# NMR of Dilute $o$-H$_2$ in Solid $p$-H$_2$ at Temperatures below 1 K

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We report some unusual observations on the NMR spectrum and the clustering rate of $o$-H$_2$ at low ortho concentration in solid H$_2$ at temperatures between 25 mK and 2 K. Evidence points towards motional narrowing of the HD impurities, the proton signal of which is observed for $T < 0.15$ K, and a hopping of $o$-H$_2$ from one pair configuration into another. Furthermore, there is an unexpected increase of the clustering rate of the other $o$-H$_2$ molecules as the temperature decreases below $\sim 0.1$ K.

We report some rather striking nuclear-magnetic-resonance results for $o$-H$_2$ in a single crystal and in two other samples of solid H$_2$ at temperatures between 25 mK and 2 K, with an average ortho concentration of $X = 0.015$ and as a function of the magnetic field orientation. Because only $o$-H$_2$ has a nuclear spin, the NMR spectrum at low concentrations shows the signature of isolated $o$-H$_2$ molecules and of isolated nearest $o$-H$_2$ neighbor pairs.[1] The signal from larger ortho configurations apparently gives broader lines[1] and will not be discussed further. Here we describe in detail only the data that appear to give novel information on the motions of $o$-H$_2$ and HD impurities below $\sim 0.15$ K, namely, (1) the spectrum close to the Larmor frequency where the natural HD impurities show strong motional narrowing of the proton NMR line, and (2) the clustering rate of the isolated $o$-H$_2$ into groups of two or more nearest ortho neighbors,[2-7] which increases strongly below $T \simeq 0.1$ K.

The solid H$_2$ samples were grown around copper wires of 0.1 mm diam in thermal contact with the mixing chamber of a dilution refrigerator. The continuous-wave (cw) measurements of the H$_2$ NMR spectrum were carried out using a low-level Robinson spectrometer operating at 12 MHz, the frequency of which was swept slowly while the magnetic field was kept constant. We have also measured at 9.5 and 25 MHz the longitudinal and transverse relaxation times ($T_1$ and $T_2$) of restricted portions of the spectrum where sharp lines were observed. This was done by applying long rf pulses (approximately 100 $\mu$sec for 90° pulses) that saturated only the sharp lines, and by using, respectively, 90°-90° and 90°-180° sequences.

On the first sample, with an initial concentration of about $X \simeq 0.02$, we recorded a spectrum with several very sharp lines that showed a strong change in intensity and also in frequency when the direction of the magnetic field was changed

with respect to the sample. These observations led us to believe that we were dealing with a single-crystal sample with a hexagonal symmetry whose orientation could be determined approximately. This crystal was studied over a period of about six weeks, during which the ortho concentration decreased from $X \simeq 0.02$ to $X \simeq 0.007$.

Our observations are as follows:

(1) Above about 0.15 K the spectrum includes, in particular, the central line $C_b$ (center, broad) at the Larmor frequency and two groups of triplets labeled $P$ and $P'$, and in addition some wider lines. The derivative of the spectrum is shown in Fig. 1(a) at $T = 0.55$ K. The line $C_b$, which we attribute to "isolated" $o$-H$_2$ molecules surrounded by $p$-H$_2$ neighbors, broadens as $T$ decreases and eventually shows a doublet structure that continues to widen until it becomes unobservable because of the masking by the additional lines mentioned above and because of clustering into pairs. This broadening, already discussed elsewhere,[8] is believed to be caused by the progressive quenching of the quasifree rotation by the crystalline field $V_c$ as $T$ decreases. Our analysis suggests that $V_c$ assumes a distribution of values with an rms of $|V_c|/k_B \approx 0.025$ K. The two triplet groups $P$ and $P'$ are spectra attributed to nearest $o$-H$_2$ pairs. From Eqs. (12) and (13) in Ref. 1, we conclude that the outer one is the signal of those whose pair axis is nearly parallel to the direction of the applied field, while the inner one represents pairs where the axis is nearly perpendicular to the field. Based on the observed variation of the NMR spectrum with the direction of the applied field, we conjecture that $P'$ represents out-of-plane pairs, namely those whose axis is not in the basal plane, while $P$ represents in-plane pairs. The structure $P'$ has been observed before[7,9] although with somewhat different splittings, no doubt because of a different crystal orientation. The pair spectrum, its anisotropy, and relaxation times will be reported and inter-
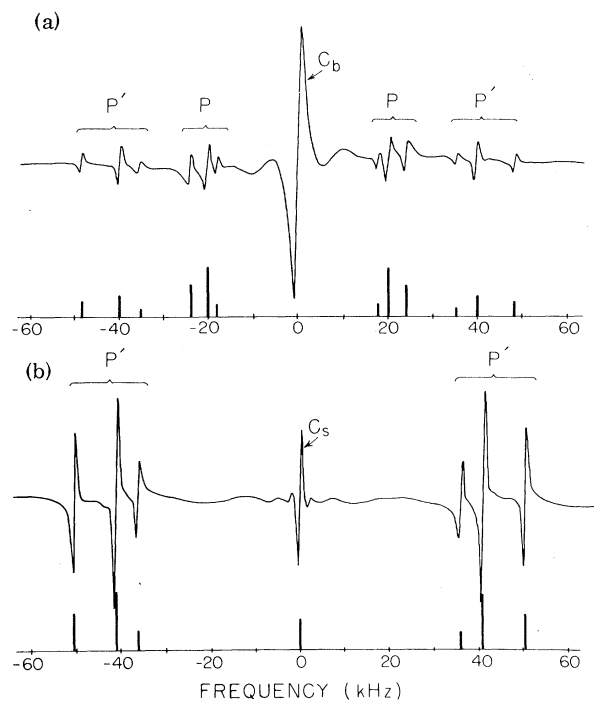
FIG. 1. (a) The derivative of the absorption spectrum of dilute $o$-$H_2$ ($X \cong 0.015$) at $T = 0.55$ K. Larmor frequency $\nu_L \approx 12$ MHz. (b) The spectrum at $T = 0.025$ K. The structures labeled $P$, $P'$, $C_s$, and $C_b$ are discussed in the text. The relative integrated intensities of the lines are shown by vertical lines on the frequency axis. No corrections were made for broadening due to field inhomogeneity.



FIG. 2. The clustering time constant $\tau$ as a function of $T$, as measured by the rate of disappearance of the structure $C_b$ as a function of time. For comparison, the experiments by Harris et al. (Ref. 1), Ramm (Ref. 5), Roffey, Boggs, and Welsh (Ref. 3), and Kohl (Ref. 7) are shown.

preted in detail elsewhere.[10]

(2) As the temperature is lowered with the crystal oriented the same way as in Fig. 1, the intensity of $P$ gradually disappears while that of $P'$ increases. Below about 0.15 K, a sharp Lorentzian line $C_s$ (center, sharp) appears at a frequency $\nu(C_s)$ slightly below the Larmor frequency $\nu_L(C_b)$ midway of the $C_b$ doublet structure.

(3) In Fig. 1(b), we present the derivative of the spectrum at $T \cong 25$ mK a few hours after cooling. Only the outer pair spectrum $P'$, the sharp line $C_s$, some additional peaks, and a broad structure are observed. The ratio of the integrated intensities of the $P'$ and the $C_s$ signals is approximately 8:1 at $X \cong 0.015$.

(4) The characteristics of the line $C_s$ are as follows: (a) The linewidth is very small, namely $T_2 = 11 \pm 2$ msec, independent of frequency, of the applied field direction, and of temperature. (b) At equilibrium, the intensity follows Curie's law and is independent of the field direction. (c) $T_1$
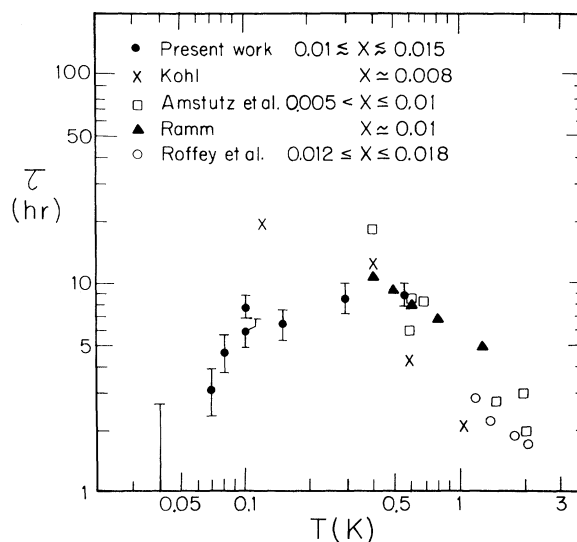
is a strong function of $T$. At $T = 0.1$ and 0.025 K, $T_1(9.5$ MHz$) \cong 2$ and 25 sec, respectively. Also $T_1(25$ MHz$)/T_1(9$ MHz$) \cong 1.5$. (d) Finally at 9.5 and 12 MHz at least, there appears to be a frequency shift $\nu_L(C_b) - \nu(C_s) \cong 0.2$ kHz which is roughly temperature independent, as determined both from cw experiments and from free-induction-decay measurements down to 0.025 K. The stability of the magnetic field was not sufficient to confirm the shift at 25 MHz.

(5) The $o$-$H_2$ clustering time constant $\tau$ at a temperature $T$ (measured from the initial intensity decrease of the $C_b$ line as a function of time after rapidly cooling the sample from 2 K) shows a broad maximum as displayed in Fig. 2. The time constant obtained from the intensity increase of the $P'$ pair spectrum during the same cooling operation also shows the maximum and is consistent with $\tau$. In Fig. 2, the data are compared with those of Amstutz, Thompson, and Meyer[2] and of Ramm[5] above 0.35 K, of Roffey, Boggs, and Welch[3] above 1.2 K, and those of Kohl[7] above 0.12 K. The previous results were also all obtained upon cooling the samples using, respectively, NMR,[2] pressure,[5] infrared absorption,[3] and NMR[7] techniques. Below 0.1 K, the clustering rate becomes quite fast. In fact, the time that it takes for the dilution refrigerator to cool from 2 to 0.05 K ($\sim$ 2 h) is comparable with, or

larger than, the clustering time constant. Such a behavior is quite unexpected from theoretical predictions.[11]

NMR measurements on the two other samples also indicated that single crystals had been grown but with their axes in a different direction from that of the first sample. The sharp line $C_s$ was again observed and the times $T_2$ and $T_1$ were consistent with those in the first sample.

We now attempt a preliminary discussion of these unusual results. First, the sharp and isotropic line $C_s$ must represent isolated HD molecules that apparently diffuse through the lattice. This conclusion is based on the line intensity in comparison with that of the whole spectrum, obtained by pulse measurements. The intensity is roughly 1.5% to 2% for the mixture with $X \simeq 0.1$, which corresponds to about 400 ppm of HD in $H_2$, which is consistent with the natural abundance, 300 ppm. The HD molecules show a diffusive type of motion: The measured line has a width $w \simeq 30$ Hz, while the calculated one for a rigid lattice with a random distribution of $o$-$H_2$ for $X \simeq 0.01$ is $w \simeq 3 \times 10^2$ Hz.[8] Hence there is appreciable motional narrowing. The longitudinal relaxation time of the $C_s$ line compares with $T_1 \sim 1$ msec for the $C_b$ line in the high-temperature regime. The difference in the Larmor frequency between the $C_b$ and $C_s$ lines suggests the possiblity of a chemical shift between $o$-$H_2$ and HD in the solid phase of hydrogen, namely $[\nu(H_2) - \nu(HD)]/\nu \simeq 20$ ppm. We are not aware that this shift has been measured before. Constable and Gaines[12] briefly reported observing the HD signal in very dilute mixtures of $o$-$H_2$ in $p$-$H_2$, and mentioned a free-induction-decay time constant of 3 msec for $X \simeq 2 \times 10^{-4}$, but no spin-echo or $T_1$ measurements. A shift in the frequency between $H_2$ and HD was not reported.

As for the disappearance of the signal from the $P$ spectrum as $T$ decreases, we suggest that since the in-plane pairs have higher ground-state energy than the out-of-plane pairs,[6] the former can transform into the latter by a jump of one $o$-$H_2$. This question will be discussed in more detail elsewhere.[10]

The obvious question is now the following: What is the origin of the motion giving the sharp $C_s$ line and the enhanced clustering? One might ask whether this is a bulk effect such as a gaslike condensate or the result of growing the $H_2$ around Cu wires, a necessary technique for the thermalization at low temperatures. Does this method lead to the formation of surface dislocations that

in turn might produce "vacancy waves"? Surface and bulk-vacancy or point-defect motions were discussed and reviewed recently by Guyer[13] and by Landesman.[13] Is the situation of bulk dilute HD and $o$-$H_2$ in $p$-$H_2$ comparable with that of He³ impurities in He⁴? Of course, the masses and molar volumes of $o$-$H_2$ and $p$-$H_2$ are equal or nearly equal, respectively, while in the He³-He⁴ system this is not so. We also note that the conditions for observing the sharp $C_s$ line in $H_2$ are greatly favored by the splitting and disappearing of the $C_b$ structure as $T$ decreases. Hence solid $H_2$ offers a unique opportunity in studying the proton signal of a small fraction of impurity molecules.

Clearly more measurements also below 25 mK should give further information on this novel phenomenon. Further investigation on these mixtures at higher frequencies and different mole fractions $X$ are in progress in this laboratory.

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# Gallium Phosphide: Observation of the $\Gamma$-$L$ Indirect Transition by Electroabsorption

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The phonon structure of the 2.67-eV indirect transition in GaP has been resolved in a transverse electroabsorption measurement. The transition is shown to be from $\Gamma_{15}$ to $L_1$, contrary to previous assignments.

In their band-structure calculations, Cohen and Bergstresser[1] predicted a conduction-band $X_1$-$X_3$ heteropolar splitting in GaP of about 300 meV. Spitzer et al.[2] observed an infrared absorption band in degenerate material which they attributed to the $X_1$-$X_3$ transition. The $\Gamma_{15}$-$X_1$ transition has been observed by many workers[3] and confirmed by observation of the phonon structure. Dean, Kaminsky, and Zetterstrom[4] observed an unresolved indirect transition at 2.67 eV, or 290 meV above the $\Gamma_{15}$-$X_1$ transition, which they attributed to $\Gamma_{15}$-$X_3$. In this Letter we report transverse-electroabsorption experiments in which the phonon structure of this transition is resolved and is seen to be appropriate to a $\Gamma_{15}$-$L_1$ transition at $2.637 \pm 0.010$ eV (78 K).

A simple signal to noise ratio analysis indicates the optimum sample thickness in a modulated absorption experiment to be $t \sim 2/\alpha$, where the absorption coefficient is about 500 cm$^{-1}$. Accordingly, samples were prepared from a boule of chrome-compensated GaP ($\rho > 10^7 \Omega$ cm) and thinned to 40–100 $\mu$m by mechanical polishing. Experimental broadening effects are thought to be small because of the extreme narrowness of an impurity peak just below the $\Gamma_{15}$-$X_1$ edge (about 2-meV peak to peak in the modulation spectrum at 78 K).

Because of the transparency of GaP at energies lower than 2.4 eV, stray light is a severe problem in a transmission experiment at 2.67 eV. We use two Corning glass filters (5-57 and 4-96) and an interference filter (International Light type WB400; pass, 300 to 500 nm). It is estimated that stray light is less than 20% at the highest energies discussed herein. Because of fluorescence, it is necessary that filtering be done between the sample and the detector.

The sample holder used is similar to one described previously.[5] The sample is mechanically clamped between insulating electrodes of 1-mm spacing. Electric fields up to 6 kV/mm were used. No effect in the modulation due to optical polarization or field orientation was observed, other than a small ($\sim 5 \times 10^{-4}$) uniform background change with polarization. The structure is quadratic in applied field, with the terms odd in field less than 5% of the even part.

The modulation of the transmitted beam was detected and normalized to the dc transmitted beam by servoing the photomultiplier-tube gain. The convention which we use is that a positive value reported is a positive $\Delta\alpha$. The quoted values for $\Delta\alpha$ are accurate only to $\pm 50\%$ because of uncertainties in sample thickness and stray light.

The electroabsorption spectrum is shown in Fig. 1. The major up-down structure near 2.67 is similar, except for width, to the resolved phonon structure in the 2.3-eV $\Gamma_{15}$-$X_1$ electroabsorption spectrum (Fig. 2).[6] The peak above 2.77 eV is thought not to be a part of the 2.67-eV structure, but relates to a higher transition—the $\Gamma_{15}$-$X_3$ transition or possibly the direct edge at 2.86 eV. (All energies refer to 78 K.) Furthermore, this peak is artificial; that is, the high-energy cutoff of the modulation is due to the dominance of stray light at higher energies as the sample becomes increasingly opaque.

The remaining spectrum shows a strong negative peak at 2.677, a weak shoulder at 2.691,

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