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THE NMR SPECTRUM OF ORTHO-H$_2$ IN DILUTED SOLID ORTHO-PARA MIXTURES

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Résumé.—Le spectre de résonance magnétique nucléaire de o-H$_2$ et des impuretés de HD dans un monocristal de H$_2$ solide avec une concentration X(o-H$_2$) = 0.015 est décrit pour 0.02 < T < 1 K. Les signaux des pairs de o-H$_2$ aussi bien dans le plan basal qu’en dehors, sont décrits ainsi que les signaux des molécules isolées de H$_2$ et de HD. Le retrécissement de la ligne HD est discuté.

Abstract.—The NMR spectrum of o-H$_2$ and HD impurities in a single crystal of solid H$_2$ with a concentration X(o-H$_2$) = 0.015 is described for 0.02 < T < 1 K. The signals from the nearest ortho pairs, both in-plane and out of the basal plane, and of isolated o-H$_2$ and HD are discussed. Motional narrowing of the HD impurities is observed.

We report a study of the NMR spectrum of diluted o-H$_2$ in solid p-H$_2$ with a mole fraction X(o-H$_2$) = 0.015 and of the proton signal of HD impurities, by means of continuous wave techniques at 12 MHz. In addition, the relaxation times $T_1$ and $T_2$ of selected portions of the spectrum were measured at 9.5 and 25 MHz. The sample was grown around thin Cu wires that were in thermal contact with a dilution refrigerator. Temperatures of ~ 20 mK were reached, as measured from the NMR signal intensity of the Cu wires and the HD. A spectrum of very sharp lines was obtained over a narrow range of directions of the applied magnetic field. In other directions, the lines were broader and difficult to resolve. There was a strong angular variation of the frequencies.

It is known that the NMR spectrum at such low concentrations is mainly made up of signals from isolated o-H$_2$ (namely those molecules with no nearest o-H$_2$ neighbour) and from isolated nearest-neighbour o-H$_2$ pairs/1,2/. The crystalline field that splits the rotational J = 1 triplet into a doublet $J_z = \pm 1$ and a singlet $J_z = 0$ can be deduced from the temperature dependence of the NMR signal width of the isolated o-H$_2$ /3/. In the present experiment the splitting was found to be $\nu_c/k = 0.025$ K. The crystalline electric field that influences the energy levels of the o-H$_2$ pairs is different /4/ for the in-plane pairs (IP) and those whose axis is out of the basal plane (OP). It appears from the analysis of microwave /4/ experiments that the ground state energy is lower for OP than for IP by about $\Delta/k = 0.035$ K.

We have studied in detail the spectrum near the Larmor frequency and the pair spectrum. In figure 1, we show the integrated spectrum taken with a magnetic field along the direction where the pair spectrum is sharpest. The sequence of curves was recorded over a narrow range of directions of the applied magnetic field. In other directions, the lines were broader and difficult to resolve. There was a strong angular variation of the frequencies.

Fig. 1 : The integrated NMR spectrum of H$_2$(X = 0.015) as a function of temperature upon cooling. The labels of the various lines are discussed in the text. The exact shape of the curves is subject to systematic errors caused by small baseline drifts of the recorded derivative spectrum. The line C$_b$ is partially saturated and no correction was made for the line broadening through the applied field inhomogeneity.
agreement with the expressions derived by Harris (equation (13) in reference /1/). We interpret the broad maxima D as the unresolved spectrum of the OP and IP pairs that are not parallel or perpendicular to the applied field.

As the temperature is decreased, a dramatic change in the spectrum is observed. The line $C_b$, representing the isolated $o$-$H_2$ splits into a well-resolved doublet under the influence of the crystalline field and disappears because of the pair formation /5/. The peaks of the pair spectrum P broaden an eventually disappear. The broad maximum D is displaced. In the middle, a sharp peak $C_s$ gradually emerges. At the lowest temperatures the only sharp features are the $P'$ and the $C_s$ spectra. Upon warming up, there is a hysteresis in the spectrum intensity. The $P$ and $C_b$ spectra reappear at a higher temperature than they have disappeared upon cooling.

The disappearance of the $P$ spectrum as $T$ decreases suggests that by means of jumps, IP pairs can change into OP pairs whose ground state is lower. It is interesting that the effects of this change-over manifests itself already at temperatures well above $\Delta/k=35$ mK. The thermal hysteresis mentioned above is presumably linked with the various time constants of the configurational changes.

We have investigated the properties of the $C_s$ line which we identify as the proton signal from the HD impurities, because its intensity corresponds to a concentration compatible with the natural abundance of HD in $H_2$. We find $T_2 = 11 \pm 2$ ms for $X = 0.01$, while the calculated $T_2$ resulting from intermolecular dipolar interaction with the $o$-$H_2$ is about $T_2 = 1$ ms. Hence there appears to be consider-

able motional narrowing, possibly by vacancy wave motion /6/. The time $T_1$ is a strong increasing function of $T^{-1}$, with $T_1 \approx 25$ s at $T = 0.02$ K, and also increases with frequency. Finally there is a frequency shift which at 12 MHz is $\nu_L(H_2)-\nu_L(HD)^+ 0.2$kHz which corresponds to a chemical shift of about 20 ppm.

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