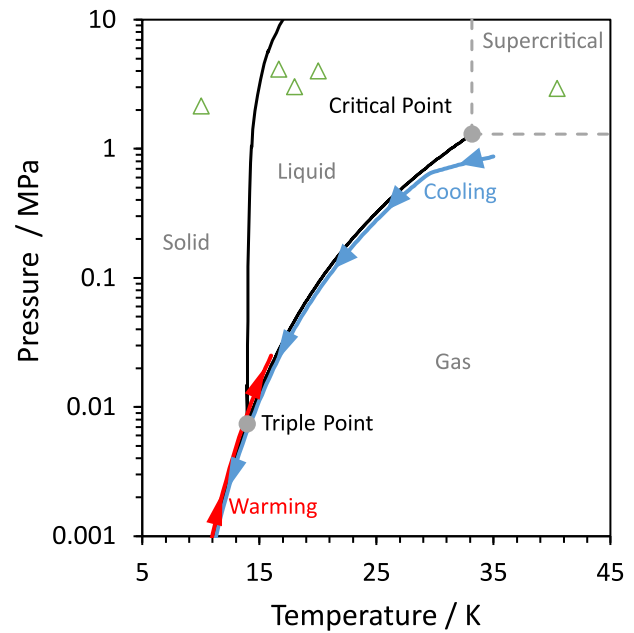


FIG. 7. Normal hydrogen pressure-temperature phase diagram as calculated in REFPROP 10.0 [24] using the Leachman *et al.* [3] equation of state for vapor-liquid equilibrium and critical points, a NIST preliminary equation for the melting line, and the default solid-fluid equilibrium model in ThermoFAST v2.1 [8] for the sublimation line. The experimental pathway for the triple-point measurement is indicated by arrows and the conversion measurement conditions reported in this work are indicated by Δ symbols.

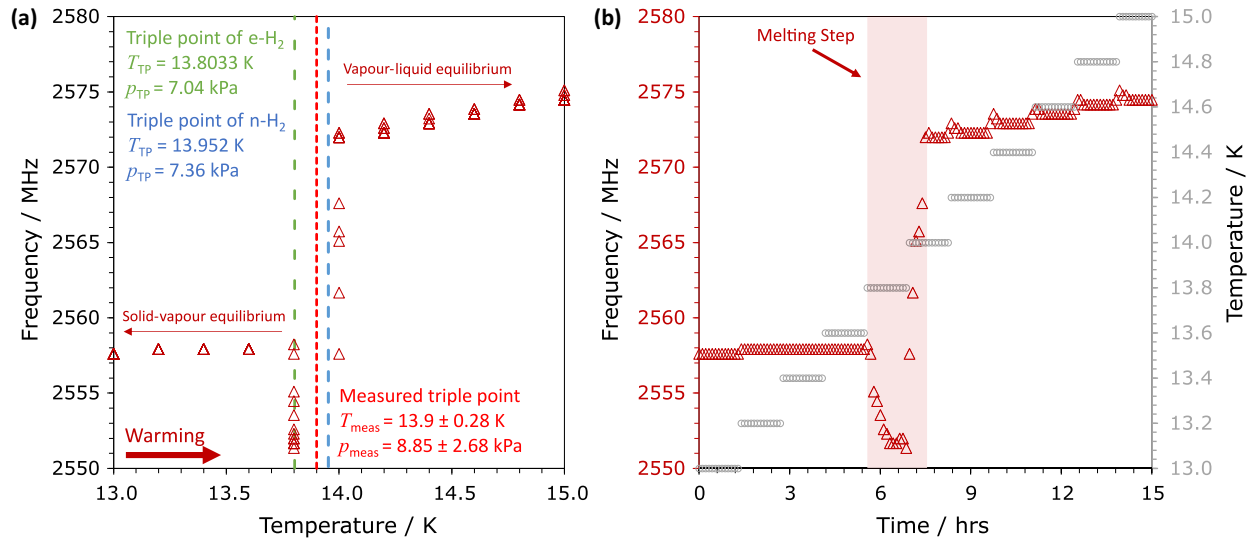


FIG. 8. (a) Measured resonant frequency data with temperature during warming experiment. The reference triple-point temperature for normal (—) [63] and equilibrium hydrogen (approximately *para*-hydrogen) (—) [64] are indicated. The measured triple-point temperature is indicated by the red dashed line (---). (b) Measured frequency (Δ) and temperature ($\circ$) data with time during warming experiment. The shaded region represents where the onset and conclusion of melting was observed to occur based on the frequency data.

(and thus density) in the solid, liquid, and supercritical gas phases, as detailed in Table II. The properties of fluid hydrogen, including density, were predicted using the Leachman *et al.* EOS for normal hydrogen [3]. The density of solid hydrogen cannot be confidently predicted, as it is dependent on crystal growth and porosity. Nevertheless, the solid density was estimated here using an empirical formula for solid hydrogen density along the melting curve detailed by Younglove [65] and thermal-expansion coefficients provided by Ahlers [66].

For all experiments, the measurement procedure began with cooling the sensor to the temperature set point while under vacuum. For the liquid and solid measurements, room-temperature hydrogen was then loaded from a 1-l sample cylinder into the cold sensor through V4, V2, and V1 (Fig. 5). The system remained in fluid communication with the sample cylinder throughout the experiment. A similar procedure was followed for the gaseous measurement; however, the sample hydrogen also flowed via the downstream Raman spectrometer during filling (see Fig. 6) to confirm the initial *o-p* composition. Due to the influx of hot gas, the resonator temperature initially increased by up to 20 K, before returning to the desired set point within the first 2 h for all experiments. This created some additional uncertainty as the initial *ortho*-fraction upon returning to the experimental temperature was assumed to be unchanged across this 2-h period. The uncertainty due to this assumption is discussed in Sec. IV B.

Frequency, temperature, and pressure were continually monitored and recorded using custom software (LabVIEW). The experiments continued for several hundred

hours, to allow time for the slow conversion to proceed and result in a significant change in *ortho*-fraction. For the 17.9-K experiment, after 422 h of conversion, hydrogen was sampled by expanding the gas into a 0.3 l sample cylinder made from 304 stainless steel and transported to an off-site Raman spectrometer (Renishaw InVia, 532-nm 200-mW source, 2400-lpm grating) for independent measurement of *ortho*-fraction concentrations within 1 h of the sample's withdrawal from the sensor. For the 40.4-K experiment, the downstream Raman spectrometer measurement cell and surroundings were evacuated up to V4, then filled from the final volume of hydrogen contained within the sensor by opening the valve and allowing the gas to expand. As there was a small volume (approximately 1.2 ml) of tubing between the cavity and the valve leading out of the cryocooler with an unknown hydrogen composition, the hydrogen was then flowed slowly (0.01 SLPM) with a mass flow controller (Alicat MC-5SLPM-D) and Raman measurements of the rotational spectral region [$S_0(J)$] were continuously acquired (approximately one per 16 s) until a constant *ortho*-fraction was recorded, representative of the composition of the bulk of the fluid previously inside the microwave resonator. This occurred after approximately 15 min of flow (<0.1-ml volume flowed from the cell). For both independent Raman measurements, the reverse (*para*-to-*ortho*) conversion expected during transfer and flow at room temperature is negligible compared to the measurement uncertainty; extrapolating the Milenko *et al.* [12] empirical natural conversion-rate formula to 293 K gives an approximated value of <0.0003 mol/mol in both cases.

TABLE II. Summary of the experimental conditions for the five conversion measurements presented in this work (displayed in Fig. 10). Densities were calculated using the Leachman *et al.* EOS for normal hydrogen [3] as implemented in the software package REFPROP 10.0 [24], or using empirical models for the solid [65,66].

Experiment Number ^a	1	2	3	4	5
Temperature/K	16.6	19.9	17.9	10.0	40.4
Pressure/MPa	4.14	4.01	3.01	2.14	2.92
Phase	Liquid	Liquid	Liquid	Solid	Supercritical
Density/kg m ⁻³	78.3	75.6	76.3	88.6	34.7
Length of experiment/h	164 ^b	202	422	160	157

^aExperiments 1 to 4 were performed in the dual-stage cryocooler (Fig. 5), 5 in the single stage cryocooler (Fig. 6).

^bData acquisition failed between $t = 100$ and 160 h.

E. Calculating *ortho*-fraction

An example of the frequency measurements acquired during conversion at 17.9 K is presented in Fig. 9. The data exhibit a characteristic curve that is indicative of a second-order reaction dependent on the square of the *ortho*-hydrogen concentration [as per Eq. (5)]. This is consistent with the model of low-temperature natural *o-p* conversion presented by Milenko *et al.* [12] and Driessen *et al.* [53]. To determine the relative concentration of *ortho*- and *para*-hydrogen from the measured frequency data, the initial frequency measurement acquired after the cavity temperature stabilized is assumed to be representative of the initially loaded equilibrium ambient hydrogen (approximately 0.749 mol/mol). The conversion model presented by Milenko *et al.* [12] suggests that the frequency data will asymptotically approach a value representative of equilibrium hydrogen at the experimental conditions. For 17.9 K, this is $x_o = 7 \times 10^{-4}$ mol/mol.

Ideally, this asymptotic frequency value, representing equilibrium hydrogen, could be calculated (in reference to the initial frequency) from predictive dielectric models and associated mixing rules for *ortho*- and *para*-hydrogen. However, this investigation has revealed that the current models [3,24,42] underestimate the magnitude of dielectric constant changes between *ortho*- and *para*-hydrogen at high-density conditions, due to a deficiency in the model that will be further discussed in Sec. IV D. In addition to the observations from this work, this discrepancy is also apparent when comparing the models to the data of Pashkov and Lobko [67].

Nevertheless, even without reliable models for the dielectric constant of cryogenic hydrogen, the asymptotic frequency value can be estimated by fitting the resonant frequency data to the second-order reaction model as in Eqs. (7) and (8) and assuming a linear mixing rule for the polarization of an *o-p* hydrogen mixture [where polarization is related to dielectric constant by Eq. (2)] as per Eqs. (9) and (10), where P_o and P_p are the pure-fluid polarizations of *ortho*- and *para*-hydrogen (respectively), and P is

the mixture polarization.

$$P = x_o P_o + (1 - x_o) P_p, \quad (9)$$

$$x_o = \frac{P - P_p}{P_o - P_p}. \quad (10)$$

Substituting Eq. (10) into Eq. (8) gives the second-order reaction model in terms of polarization (P):

$$\ln \left(\frac{P - P_p}{P - P_{eq}} \right) = \frac{P_{eq} - P_p}{P_o - P_{eq}} kt + \ln \left(\frac{P^i - P_p}{P^i - P_{eq}} \right), \quad (11)$$

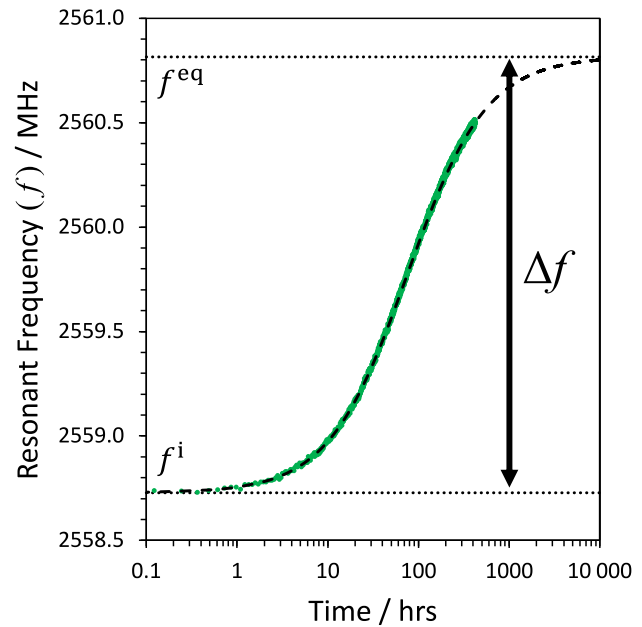


FIG. 9. Measured resonant frequency data as a function of time for the 17.9-K experiment (●). Data is fitted to a second-order model (---) as per Eqs. (7) and (8), and extrapolated out to 10 000 h. The initial frequency (f^i) corresponds to the initially loaded hydrogen (normal hydrogen), the equilibrium frequency (f^{eq}) corresponds to the extrapolated frequency for equilibrium hydrogen at the experimental temperature of 17.9 K.

where P^i is the initial polarization at time (t) = 0, P^{eq} is the polarization of an equilibrium o - p hydrogen mixture at the experimental conditions, and k is the conversion reaction constant [carried over from Eq. (8)]. Substituting Eq. (2) into Eq. (11) achieves the model for the natural conversion of hydrogen in terms of the measured dielectric constant (ε):

$$\ln \left(\frac{\varepsilon - \varepsilon_p}{\varepsilon - \varepsilon^{\text{eq}}} \right) = \left(\frac{\varepsilon^{\text{eq}} - \varepsilon_p}{\varepsilon_o - \varepsilon^{\text{eq}}} \right) \left(\frac{\varepsilon_o + 2}{\varepsilon_p + 2} \right) kt + \ln \left(\frac{\varepsilon^i - \varepsilon_p}{\varepsilon^i - \varepsilon^{\text{eq}}} \right). \quad (12)$$

For each dielectric constant value (ε), Eq. (1) is substituted into Eq. (12) to yield a relationship in terms of measured frequency (f):

$$\ln \left(\frac{1/f^2 - 1/f_p^2}{1/f^2 - 1/f^{\text{eq}2}} \right) = \left(\frac{1/f^{\text{eq}2} - 1/f_p^2}{1/f_o^2 - 1/f^{\text{eq}2}} \right) \left(\frac{(f^\emptyset/f_o)^2 + 2}{(f^\emptyset/f_p)^2 + 2} \right) kt + \ln \left(\frac{1/f^{i2} - 1/f_p^2}{1/f^{i2} - 1/f^{\text{eq}2}} \right), \quad (13)$$

where $f^\emptyset$ is the vacuum frequency of the sensor at the experimental conditions. Both f_p and f_o can be calculated in terms of the initial and equilibrium frequencies (f^i and f^{eq}) through application of Eq. (10) and converting to dielectric constant via Eq. (2) at known compositions x_o^i (the initial *ortho*-fraction) and x_o^{eq} (the equilibrium *ortho*-fraction as in Fig. 1):

$$P_p = \frac{x_o^{\text{eq}} P^i - x_o^i P^{\text{eq}}}{x_o^{\text{eq}} - x_o^i}, \quad (14)$$

$$\Rightarrow f_p = \frac{f^\emptyset}{\sqrt{(1 + 2P_p)/(1 - P_p)}}, \quad (15)$$

$$P_o = \frac{(1 - x_o^i) P^{\text{eq}} - (1 - x_o^{\text{eq}}) P^i}{x_o^{\text{eq}} - x_o^i}, \quad (16)$$

$$\Rightarrow f_o = \frac{f^\emptyset}{\sqrt{(1 + 2P_o)/(1 - P_o)}}, \quad (17)$$

where, P^i and P^{eq} are calculated in terms of frequency (f^i and f^{eq}) via application of Eqs. (1) and (2). Hence, by fitting Eq. (13) [including the relations in Eqs. (14)–(17)] to the experimental data for f over time (t), f^{eq} (the asymptotic frequency value for natural conversion at the experimental conditions) and k (the reaction constant) can be calculated for each experiment. In this work, the fits were performed using a nonlinear least-squares method as implemented by Python 3.13.0's "scipy.optimize.curve_fit" function [68].

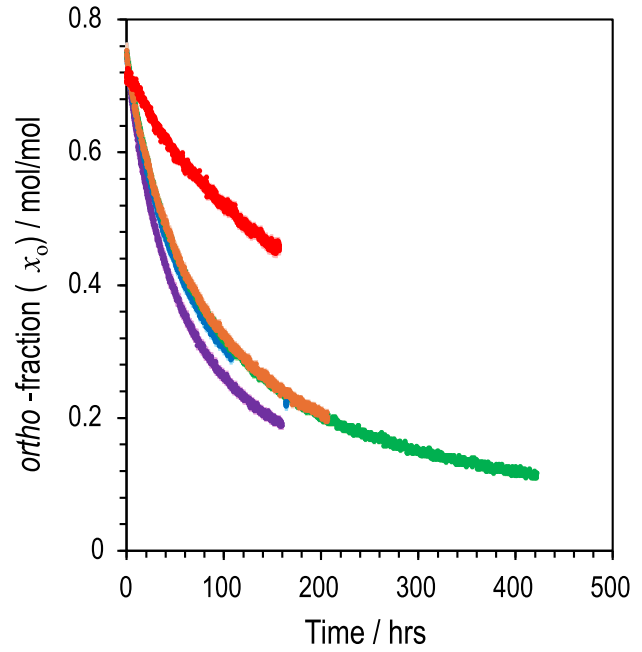


FIG. 10. Microwave cavity measured experimental *ortho*-fraction (x_o) data for the natural conversion experiments at 10.0 K (●), 16.6 K (●), 17.9 K (●), 19.9 K (●), and 40.4 K (●). For each dataset, the shaded lines represent the point-wise uncertainty (lighter shading) as discussed in Sec. IV B (mostly not visible on the plot, on the order of the scatter in the data). Experimental details are available in Table II.

Following fitting of f^{eq} and k , the *ortho*-fraction over time for each experiment (x_o) was calculated by substituting Eq. (2) into Eq. (10) where ε was related to the measured frequency, f , via Eq. (1), and f_p and f_o were calculated from Eqs. (15) and (17):

$$x_o = \frac{(\varepsilon - \varepsilon_p)(\varepsilon_o + 2)}{(\varepsilon_o - \varepsilon_p)(\varepsilon + 2)}. \quad (18)$$

IV. RESULTS AND DISCUSSION

A. Spin-isomer conversion

The fitted *ortho*-fraction over time for each natural conversion experiment is shown in Fig. 10. The results of the fit to Eq. (13) [the conversion constant (k), and the expected frequency change from approximately normal to equilibrium H_2 ($\Delta f = f^{\text{eq}} - f^i$)], as well as the final *ortho*-fraction (x_o) (an average of the final hour of measurement) are recorded in Table III.

For the 17.9-K experiment, the predicted final *ortho*-fraction after 422 h was determined to be 0.113 ± 0.005 mol/mol [represented in Fig. 11(a)]. As outlined in Sec. III D, the o - p composition of the final *para*- H_2 -rich fluid was verified with a Raman spectrometer within an hour of the final microwave cavity measurement. The rotational [$S_0(J)$] excitations of the hydrogen molecule were

TABLE III. Experimentally determined rate constants (k), magnitude of frequency change from the initial to equilibrium H_2 ($\Delta f = f^{\text{eq}} - f^{\text{i}}$), and final *ortho*-fraction (x_o) for each experiment.

Experiment	Measured rate constant (k)/ 10^3 h^{-1}	Magnitude of total conversion frequency shift (Δf)/MHz	Measured final <i>ortho</i> -fraction (x_o)/mol/mol
10.0 K, 2.14 MPa	24.8 ± 0.6	1.96 ± 0.01	0.188 ± 0.008
16.6 K, 4.14 MPa	19.2 ± 0.6	2.12 ± 0.02	0.221 ± 0.009
17.9 K, 3.01 MPa	17.8 ± 0.3	2.09 ± 0.01	0.113 ± 0.005
19.9 K, 4.01 MPa	17.6 ± 0.4	1.99 ± 0.01	0.200 ± 0.007
40.4 K, 2.92 MPa	5.8 ± 0.3	1.97 ± 0.10	0.456 ± 0.009

analyzed (350–1045 cm^{-1}), as illustrated in Fig. 11(b). The separate peaks reflect different molecule rotational quantum numbers, J , with $J = 2n$ peaks corresponding to *para*-hydrogen and $J = 2n + 1$ peaks representing *ortho*-hydrogen [69].

Calculation of *ortho*-fraction based on these spectra was completed through Gaussian function integration of the peak areas of each of the first four peaks and taking the ratio of the total *ortho*-peak area ($J = 1, 3$) and the total peak area of all four peaks. As with the other in-line spectrometer on the single-stage pulse-tube apparatus, the raw integrated areas and total ratio were scaled in accordance with the *ortho-para* Raman calibration method outlined in Luther *et al.* [20], including correction for the molecules at higher-energy states not included in the analysis of only four peaks. The final calculated *ortho*-fraction from the Raman analysis was found to be 0.111 ± 0.008 mol/mol with the uncertainty taken to be the standard deviation of three repeated scans.

Measurement of hydrogen taken from the same sample cylinder (held at room temperature) 24 h later yielded a mean increase in *ortho*-fraction of 0.02 mol/mol, suggesting that the initial measurement of *ortho*-fraction was indeed representative of the microwave experiment's end point, and, as predicted, no significant conversion occurred during the 60-minute transport of the sample to the spectrometer.

As shown in Fig. 6, the measurements at 40.4 K were conducted in an apparatus with an in-line Raman spectrometer downstream of the microwave resonator. After 157 h, the final *ortho*-fraction was measured by the microwave sensor to be 0.455 ± 0.009 mol/mol [represented in Fig. 11(c)]. The average Raman spectra of the sample is shown in Fig. 11(b). After analysis of the Raman spectra as described above for the 17.9-K experiment, the final *ortho*-fraction was found to be 0.452 ± 0.015 mol/mol. The largest uncertainty contribution for the Raman measurement is associated with the unknown hydrogen concentration in the dead volume between the resonator and the cryocooler valve.

B. Uncertainty

The uncertainties in both the regression generated constants—equilibrium frequency (f^{eq}) and conversion rate constant (k)—and the calculated *ortho*-fraction over time (as in Fig. 10) primarily arise from the noise in the measured frequency data (f); and from the uncertainties in the values of the vacuum frequency (f^{v}), initial frequency (f^{i}), the initial *ortho*-fraction (x_o^{i}), and the equilibrium *ortho*-fraction (x_o^{eq}). It should be noted that additional contributions may arise from the assumption of linear mixing of *ortho-para* polarizations; however, these could not be quantified and were therefore neglected.

For the regression-generated constants, the contribution from the frequency noise was determined directly from the regression statistics (via the covariance matrix). Then, the uncertainty contributions from the input parameters were estimated through sensitivity analyses, where each term was perturbed across its uncertainty range to assess its impact on f^{eq} and k , in accordance with the recommendations in the GUM [70] for this type of nonlinear analysis framework.

The uncertainty in f^{v} was estimated as outlined by Tsankova *et al.* [71]. The uncertainty in f^{i} was estimated as the mean absolute deviation of the first hour of frequency measurements about their mean for each experiment. The maximum change in *ortho*-fraction expected after 2 h of natural conversion at the experimental temperature was estimated using the kinetic model [as per Eq. (7) using conversion constants as in Table III] and then converted to a standard uncertainty for x_o^{i} by assuming a rectangular distribution (division by $\sqrt{3}$) [70]. This accounts for the possible difference between the assumed and actual initial composition at the start of measurement, due to natural conversion over the time required for the system to reach steady state following the initial influx of hot gas (as mentioned in Sec. III D). The uncertainty in x_o^{eq} was attributed solely to the uncertainty in the experimental temperature (T), which affects its calculation via the Boltzmann probability distribution [5–7].

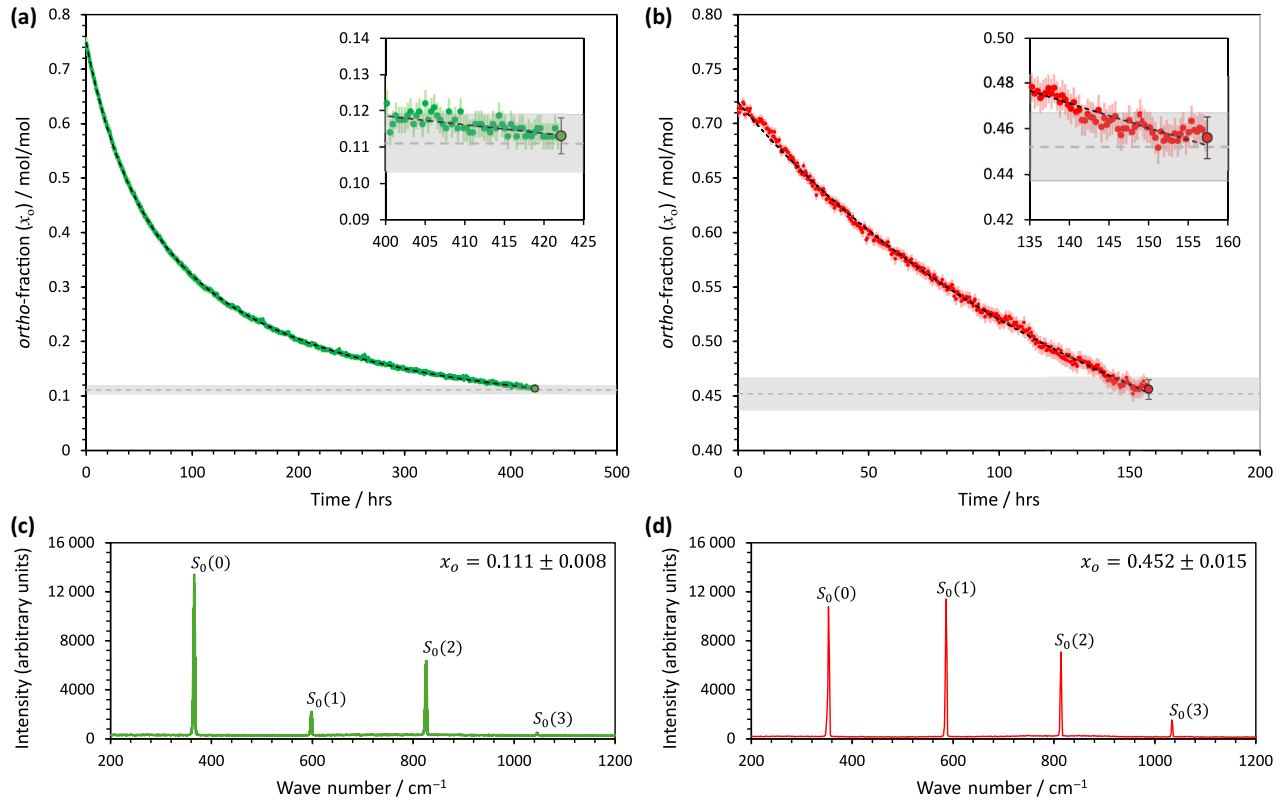


FIG. 11. Top: *ortho*-fraction data for the (a) 17.9-K (●) and (b) 40.4-K (●) experiments with fitted model [Eq. (7)] overlaid (---). Each point represents the average of approximately 20 min of data. As with Fig. 10, the shaded lines represent the point-wise uncertainty (lighter shading) as discussed in Sec. IV B. Insets show the final approximately 20 h of data. The measured concentration from the microwave cavity at the conclusion of the experiment is indicated (●) (with uncertainty bars in black), as well as the value measured using Raman spectroscopy (---). The gray shading is indicative of the Raman measurement uncertainty. Bottom: measured Raman spectra showing the rotational $S_0(J)$ wave-number ranges for hydrogen sampled at the end of the (c) 17.9-K experiment and (d) 40.4-K experiments including their calculated *ortho*-fraction values and uncertainties.

Uncertainty contributions to the calculated *ortho*-fraction (x_o) were determined similarly. The input coefficients were perturbed and their impact assessed through sensitivity analysis, while the contribution from frequency noise (f) was evaluated as the mean error resulting from perturbing the calculations by the standard deviation of the noise about the mean.

All uncertainty contributions for f^{eq} , k , and x_o were assumed to be independent and combined quadratically. A detailed breakdown of the standard uncertainty contributions for the 17.9-K experiment is given in Table IV, along with the combined uncertainty for each calculated parameter.

C. Comparison to natural-conversion models

In their study of the natural conversion of hydrogen, Milenko *et al.* [12] developed an empirical function to calculate conversion rate, k (in 10^{-3} h^{-1}), in terms of temperature (T in K) and density (ρ in g cm^{-3}) for both liquid and gaseous hydrogen. The functional form [Eqs.

(19)–(21)] was derived from theory, with empirical constants ($\Lambda_0, \eta, \Gamma_0, \Psi, \mu, \xi$) determined through interpolation of their own experimental data (note, the symbols used here are different from those reported in Ref. [12]). The deviation of their experimental data from the empirical function did not exceed 4.8% for liquid or gaseous hydrogen.

$$k(\rho, T) = \Lambda(T)\rho + \Gamma(T)\rho^\xi, \quad (19)$$

$$\Lambda(T) = \Lambda_0 T^\eta, \quad (20)$$

$$\Gamma(T) = 5 \cdot 10^4 (\Gamma_0 + \Psi T^{-\mu}). \quad (21)$$

The calculated conversion rates (k) from the Milenko *et al.* [12] empirical equation (with a 4.8% uncertainty) are available in Table V. Notably, the rate constant values from this work for liquid and supercritical gas hydrogen are consistently higher than those of Milenko *et al.* [12]. This could be due to several possible causes.

Firstly, it is well established in the literature [58,72,73] that the interaction of hydrogen molecules with ferro- or paramagnetic metallic surfaces can facilitate spin-isomer

TABLE IV. Contributions to combined standard uncertainty and their values for the calculation of equilibrium frequency (f^{eq}), natural conversion rate constant (k), and *ortho*-fraction (x_o) for the 17.9-K experiment.

Contribution	Value	Error in f^{eq} /MHz	Error in $k/10^3 \text{ h}^{-1}$	Error in $x_o/\text{mol/mol}^a$
f/MHz	0.00 864	5.4×10^{-4}	0.017	0.0031
f^0/MHz	0.0201	2.9×10^{-8}	1.0×10^{-6}	4.6×10^{-10}
f^i/MHz	0.00 764	0.0015	0.099	4.6×10^{-4}
$x_o^i/\text{mol/mol}$	0.0112	1.4×10^{-5}	0.27	0.0038
T/K^b	0.0115	5.6×10^{-6}	2.5×10^{-5}	2.7×10^{-6}
f^{eq}/MHz	0.00 157	...	...	3.7×10^{-4}
Total standard uncertainty		0.002	0.3	0.005

^aAll contributions are the mean error across the entire experiment.

^bThe uncertainty in temperature is assumed to only influence the calculation of x_o^{eq} .

conversion through adsorption and electron transfer. The extent of *o-p* conversion is influenced mainly by the magnetic properties of the metal and the surface-to-volume ratio of the containment cell [73]. In the study by Milenko *et al.* [12], a 2-cm³ Br-B2 beryllium bronze cylindrical cell (surface-area-to-volume ratio approximately 0.5) was used, whereas this work employed a 14.9 cm³ Aluminum 6061 internally conical cell (surface-area-to-volume ratio approximately 2.5). Given these values, the observed difference in conversion rates (Table V) can potentially be attributed in part to the different surface-area-to-volume ratios.

Secondly, and more significantly, in the work of Milenko *et al.* [12], the conversion-rate constant was fit to data acquired over a relatively short time period with a limited extent of conversion, starting from approximately normal hydrogen at 74.9 mol% and finishing at or above 64 mol% for all temperatures. This limited range of composition leads to increased uncertainty in the fitted model parameters, particularly for lower temperatures where the equilibrium *ortho*-fraction is significantly lower than 64 mol%. Figure 12 illustrates the variation in the fitted k -value if the data are truncated at varying amounts of conversion, which is examined using the 19.9-K experimental data from this work (equilibrium *ortho*-fraction of 0.17 mol%). Here, k_{full} is the fitted rate constant to the full dataset (as in Table III), and k_{fit} is the refitted rate constant

to the data truncated at the respective *ortho*-fraction. The right-most point corresponds to the dataset truncated to an *ortho*-fraction of 64 mol% and has a relative deviation in k_{fit} of over 100% from k_{full} . The estimate for k_{fit} only converges to a consistent value (k_{full}) within the experimental uncertainty at *ortho*-fractions below approximately 35 mol % when the dataset spans a large enough conversion range such that the fitted parameters k and f^{eq} become sufficiently independent of one another, reducing the sensitivity of the fit parameters to small changes in curvature.

Considering these potential sources of discrepancy, there is agreement between the natural conversion-rate constants (k) obtained in this study and those reported by Milenko *et al.* [12]. The strong correlation between the second-order reaction model presented by Milenko *et al.* [12] and experimental data confirms that the observed signal changes were dominated by natural *o-p* hydrogen conversion.

D. Comparison to thermophysical property models and data

The measured dielectric constant of *para*-hydrogen [from f_p , Eqs. (14) and (1)] for each experiment in this work was converted to specific polarizability (P/ρ) via Eq. (2) for comparison with previous literature data. The values are presented in Table VI.

TABLE V. Experimentally determined rate constants (k) and those predicted by Milenko *et al.* [12] empirical equation based on interpolation of their data. Densities were calculated using the Leachman *et al.* EOS for normal hydrogen [3] as implemented in REFPROP 10.0 [24] or empirical models for solid H₂ [65,66].

Experiment	Density/kg m ⁻³	Measured rate constant (k)/10 ³ h ⁻¹	Milenko <i>et al.</i> rate constant (k)/10 ³ h ⁻¹
10.0 K	88.6	24.8 ± 0.6	35.77 ± 1.72^a
16.6 K	78.3	19.2 ± 0.6	15.15 ± 0.73
17.9 K	76.3	17.8 ± 0.3	13.87 ± 0.67
19.9 K	75.6	17.6 ± 0.4	13.26 ± 0.64
40.4 K	34.7	5.8 ± 0.3	5.24 ± 0.25

^aCorrelation not recommended for use with solid hydrogen but is shown here for comparison.

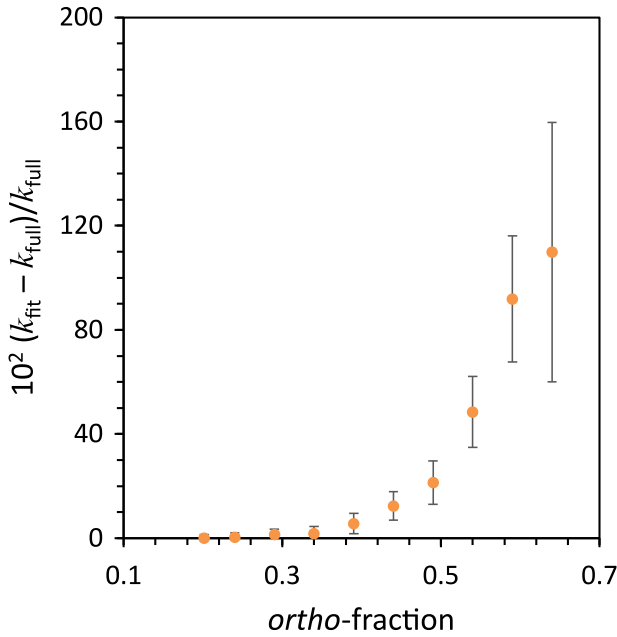


FIG. 12. Relative deviation of the fitted k value (k_{fit}) for experimental conversion data ending at the indicated *ortho*-fraction (initially normal hydrogen), based on the 19.9-K (●) dataset. The fitted k value converges on a stable value as the end *ortho*-fraction approaches the lowest value. The results for each intermediate *ortho*-fraction were obtained by truncating the experimental datasets from this study to end at different *ortho*-fraction values and comparing the result to the full dataset (k_{full}). The error bars are the uncertainty as calculated via the method outlined in Sec. IV B.

These results for specific polarizability are compared with literature values in Fig. 13. The values measured in this work are well within the scatter of the historical data. More important for the analysis of conversion measurements and *o-p* compositions is the difference in polarizability between normal and *para*-hydrogen. Figure 14 illustrates the effective frequency shift observed between normal hydrogen and *para*-hydrogen in this work, that of Pashkov and Lobko [67], and the expected shift based on the default models implemented in REFPROP 10.0 [24],

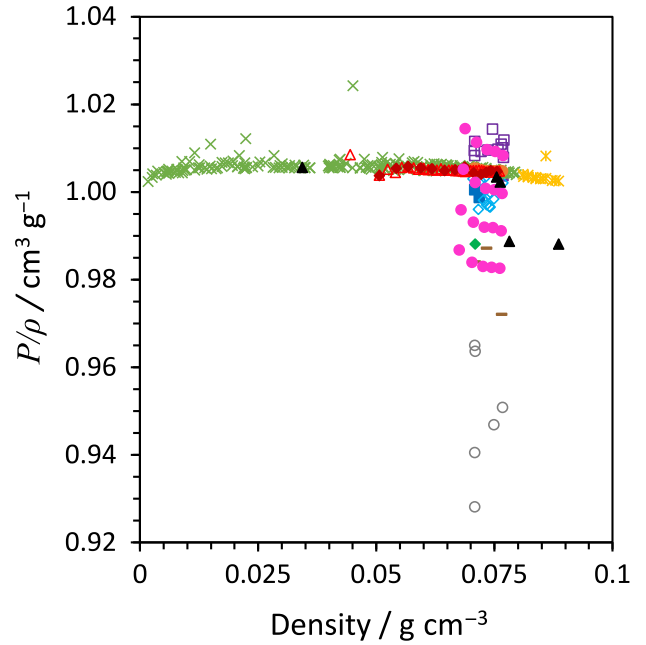


FIG. 13. Experimentally measured specific polarizabilities of fluid *para*-hydrogen as a function of density from the literature. (○) Breit 1924 [74], (—) Wolfke 1924 [75], (□) Werner 1925 [76], (■) Johns 1937 [77], (◇) Guillien 1940 [78], (●) van Itterbeek 1942 [79], (×) Stewart 1964 [80], (★) Younglove 1968 [65], (●) Milenko 1975 [46], (△) Pashkov 1979 [81], (●) Pashkov 1980 [67], (●) Charignon 2007 [82], (▲) this work (note: the largest density point is for solid).

which uses the EOS from Leachman *et al.* [3] for density, and the dielectric virial coefficient model from Harvey and Lemmon [42]. As in Sec. III E, the polarizations for *ortho*- and *para*-hydrogen were assumed to mix linearly for calculation of the dielectric constant of normal hydrogen.

Within the dielectric model implemented in REFPROP 10.0 [24], there appears to be a misrepresentation of the dielectric behavior of normal and/or *para*-hydrogen under cryogenic conditions. The data from Pashkov and Lobko [67] has a mean absolute deviation of their measured dielectric constant from the predictive model at the same

TABLE VI. Experimental data and calculated polarizability (P/ρ) of fluid *para*-hydrogen for the experiments conducted in this work. Densities were calculated using the Leachman *et al.* EOS for *para*-hydrogen [3] as implemented in the software package REFPROP 10.0 [24], or using empirical models for solid [65,66].

T/K	p/MPa	$\rho_p/\text{g cm}^{-3}$	f^θ/MHz	f_p/MHz	ϵ_p	$P/\rho / \text{cm}^3 \text{ g}^{-1}$
10.0	2.14	0.0886	2870	2529	1.288	0.988
16.6	4.14	0.0782	2870	2566	1.251	0.989
17.9	3.01	0.0763	2861 ^a	2561	1.248	1.002
19.9	4.01	0.0755	2863 ^a	2565	1.246	1.004
40.4	2.92	0.0343	2853 ^a	2711	1.107	1.006

^aExperiments performed after resealing the cavity, altering vacuum frequency.

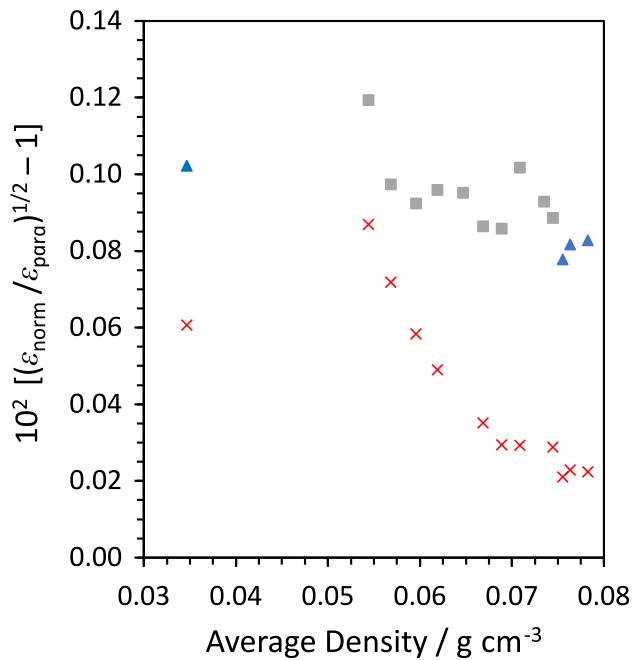


FIG. 14. Effective frequency shift ($= 10^2[(\epsilon_{\text{norm}}/\epsilon_{\text{para}})^{1/2} - 1]$) arising from the transition between normal and *para*-hydrogen (experimental or predicted), plotted as a function of density. The plot compares experimental values from this work ($\blacktriangle$), the work of Pashkov and Lobko [67] ($\blacksquare$), and the corresponding predictions using REFPROP 10.0 [24] ($\times$). Note: the displayed density is the average between normal and *para*-hydrogen at the measurement conditions.

conditions of 9.15×10^{-4} for normal hydrogen, 3 times larger than the deviation for *para*-hydrogen (2.91×10^{-4}). This suggests that the model currently underperforms in predicting the behavior of *ortho*-hydrogen-rich mixtures at these low-temperature, high-density conditions. For context, the coefficients of the Harvey and Lemmon virial dielectric model for hydrogen [42] implemented in REFPROP 10.0 [24] [see Eq. (3)] were each regressed as linear functions of temperature, where the focus was for natural gas relevant conditions between (100 and 500) K. The first virial coefficient, A_ϵ , was fitted to *ab initio* calculated static polarisabilities from Rychlewski [83] over this temperature range. However, below 100 K, where only the lowest rotational states are occupied, these same calculations predict A_ϵ to approach a constant value, which is not captured by the model's linear form. The linear temperature dependencies of B_ϵ and C for both *para*- and normal-hydrogen were fitted to a single truncated experimental dataset measured only for *para*-hydrogen by Stewart [80] between (50 and 100) K. The resulting coefficients were assumed to be equal between *para*- and normal-hydrogen. Although these dielectric virial coefficient values have been validated for normal hydrogen at room temperature by May *et al.* [47] using a quasispherical microwave resonator, it is likely that

the approach becomes inadequate at lower temperatures (and higher densities) where deviations from linearity and stronger intermolecular interactions become significant. Milenko and Sibileva [46] assume that the observed differences in behavior of dense hydrogen mixtures could be a result of the quadrupole moment of *ortho*-hydrogen molecules, which is supported by Podgorny and Pashkov [84]. The multiparticle interactions, such as quadrupole effects, are generally very difficult to determine theoretically through *ab initio* calculations and often require robust datasets to calculate [85]. Milenko and Sibileva [46] estimated the quantum correction to the second dielectric virial coefficient for *ortho*- and *para*-hydrogen using statistical mechanics but found it did not lead to satisfactory results below 50 K.

Currently, there is insufficient experimental data for hydrogen *o-p* mixtures to improve significantly on the hydrogen dielectric model at temperatures below 100 K. The data that is available is either: (i) only for normal or *para*-hydrogen [49,65,80,81,86]; (ii) assumes *o-p* hydrogen compositions without any verification [49,81,86]; (iii) does not state any *o-p* hydrogen composition [74,76,78]; and/or (iv) was acquired using outdated techniques and without necessary detail [74–76]. Thus, generating high-accuracy hydrogen dielectric data, and indeed thermodynamic-property data more broadly, at low temperatures is critical, not only for improving and validating predictive property models for normal, *ortho*- and *para*-hydrogen, but also for verifying mixing rules for *o-p* hydrogen mixtures.

V. CONCLUSIONS

This work presents a novel sensor based on a microwave cavity resonator for quantifying hydrogen spin-isomer composition *in situ* at cryogenic temperatures, validated through measurements of the natural *o-p* conversion of hydrogen in solid (10.0 K), liquid (16.6 K, 17.9 K, and 19.9 K), and supercritical (40.4 K) states with an average combined standard uncertainty of 0.007 mol/mol. By monitoring the cavity's resonant frequency change over time—corresponding to polarizability changes due to the evolving spin-isomer composition—the *ortho*-fraction of hydrogen was precisely tracked, with the final state value confirmed through independent Raman spectroscopy measurements. The observed microwave frequency shift followed a second-order reaction model, consistent with theoretical predictions and prior experimental studies on the natural conversion of hydrogen [46,50,53].

Moreover, the conversion-rate constants (k), determined via correlation with the second-order model, aligned well with the empirical model of Milenko *et al.* [12], further validating the sensor's accuracy. These results demonstrate the microwave cavity resonator's capability to precisely measure both *o-p* composition and conversion dynamics

under cryogenic conditions. These results also show that the range of conversion captured in experimental data should be carefully considered if accurate determination of conversion-rate constants is required.

This study also revealed that the polarizability changes from normal to *para*-hydrogen measured in this work are consistent with the previous literature [67] but exhibit significant discrepancies when compared to current predictive models for hydrogen's dielectric properties [3,24,42]. This highlights the urgent need to reassess hydrogen dielectric models, especially in the cryogenic temperature regime.

Overall, the microwave cavity resonator sensing method presented here holds potential for further development as an in-line instrument for monitoring hydrogen liquefaction industrial processes, particularly for real-time monitoring of hydrogen *o-p* catalyst performance at cryogenic conditions.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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