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Spin Isomer Conversion Kinetics in Supercritical Fluid Hydrogen

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A detailed kinetic study of para-ortho hydrogen conversion under supercritical conditions using rotational Raman scattering is presented. Isochoric measurements over temperatures $32<T<280$ K and densities $0.014<\rho<0.060$ g/cm^3, revealed autocatalytic conversion constants in the range $0.1<k<0.6$ hr^{-1}, consistent in magnitude with previous results. However, our results demonstrate that k decreases with T, contrasting previous measurements based on thermal conductivity, but similar to the original predictions of Wigner.

Molecular hydrogen consists of two protons with nuclear spin 1/2, thus obeying the Pauli principle requiring the total wave function of the system to be antisymmetric with respect to the permutations of the nuclei. The two proton spins can form a singlet (total nuclear spin 0) or a triplet (total nuclear spin 1) state, which are referred to as para -H_2 or ortho-H_2 respectively. Since the nuclear spin wave function of the para (ortho) configuration is antisymmetric (symmetric), the rotational wave function must be symmetric (antisymmetric), thus allowing only even (odd) values for the rotational quantum number J.[1] As a result, the conversion from the ortho state with J = 1 to the ground state with J = 0 is strictly forbidden for an isolated H_2. However, the presence of a nearby magnetic gradient is known to decouple the spin wave functions and enable this transition.[2] This magnetic field gradient may be supplied by foreign paramagnetic[3] and diamagnetic[4] atoms, or by any existing ortho-H_2 molecules themselves in a second-order autocatalytic process.[5] In addition, energy conservation requires coupling to either collisions or collective excitations (e.g. lattice phonons), the latter having profound implications in solid H_2 at high pressures.[6-7] Thermodynamically, the spin transition from ortho to para (para to ortho) is exothermic (endothermic), with an enthalpy of conversion of 706 kJ/kg at 20.3 K.[8] Until recently, there was little need to study the para/ortho-H_2 conversion kinetics in fluids as hydrogen was stored only at near constant temperature (as a liquid, 20.3 K, where hydrogen is 99.8% para, or as a compressed room temperature gas, 75% ortho and 25% para). Contrary to those technologies, cryogenic high pressure storage operates at varying temperatures (between liquid temperature and 100 K, and above), conditions under which the equilibrium fraction of para and ortho varies quite a lot. The interesting consequence is that the endothermic para to ortho reaction could absorb a non-negligible amount of energy and thus reduces the self-pressurization of cryogenic high pressure H_2 storage system, a phenomenon that is critical for the technology (boil off losses). Yet while several fundamental studies have been performed on ortho-to-para (o-p) conversion in the solid state,[4, 6-7, 9-11] surprisingly few studies exist on conversion kinetics of fluid H_2 in the supercritical region. The earliest known studies of ortho-to-para conversion kinetics in isothermal liquid H_2 were from Cremer and Polanyi[5] who found a rate constant k= 12x10^{-3} hr^{-1} at 20 K. More recently, Milenko et al.[12] presented o-p conversion data on both liquid (17 - 32 K) and gaseous/supercritical (40 - 120 K) up to densities of 0.09 g/cm^3 based on H_2 thermal conductivity measurements. A semi-empirical model was also presented which supplemented the well-known Wigner model[2] by including the dependence on velocity of the approach distance between colliding molecules in the derivation of k. While the conversion rate constant was observed to scale (roughly) linearly with density, their data showed an *increase* in conversion rate with temperature, in contrast to the ~T$^{-1/2}$ law expected from Wigner's theory. Because of the dramatic effect this difference can have on the low temperature kinetics, and therefore dormancy, of future cryogenic fuel storage systems, additional study is of interest, particularly at small initial ortho concentrations.

In this letter, we report a study of para-ortho (p-o) conversion of supercritical fluid H_2 under high density cryogenic conditions using rotational Raman scattering. The range of % ortho, density and temperature was chosen for practical interest for cryogenic high pressure storage applications, but also to extend fluid H_2 kinetic modeling beyond what has been previously published.[5, 12-13] J=0 and J=1 rotational transitions were successfully used to quantify spin isomer concentrations. Consistent with previous observations below 120 K, a roughly linear dependence of k on density was found. However, for the ranges studied here, k was observed to decrease slightly with temperature, in disagreement with other published work. The

relevance of the observed spin isomer kinetics on cryogenic high pressure H_2 storage energy absorption is also discussed.

Details of the high-pressure cryogenic tank design are given elsewhere.[14] Briefly, a 151 L Al-lined cryogenic storage vessel was used for the conversion experiments. The H_2 used in this study was 99.997% pure. All experiments began with an initially pure (>99%) para-H_2 sample at 20.3 K, which was allowed to warm and pressurize to a maximum working pressure 35 MPa. A Si diode was used to measure temperature to an accuracy of better than 0.12% while the pressure transducer used had an accuracy of +/- 0.17 MPa. Fluid H_2 density curves were derived from measured state variables (P and T) using the Younglove equation of state for hydrogen.[15] The uncertainties in density for the equation of state are 0.1% in the liquid phase, 0.25% in the vapor phase, and 0.2% in the supercritical region. Following an initial small venting procedure ($\Delta P<0.06$ MPa), H_2 gas samples were extracted from a bleed valve into a 12.5 mm diameter, 60 mm long Cu vessel equipped with 5 mm thick fused silica windows, at room temperature. Raman scattering measurements were carried out using a diode-pumped frequency-doubled Nd-YVO_4 CW laser operating at 532 nm in a back-scattering confocal collection geometry. Filtered Raman light was dispersed through an f/4 spectrometer onto a LN-cooled 1100x330 pixel back-illuminated CCD, yielding a spectral resolution and accuracy of ~4 cm^{-1} and <1 cm^{-1}, respectively. A quartz-tungsten-halogen lamp was used for absolute intensity calibration. The total integration time for each spectrum was 60 s.

Figure 1 shows the observed change in H_2 rotational Raman scattering measured from samples taken at 72 and 168 K (20 and 35 MPa respectively) corresponding to a density of 0.051g/cm^3. Between 200 and 700 cm^{-1} two peaks at 354 and 587 cm^{-1} are observed corresponding to the $S_0(0)$ rotational transition ($J=2\leftarrow 0$) of para-H_2 and the $S_0(1)$ transition ($J=3\leftarrow 1$) of ortho-H_2 respectively. Raman peaks corresponding to $S_0(2)$ and $S_0(3)$ transitions (>700 cm^{-1}) were observed but not used for relative concentration measurements. The observed Raman bands were well fit (least-squares) to a Gaussian, from which the area of each peak was numerically evaluated. The concentration x_J of para- (J=0) and ortho-H_2 (J=1) isomers was derived from integrated scattering intensities I_J given proportionally by[16]

$$I_J = \frac{(J+1)(J+2)}{(2J+1)(2J+3)} x_J p_J \gamma_J^2 \omega_s^3 \qquad (1)$$

where p_J is the Boltzmann-distributed population of the initial J^{th} level (at room temperature, T=295 K), γ_J is the anisotropy of the polarizability tensor[17] and ω_s is the scattered light angular frequency. A sample of normal H_2 (o:p ratio of 3:1) was used to verify our method, yielding a value of x_0=0.752±0.026. Independently, calorimetry was used to calculate total heat flux and monitor the endothermic conversion process in order to compare with our measured conversion rates. For example, for our ρ=0.051 g/cm^3 trial, 9400 kJ was absorbed by the system, indicating a gain of 2400 kJ due to spin isomer conversion, peaking at T~220 K in good agreement with peak conversion rate as determined by Raman measurements.

Depending on the target density, our pressure vessel was filled then vented over a series of steps to maintain a single supercritical phase, resulting in starting o-H_2 concentration between 0.2 and 10 %. The spin isomer conversion was monitored as a function of time and temperature over several days to weeks. Figure 2 shows the relative time evolution of o-H_2 for 0.014, 0.028, 0.051 and 0.060 g/cm^3 systems. For clarity, the time axis has been offset for each case. Given that the temperature range for each density is comparable (see inset), the density dependence on conversion is evident. As shown in Fig. 2 (inset), the gradual approach of o-H_2 towards

equilibrium can be confirmed by comparing our data with the calculated equilibrium ortho concentration based on the quantized rigid rotator partition function.[9]

One concern about this study on natural para-ortho conversion kinetics is the possible effect of catalysis near the wall of the tank. If the diffusion time is small enough within the hydrogen tank, the catalytic effect could outrun the intrinsic effect. To explore this possibility, we modeled the diffusion time of molecular ortho-H_2 across the dimensions[14] of our system using the Stokes-Einstein equation with calculated viscosities[15] and the Fick's laws. By fixing the initial slope of the modeled extrinsic conversion to our observed values, we find that this diffusive-catalytic effect is negligible above ortho fractions of ~1%. Kinetics rate constants obtained at ortho fraction lower than 1% should thus be disregarded.

In order to examine the p-o conversion kinetics and $k(\rho,T)$ specifically in more detail, and over a wider temperature range than previously reported, we now focus attention on the 0.028 and 0.051 g/cm^3 cases for which more finely spaced (in time) Raman data was taken. The kinetic equation governing the autocatalytic evolution of the two spin isomer concentrations towards equilibrium can be described by[12]

$$\frac{dx_0}{dt} = k\,\frac{x_0\left(x_0 - x_e\right)}{1 - x_e} \tag{2}$$

where $k=k(\rho,T)$ the ortho-to-para conversion rate constant and x_e the equilibrium fraction of o-H_2 as a function of temperature. Using our measured T and EOS-derived ρ, we first constructed $k(\rho,T)$ using the form derived by Milenko, and solved Eq. (2) to find $x_0(t)$. In all cases, we observed a more rapid conversion than the calculated values, except when $x_0 \approx x_e$, as can be seen by comparing the data of 0.028 and 0.051 g/cm^3 in Fig. 2 to calculated curves (dashed lines).

We next numerically evaluated Eq. 2 for each time-temperature step, and derived k for each density case. The results, for x_0>1%, are shown in Fig. 3 where we have taken the liberty of normalizing k by ρ. Although weakly temperature dependent, a slight decrease in k was observed, in contrast to previous work (dashed curve). Both comparison of our measured $x_0(t)$ and extracted $k(\rho,T)$ suggest revisiting the original work of Wigner, who first described the influence of a perturbing magnetic field gradient on the H_2 ortho-para conversion rate.[2] According to Wigner's theory, the transition rate is given by

$$Z_{o-p} = \frac{\mu_P^4}{9r^6 B k_B T} \tag{3}$$

where r is the (temperature independent) collision distance and μ_P is the proton magnetic moment. Assuming ideal gas collision rate statistics, the resulting form of the kinetic constant follows $k \sim \rho T^{-1/2}$. However, Milenko et al. showed that by accounting for a plausible temperature dependence on the collision distance, $k \sim T^{7/12}$, fundamentally in disagreement with Wigner's theory. Unfortunately, due to the strong dependence of Z_{o-p} on r in Eq. (3), quantitative evaluations of either model are rather difficult. However, for qualitative comparison with our results, we consider a very short collision distance r=50 pm (considerably shorter than the hard core Lennard-Jones diameter of 300 pm). Figure 3 shows the result of this conversion rate calculation (normalized by ρ), along with the experimentally-derived formula from previous results.[12] While the overall magnitude of our normalized k's based on Raman agree well with previous measurements based on thermal conductivity, the slight decrease with increasing temperature appears to favor Wigner's original theory. Because our study focused on low ortho concentrations, one possible explanation of the difference could transient local phase

separation in higher ortho mixtures that enhances conversion. Alternatively, if the velocity dependence of the turning (collision) distance as previously described were weaker, a slower conversion rate would be observed.

The kinetics of para-ortho hydrogen conversion under cryogenic, high-pressure conditions relevant to H_2 fuel storage technologies was presented. Rotational Raman scattering measurements of initially low % ortho-H_2, revealed autocatalytic conversion constants which were weakly temperature-dependent, agreeing in magnitude with previous results, but of opposite sign. Below 1% ortho concentration, extrinsic effects associated with particular paramagnetic impurities could be responsible for the observed deviation from prior work. Resolving the exact nature of para-ortho conversion at low % ortho-H_2 will likely be an important issue for understanding the exact contribution of para/ortho conversion in the energy absorption process under different cryogenic high pressure conditions.

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FIGURE CAPTIONS

Figure 1: Room temperature rotational Raman spectra of H_2 spin isomer mixtures corresponding to a density of 0.051g/cm^3, sampled at two different temperatures and pressures: 109 K, 34 MPa (blue) and 68 K, 17 MPa (red).

Figure 2: Concentration of ortho-H_2 as a function of relative time (main graph) and absolute temperature (inset) for densities 0.014, 0.028, 0.051 and 0.060 g/cm^3. Model predictions for the 0.028 and 0.051 g/cm^3 cases, as discussed in the text, are also shown (dashed: Ref. 13, solid: Ref. 2). Also shown in the inset is the calculated equilibrium concentration based on the quantized rigid rotator partition function (dashed line).

Figure 3: Normalized conversion rate constant k/ρ vs T for ρ =0.051 g/cm^3 (blue symbol) and ρ=0.028 g/cm^3 (red symbol) compared with model curves (see text).

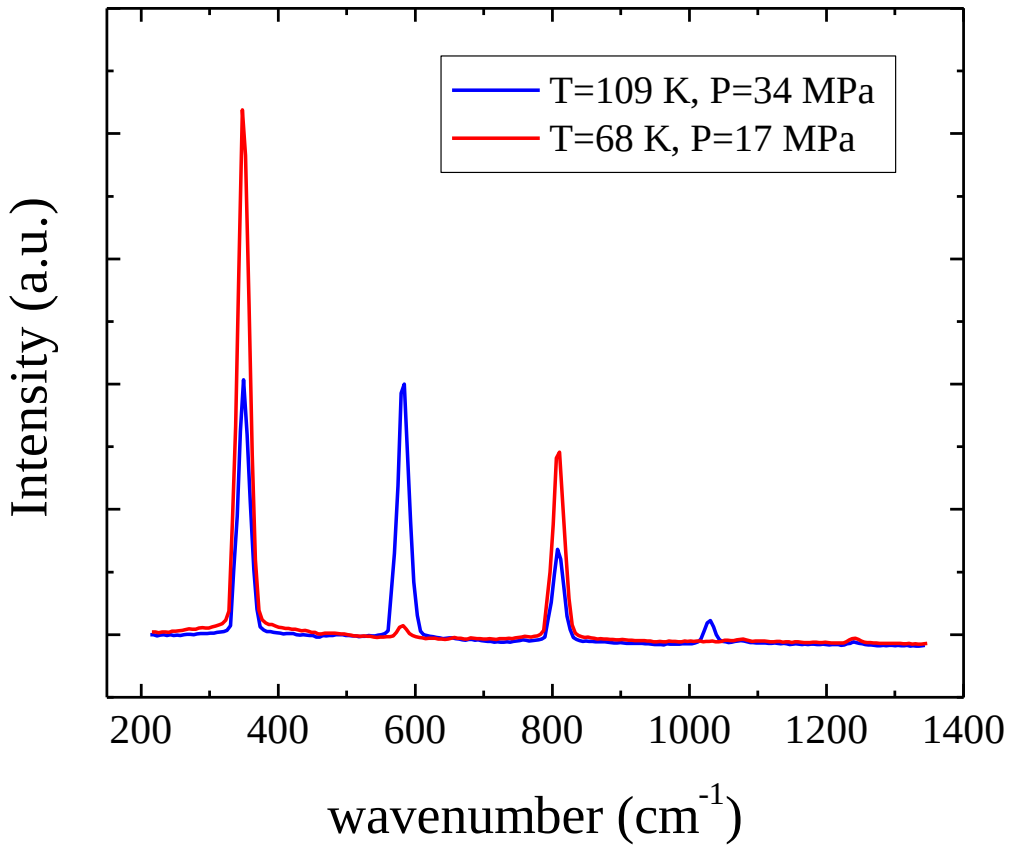
T=109 K, P=34 MPa
T=68 K, P=17 MPa
Intensity (a.u.)
200
400
600
800
1000
1200
1400
wavenumber (cm-1)

FIGURE 1

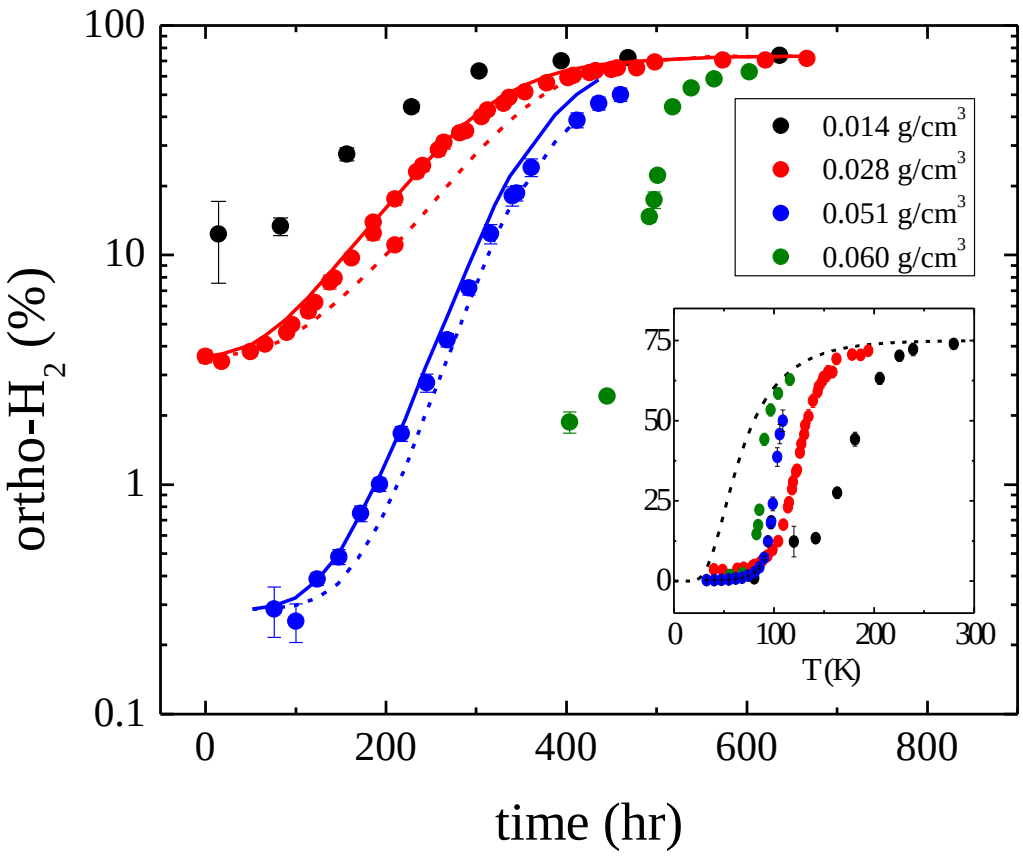
100
10
1
0.1
ortho-H2 (%)
0
200
400
600
800
time (hr)
0.014 g/cm3
0.028 g/cm3
0.051 g/cm3
0.060 g/cm3
75
50
25
0
0
100
200
300
T(K)

FIGURE 2

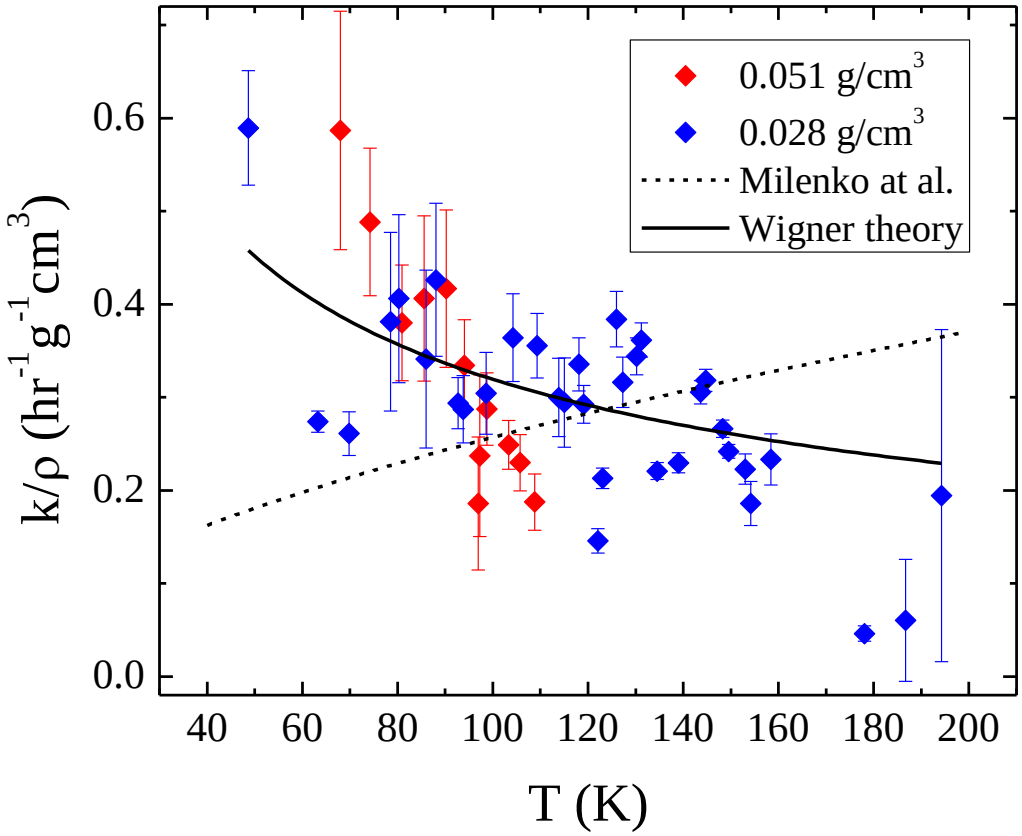
0.051 g/cm3
0.028 g/cm3
Milenko at al.
Wigner theory
0.0
0.2
0.4
0.6
40
60
80
100
120
140
160
180
200
T (K)
κ/ρ (hr-1 g-1 cm3)

FIGURE 3