NMR Study of Ortho-Para Conversion at High Pressure in Hydrogen

Michael G. Pravica and Isaac F. Silvera
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 27 May 1998)

We have studied ortho-para conversion of hydrogen to high pressures in a diamond anvil cell using NMR. The conversion rate equation is modified for high temperatures to include a first order process related to the known quadratic rate constant. The rate constant which is 1.9%/h at zero pressure, rises, dips, and then increases to 58%/h at our highest pressure, 12.8 GPa. [S0031-9007(98)07610-8]

PACS numbers: 62.50.+p, 67.80.Jd

Molecular hydrogen has the remarkable property of having two species, ortho and para, due to the requirement that the wave function be antisymmetric under exchange of the spin-$\frac{1}{2}$ protons. The single-molecule wave functions for para-hydrogen (p-H_2) have nuclear spin 0 and even rotational states with quantum numbers J, M, while ortho-hydrogen (o-H_2) has total spin 1 and odd rotational states [1]. Since at low temperature, para is a spherically symmetric molecular state in the $J = 0$ free rotor state, while ortho is in the orientationally nonuniform $J = 1$ states, solids of the two species have profound differences, both in their structures and excitation spectra. In recent years there have been extensive studies of phases of hydrogen at high pressure with little knowledge of the ortho-para (o-p) concentration, except perhaps for limiting values. As there is a continuous variation of ortho concentration between 0 and 1, there is a continuum of phase diagrams which should be labeled by their ortho concentration. In this Letter we report an NMR study of the o-p conversion rate constant as a function of pressure or density to 12.8 GPa (128 kbar).

Pure solid o-H_2 converts towards equilibrium at a rate of 1.9%/h at zero pressure [1–4]. Low pressure studies (to ~0.6 GPa) have shown the rate constant to increase to several percent/h [1–4] and then decrease [3–4]. There are two fundamental methods of measuring o-p conversion: (1) the method we have used, NMR: the ortho molecules with $I = 1$ contribute to the nuclear magnetization and thus the NMR signal, while the $I = 0$ molecules do not, and (2) measurement of the heating due to conversion energy liberated and absorbed by the lattice. The NRM method should remain valid to the highest pressures as the nuclear states are expected to be little perturbed by pressure until the molecules dissociate into the atomic state, which is expected at multimegabar pressures [5]. The highest previous NMR study of hydrogen in a diamond anvil cell (DAC) was to 6.8 GPa [6], but o-p conversion rates were not measured. We have developed a novel pulsed NMR system [7] allowing us to study o-p conversion in a DAC. Although the rate constant is only 2%/h at our lowest pressure of 4 GPa, it rapidly increases, rising to 58%/h at our highest pressure.

A recent study by Eggert *et al.* [8,9] reports o-p conversion rate data at pressures above 100 GPa, showing data to 25 GPa. They used the ratio of the Raman intensities of the rotational lines to determine the o-p concentration. In the region of overlap our results agree with theirs at low pressure but deviate substantially at pressures above about 8 GPa. Earlier work using this method to study conversion in deuterium to pressures higher than the broken symmetry phase transition (28 GPa) was not published, because reliable results could not be obtained [10]. Knowledge of the rotational states as a function of pressure is vital for interpretation of this type of data. At low pressure the Raman method is known to yield accurate results. This is due to the valid usage of the Van Vleck sum rule which greatly simplifies relating theory and experiment. This states that the integrated intensity of the transitions is independent of the quantum states used as long as the transitions are from one complete manifold of states to another, and a sum is made over all states of the manifolds ($J = 1$ and 0) [11]. At high pressure, the spherical harmonic rotational states become mixed [12,13], so that the Van Vleck sum rule is not applicable, thus requiring a very sophisticated analysis as the rotational states depend both on density, phase, and temperature. Unlike the nuclear states, the orientational states are highly deformed by pressure so that interpretation of conversion data by this method is demanding and requires a new analysis.

Intrinsic o-p conversion in solid hydrogen was first studied theoretically by Motizuki and Nagamiya [14]. Conversion involves a change of nuclear spin as well as rotation state. The microscopic mechanism for conversion of a central ortho molecule is magnet field gradients arising from the magnetic dipolar fields of neighboring ortho molecules. At modest temperatures the central ortho molecule is in the $|Im; JM\rangle = |1m; 1M\rangle$ state and converts to the $|00; 00\rangle$ state. Since conversion depends on the presence of another ortho molecule, the rate equation is second order in the ortho concentration c,

$$\frac{dc}{dt} = -Kc^2, \tag{1}$$

where K is the conversion rate constant. In the conversion process energy must be conserved. The energy change is primarily the rotational energy $BJ(J+1)$ which changes by $2B/k_B = 170.7$ K, where B is the rotational constant. This energy is taken up by the lattice via phonon emission or absorption. At zero pressure the rate is quite slow as it is bottlenecked by a low density of final states. At this pressure two phonons are required to conserve energy. Berlinsky [15] developed the theory of conversion for modest increases in pressure. He found that a small pressure change increases the phonon energy, so that single phonons can conserve energy with a resulting increase in the rate constant, as observed experimentally [2–4]. However, the rate constant is expected to peak and then fall as the phonon density of states at the conversion energy decreases with rising pressure. Silvera [5] has proposed that the rate again increases due both to stronger spin-spin coupling with higher pressure, but mainly due to the availability of rotational states which should be more strongly coupled than the phonons and take over the role of final states energy conservation in a conversion event.

Our experimental system consists of a nonmagnetic beryllium copper DAC [16] in the bore of a high homogeneity superconducting magnet in a helium bath, along with a homemade quadrature pulsed NMR spectrometer described in Ref. [7]. The DAC can be varied in temperature from 1.2 K to above room temperature. Pressure was determined using the ruby fluorescence scale [17] to a precision of 0.15 GPa at the highest pressures. At pressures below 100 GPa hydrogen is known to be quasihydrostatic, so we expect pressure variation across the sample to be quite small. We have developed a new geometry for doing NMR with enhanced sensitivity in a DAC, reported in detail elsewhere [7]. Our gasket is made of rhenium metal, but instead of a disc shaped hole for the sample, we machined a keyhole shaped hole and filled the slot of the "keyhole" with an insulator, so that the sample is confined in the circular section. In this way an rf field normal to the gasket can fully penetrate the sample resulting in a large filling factor. Although the gasket itself can be used as a single-loop inductor, we used a separate, similarly shaped copper inductor above the gasket to couple the rf signal in and out of the sample. This was part of an LC tank circuit which was connected to matching and tuning circuitry at low temperature which could be adjusted *in situ* by mechanical rods extending outside of the cryostat. We estimate an enhanced sensitivity of 50–100.

We used beveled diamonds with 300 μm diameter culet flats; the initial gasket hole diameter was 205 and 120 μm thick. We estimate that 1×10^{17} molecules were in the resulting sample. The DAC was carefully cooled, and high purity hydrogen gas was condensed and sealed in the gasket hole. The main impurity in the sample was a very small concentration of the isotopes D_2 and HD, which do not have a significant effect on the conversion of hydrogen. We studied o-p conversion at a series of pressures up to 12.8 GPa. We had earlier loaded a sample of hydrogen to 25 GPa, but this had significant impurity signals and could not be reliably interpreted. The experimental measurements described below were taken over a period of seven weeks.

The strategy for studying o-p conversion takes advantage of the known equilibrium o-p concentration in which the ortho concentration c is almost 0.75 at room temperature, 0.493 at liquid nitrogen temperature (77.3 K), and is essentially 0 below 20 K (0.001 75 at 20.4 K). The sample was brought to equilibrium at 77.3 K, so that the concentration was known, and an NMR signal was measured to calibrate the signal voltage in terms of concentration. The sample was then rapidly lowered in temperature below 20 K, the signal immediately measured and then sampled in regular time intervals as it converted towards the new equilibrium. When the conversion constant was determined, the sample pressure was then changed. The sample was then rapidly warmed to a new temperature, and the pressure and NMR spectra were measured as it converted towards its new equilibrium. We expect the rotational spectrum to change at high pressure and therefore the equilibrium o-p concentration. This can be measured by changing the pressure of an equilibrium sample at a fixed temperature for which the equilibrium concentration, c_{eq}, is nonzero and observing the change to the new equilibrium. This would be an interesting phenomena to study and may require a focused experiment as the changes may be small and occur only at higher pressures. We saw no evidence of such a change within our noise limits, although it was not carefully studied for all pressures. Finally, we mention here that there is an orientational order-disorder line for hydrogen which depends on concentration and pressure [18]. For pure ortho, ordering takes place at 2.8 K at zero pressure and the transition temperature scales as the $\frac{5}{3}$ power of the density. We found a change in the NMR spectrum when we entered the ordered phase, as expected. However, in the present work we restricted our studies to the disordered phase, as we expect the conversion rate to depend on the state of order [19]. We carried out the low temperature studies above the estimated critical temperature.

In all previous reported studies of o-p conversion, the sample was allowed to convert to a low temperature equilibrium so that Eq. (1) was used to fit the data. In our work we also allow the sample to convert to equilibrium at high temperatures so that c_{eq} is nonzero. In this case there is also a first order conversion rate term as required for detailed balance and the rate equation becomes

$$\begin{aligned}\frac{dc}{dt} &= -Kc^2 + K'c(1-c)\\ &= -Kc(c-c_{\mathrm{eq}})/(1-c_{\mathrm{eq}}). \qquad (2)\end{aligned}$$

Here K' is the back conversion rate constant for the change of a para molecule to an ortho due to an ortho neighbor. The second expression is found by solving

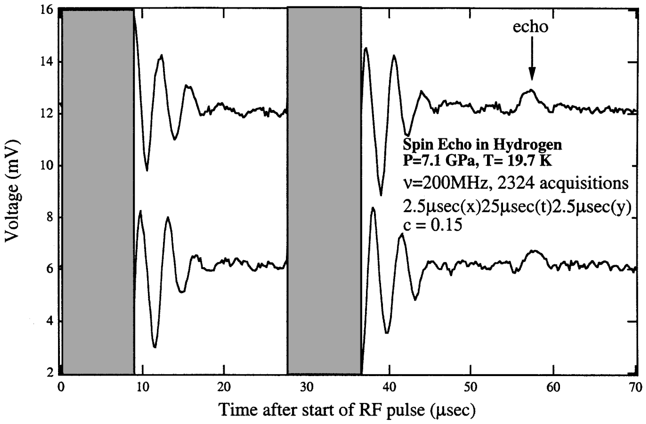

FIG. 1. An FID and a spin echo at 200 MHz. The pulses were 2.5 μs long with a 25 μs delay for the echo pulse. The spectrometer is blanked off for approximately 4 μs after a pulse.

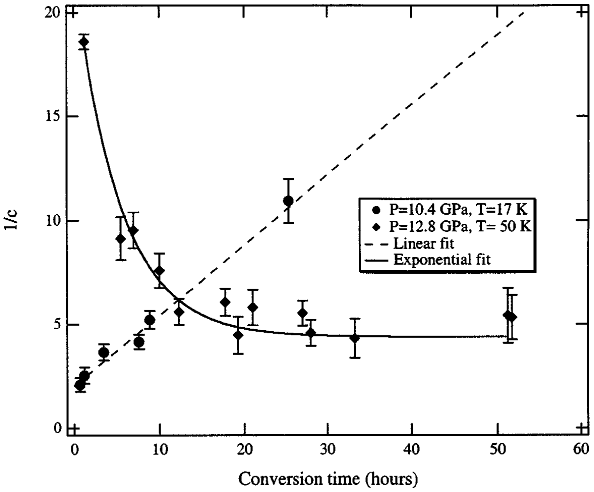

FIG. 2. A plot of $1/c$ vs time for measurements at high and low temperatures. The lines are fits to the data using Eqs. (1) and (2).

K' in terms of K at equilibrium, where dc/dt is zero and $c = c_{\mathrm{eq}}$; the equation can be integrated analytically for comparison with experiment. In the back-conversion process a para molecule in the presence of a spectator ortho is converted to ortho.

To determine the ortho concentration we studied NMR free induction decays (FIDs) as well as spin echoes. Both are expected to have Gaussian line shapes in the temperature range we studied [20] with a peak amplitude proportional to the magnetization [21]. In Fig. 1 we show an FID and a spin echo at $T = 19.7$ K for hydrogen at a pressure of 7.1 GPa for the two channels of our quadrature NMR spectrometer. Much stronger echoes were observed at 4.2 K, but the FID was distorted due to the orientational ordering. The echo signal could be fit to a Gaussian modulated by a sine function [22]. Ideally the magnetization would be determined from the peak of the echo. In hydrogen T_2 is of the order of a few microseconds, and as a consequence the echo is highly attenuated if the echo time τ is longer than T_2, which is the case. On the other hand, in our spectrometer we use a single coil for the pulse and detection. The receiver is blanked off for about 4 μm after the pulse ends, so that we cannot observe the peak of the FID. Since the FID has a much larger signal than the echo, we fit the tail of the FID to the product of a Gaussian and a sine to determine the peak value and, thus, the ortho concentration. The dominant error in the concentration determination is then the error in the fit to a Gaussian. In Fig. 2 we show results for the measurement of c^{-1} vs time at pressures of 10.4 and 12.8 GPa from which we extract conversion constants. In the lower pressure case conversion is towards an equilibrium concentration of almost zero while the higher pressure measurement is up-conversion towards a nonzero equilibrium value, $c_{\mathrm{eq}} = 0.228$. In Fig. 3 we show the pressure dependence of the conversion rate constant and have included data from other researchers. The error bars here are determined by the fit to the rate equation and are one sigma values. Note that the error bars are large for some pressures and small for others. In general, this is due to the temperature of the measurement. The concentration is highest at 77.3 K (the highest temperature we studied), but the signal is proportional to the magnetization times the circuit Q. The magnetization scales as T^{-1} due to the Boltzmann factor, while the Q scales roughly as $T^{-1/2}$, so that the signal scales as $c/T^{3/2}$. The two highest pressure points (Fig. 2) were determined at 17 and 50 K and thus have a larger relative error than other points.

The conversion rate is seen to increase and then decrease with rising pressure below 1 GPa, as explained in the introduction. At our lowest pressure point, the

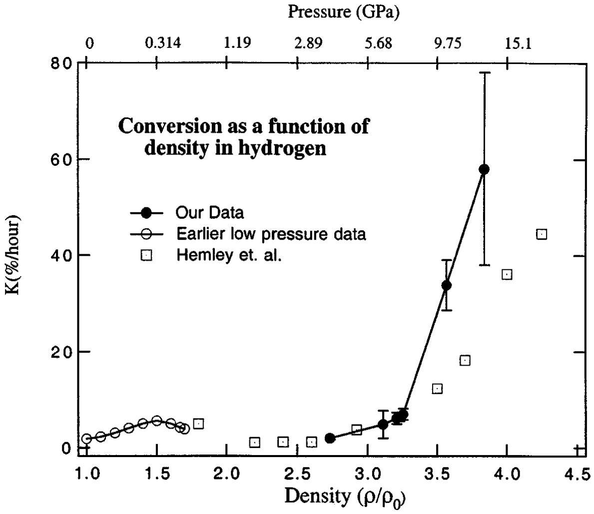

FIG. 3. The rate constant vs density ($\rho_0 = 0.04318$ mole/cm^3) and pressure; the earlier data is from Refs. [2–4]. The lines are guides to the eye.

conversion rate has reduced to around the zero pressure value. The rapid increase with increasing pressure seen in our data is most likely due to a new final states channel in which a density of rotational states shifts to lower energy and can perform in the energy conserving role.

In Fig. 3 we show the deviations between our results and those of Eggert *et al.* and Hemley *et al.* [8,9] who studied conversion in hydrogen using Raman scattering. At low pressures our measurements are in agreement, while for pressure points above 10 GPa our rate constant values are about twice theirs. We remark that NMR is a fundamental technique for this type of study, whereas the theory for a Raman study at high pressures where J is no longer a good quantum number has not yet been developed. Not only are the rotational states highly distorted by pressure, but the rotational excitations overlap a phonon mode with strong mode mixing, which must be carefully considered in use of the Van Vleck sum rule. Since the techniques used by Eggert *et al.* are not discussed in detail, it is useful to discuss other possible sources for the deviations. Since our rates are higher (in the higher pressure region), one might suspect impurities, as impurity conversion can only increase the rate. We were careful to avoid impurities in our sample. Our gasket and gasket materials were nonmagnetic. Even so, magnetic impurities can introduce a transient rapid conversion in the region around the impurity while the bulk conversion is minimally affected. Schmidt [23] saw little effect on the conversion rate constant at ambient pressure with a hydrogen sample that included 20% paramagnetic oxygen. Furthermore, if our sample was contaminated we would expect disagreement for all pressures, which is not the case. Another explanation might be that conversion was measured at different temperatures. Our work was performed near or below 77.3 K. At higher temperatures we expect the conversion rate to change as the $J = 2$ level is thermally occupied, so that conversion involves the $J = 2$ and 1 rotational states (rather than 1 and 0), and therefore the final states energy is $4B$ rather than $2B$, so that different conversion channels are open for conserving energy. This would most likely increase the rate constant. At low temperature, orientational ordering will effect the rate constant; all of our work was carried out in the disordered state. Berlinsky's calculation was carried out for very low pressure with decay to two-phonon final states. The change of the conversion rate is not negligible, but his calculation does not apply to the high pressure regime. Finally, we mention that at low temperature quantum diffusion of ortho can lead to clustering and formation of pairs, so that the distribution in the lattice is nonrandom. In this case an ortho molecule has more than the average number of ortho neighbors and the conversion rate increases, leading to upward curvature in a $1/c$ vs time plot [23]. In such a case in order to extract the rate constant a more complex analysis must be implemented. However, in our study, to within experimental accuracy, we observed only linear behavior in such plots.

We thank Robert Pound, Frederic Datchi, and Jon Eggert for useful discussions. This work was supported under NSF Grant No. DMR-9701500.

[1] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[2] G. Ahlers, J. Chem. Phys. **40**, 3123 (1964).

[3] P. Pedroni, H. Meyer, F. Weinhaus, and D. Haase, Solid State Commun. **14**, 279 (1974).

[4] A. Driessen, E. van der Poll, and I. F. Silvera, Phys. Rev. B **30**, 2517 (1984).

[5] I. F. Silvera, J. Low Temp. Phys. **112**, 237 (1998).

[6] S.-H. Lee, M. S. Conradi, and R. E. Norberg, Phys. Rev. B **40**, 12 492 (1989).

[7] M. G. Pravica and I. F. Silvera, Rev. Sci. Instrum. **69**, 479 (1998).

[8] J. H. Eggert, E. Karmon, H. K. Mao, and R. J. Hemley, Bull. Am. Phys. Soc. **41**, 615 (1996).

[9] R. J. Hemley, A. F. Goncharov, H.-k. Mao, E. Karmon, and J. H. Eggert, J. Low Temp. Phys. **110**, 75 (1998).

[10] I.F. Silvera and R. Wijngaarden (unpublished); Rapid changes in the Raman spectral intensity were observed at high pressure (in the vicinity of the broken symmetry phase transition at which J breaks down as a good quantum number) indicating conversion, but rate constants could not be reliably extracted using the low pressure spectroscopic analysis.

[11] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University, London, 1932).

[12] P. J. Berkhout and I. F. Silvera, Commun. Phys. **2**, 109 (1977).

[13] J. C. Raich and R. D. Etters, J. Low Temp. Phys. **6**, 229 (1972).

[14] K. Motizuki and T. Nagamiya, J. Phys. Soc. Jpn. **11**, 93 (1956).

[15] A. J. Berlinsky, Phys. Rev. B **12**, 1482 (1975).

[16] I. F. Silvera, and R. J. Wijngaarden, Rev. Sci. Instrum. **56**, 121 (1985).

[17] G. J. Piermarini and S. Block, Rev. Sci. Instrum. **45**, 973 (1975).

[18] I. F. Silvera and R. Jochemsen, Phys. Rev. Lett. **43**, 337 (1979).

[19] A. J. Berlinsky and W. N. Hardy, Phys. Rev. B **8**, 5013 (1973).

[20] L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, Phys. Rev. **181**, 589 (1969).

[21] For optimum results we slightly detune from the Larmor frequency. The resulting signal is a Gaussian modulated by $\sin[(\omega_L - \omega)t + \phi]$, where ω_L is the Larmor frequency and ω the rf frequency.

[22] D. S. Metzger and J. R. Gaines, Phys. Rev. **147**, 644 (1966).

[23] F. Schmidt, Phys. Rev. B **10**, 4480 (1974).