CRYSTAL-FIELD SPLITTING OF ORTHOHYDROGEN IN SOLID PARAHYDROGEN*

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From nmr measurements we have estimated the crystal-field splitting of an ortho-H_2 molecule in solid para-H_2 to be 8.2×10^{-3} °K. This lowers the existing upper limit on the splitting by a factor 5.

There has been considerable speculation in the past decade as to the magnitude of the splitting, ϵ, of the $J = 1$ rotational state of ortho-H_2 in solid para-H_2. Nakamura[1] fitted the specific-heat data of Hill and Ricketson[2] with an expression containing a linear and a quadratic term in the ortho-H_2 concentration. Assuming a two-level model ($m_J = 0$ level below the $m_J = \pm 1$ level) he predicted a value $\epsilon/k = 2.2$°K from the coefficient of the linear term. In a theoretical calculation, Nakamura and Uryu[3] used the Einstein model of lattice vibrations to estimate ϵ and obtained $\epsilon/k = 0.52$°K. Orttung[4], using a more refined theory of the anomalous heat capacity and additional specific-heat data, predicted $\epsilon/k = 2.6$°K for a two-level model and $\epsilon/k = 1.89$°K for a three-level model. Sears and Van Kranendonk[5] were able to estimate ϵ from the difference in the separations of the components of the rotational Raman triplet $S_0(0)$ ($\Delta v = 0$, $\Delta J = 2$) in pure para-H_2.[6,7] Under the assumption that the crystalline potential giving rise to the splitting is the same for the $J = 1$ and $J = 2$ states, they obtained $\epsilon/k = 0.03 \pm 0.02$°K. Recently, Van Kranendonk and Sears[8] have presented a detailed theory of the interaction between the rotational motion of the molecules and the lattice vibrations, and gave a revised value of 0.29°K for ϵ/k. These authors have emphasized the large uncertainty in this estimate due to uncertainty in the parameters of the intermolecular potential. Harris and Hunt[9] have deduced a value of about 0.3°K for the rms splitting of the $J = 1$ level from measurements of the second moment of the nmr line in solid H_2. However, as we shall see later, at the high ortho-H_2 concentrations where their measurements were made, the splitting of the $J = 1$ level is completely dominated by the electric quadrupole interactions between ortho molecules. The present note describes a measurement of ϵ/k by observation of the nmr free-induction decay at low temperatures in samples with low ortho-H_2 concentrations.

Consider an ortho-H_2 molecule in an infinite crystal of para-H_2: Because of the hexagonal close-packed structure of para-H_2, the $J = 1$ level of ortho-H_2 is expected to be split into three sublevels labeled by $\bar{m}_J$, the projection of the angular momentum along the crystal c axis, with the $\bar{m}_J = 0$ state separated from the $\bar{m}_J = \pm 1$ levels by the crystal-field energy ϵ.[5,8] The value of ϵ is dependent on the c/a ratio of the crystal and is zero for an ideal, rigid hcp structure.[5] Following Reif and Purcell,[10] the nmr spectrum of such a molecule is described by the energy-level scheme

$$h^{-1}E_{m_I, \bar{m}_J} = am_I + c\gamma m_I \bar{m}_J$$
$$+ d(3\gamma^2 - 1)(1 - \tfrac{3}{2}\bar{m}_J{}^2)(1 - \tfrac{3}{2}m_I{}^2), \quad (1)$$

where a is the Larmor frequency of the protons (20 MHz in our case) and $c = 113.8$ kHz and $d = 57.7$ kHz express the spin rotation and dipolar interactions within the molecule, respectively. m_I is the projection of the total nuclear angular momentum along the external field, and γ is the cosine of the angle between the crystal c axis and the magnetic field.

The nmr transitions $m_I = -1 \rightarrow m_I = 0$ and $m_I = 0 \rightarrow m_I = 1$ are both split into three components corresponding to the three values of $\bar{m}_J$. However, if the rate of transitions among the molecular $\bar{m}_J$ levels is fast compared with these splittings,[11] then each of the triplets is reduced to a single line having a frequency equal to the average over the $\bar{m}_J$ states, or

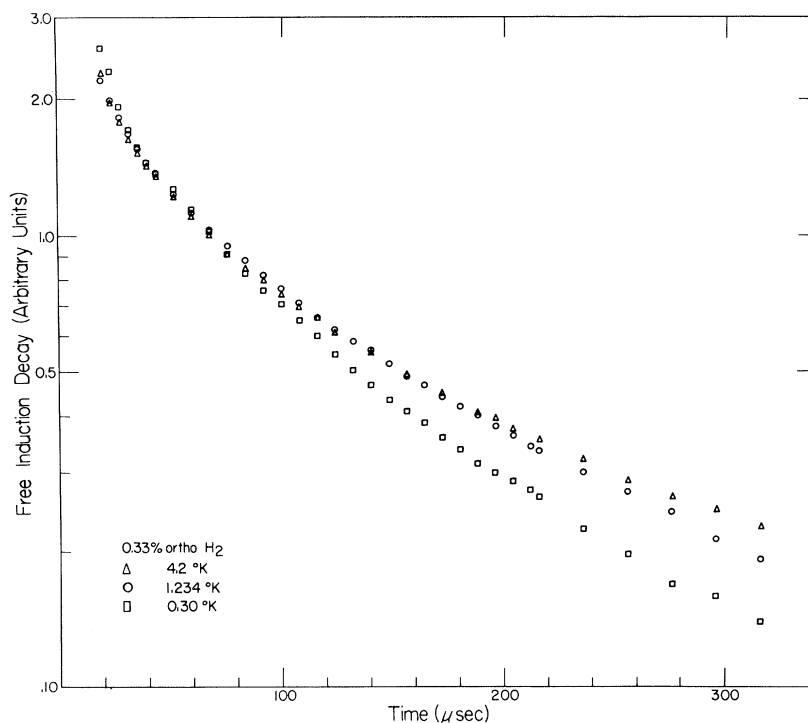$$v_{\text{Larmor}} = a \pm \tfrac{3}{4}d(3\gamma^2 - 1)[2p_0 - (p_1 + p_{-1})], \quad (2)$$

FIG. 1. Detected free-induction decay in solid H_2 with 0.33% ortho.

where p_0, p_1, and p_{-1} designate the populations of the states $\bar{m}_J = 0$, 1, and -1, respectively. The angular dependence of the splitting is just that of a normal Pake doublet[12]; the magnitude of the splitting, however, is temperature dependent. The envelope of the Fourier transform of a Pake doublet averaged over a polycrystalline sample is given by[13]

$$G(t) = \left(\frac{\pi}{6}\right)^{1/2}\left\{\frac{\cos\alpha t}{(\alpha t)^{1/2}}C(3\alpha t) + \frac{\sin\alpha t}{(\alpha t)^{1/2}}S(3\alpha t)\right\}, \quad (3)$$

where $\alpha = \frac{3}{4}d[2p_0 - (p_1 + p_{-1})]$, and C and S are the real and imaginary parts of the Fresnel integral ($3\alpha t = z$ in the tables of Jahnke and Emde[14]). Our intent was to lower the temperature of the sample so that by observation of the nmr free-induction decay the zeros of the function $G(t)$ and hence the values of $[2p_0 - (p_1 + p_{-1})]$, and then ϵ, could be determined.

The detected free-induction decay in H_2 with 0.33% ortho at 4.2, 1.23, and 0.3°K is given in Fig. 1, suitably normalized to account for changes in temperature. In order to extract the temperature-dependent part of the free-induction decay we have divided the signal at 0.3°K by the high-temperature signal (i.e., signal at 4.2°K) and the result is shown in Fig.

2 (curve A). It is evident that even at 0.3°K the first zero of $G(t)$ has not been observed. [The small oscillation in the detected signal
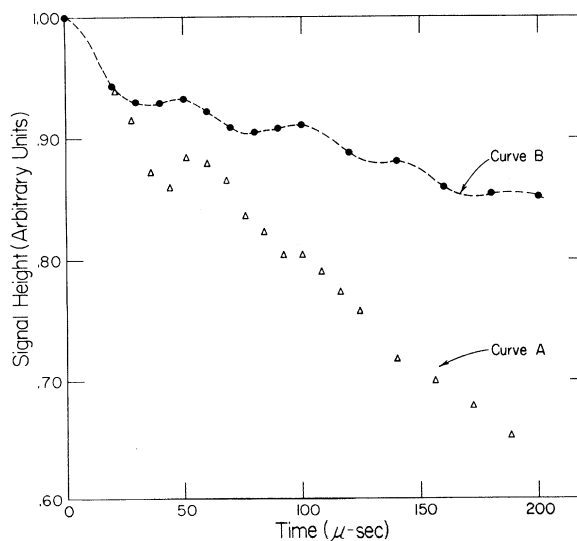

FIG. 2. Temperature-dependent part of free induction decay. Curve A obtained by dividing signal at 0.3°K by signal at 4.2°K. Curve B shows effect of residual quadrupole-quadrupole interactions at 0.3°K (theoretical).

near the origin ($t < 60$ μsec) has been shown
to be the result of a residual nmr signal from
the empty sample cell.] Provided allowances
are made for all other sources of broadening,
it is still possible to deduce a value for ϵ.

Broadening from inhomogeneities in the ex-
ternal magnetic field and from residual inter-
molecular dipolar interactions is only a slight
perturbation on the natural linewidth and in
addition can be safely assumed to be temper-
ature independent. The main source of broad-
ening is due to the intramolecular dipolar and
spin-rotational interactions, i.e., the same
interactions giving rise to the splitting of the
nmr line. If it is assumed that the molecular
transition rates are not intrinsically temper-
ature dependent, then it can be shown that the
fractional change in broadening due to depop-
ulation of the upper $\bar{m}_J$ level (or levels) is of
the order of $(\epsilon/kT)^2$, and this is negligible a
posteriori. In the temperature range 4.2 to
0.3°K one expects the change in molecular re-
orientation rates to be small, as the majori-
ty of the molecules in a 0.3% ortho sample have
nearest-neighbor ortho-ortho interactions small-
er than 10^{-3} °K. However, those ortho mole-
cules having a sizable electric quadrupole cou-
pling with a neighboring ortho molecule do ex-
hibit a temperature-dependent line shape and
we have devised a simple model to estimate
their effect on the free-induction decay.

Consider a single pair of ortho-H_2 molecules
in a crystal of para-H_2 and for simplicity as-
sume that the crystal-field splitting due to or-
tho-para interactions is zero. The energy lev-
el scheme of a pair of ortho-H_2 molecules has
been calculated by Orttung[4] and consists of
nine levels (several of which are degenerate)
having a total energy span of 7.43°K for ortho
molecules at the nearest-neighbor distance,
a_0, in solid para-H_2.[15] Assuming fast transi-
tions among the molecular levels, one again
finds a temperature-dependent splitting of the
nmr line. For a given temperature it is pos-
sible to calculate the free-induction decay char-
acteristic of each ortho-ortho separation. If
we confine our attention to times $\leqslant 200$ μsec,
then at 0.3°K only pairs of molecules separated
by $r^2 \leqslant 5a_0^2$ contribute significantly to the damp-
ing of the free-induction decay. For an ortho
concentration of 0.33%, the majority of near-
est-neighbor pairs having $r^2 \leqslant 5a_0^2$ are isolat-
ed pairs, i.e., the two molecules are nearest
neighbors of each other. Guided by the fact

that the quadrupole-quadrupole interaction is
fairly short ranged ($1/r^5$), we have assumed
that to a first approximation the interaction
of an isolated pair with other ortho molecules
can be neglected. It is then possible to sum
up all contributions to the free-induction de-
cay (assuming a random distribution for the
ortho molecules) and the result is shown in
Fig. 2 (curve B).

If the above source of damping is extracted
from the experimental free-induction decay
by dividing curve A by curve B, then the re-
sulting curve can be compared with the short-
time expansion of $G(t)$: $G(t) = 1 - \frac{2}{5}\alpha^2 t^2$.[10] The
result gives $\epsilon/k = (8.2 \pm 2.1) \times 10^{-3}$ °K. It is not
possible to say whether the $\bar{m}_J = 0$ state lies
above or below the $\bar{m}_J = \pm 1$ states since $T \gg \epsilon/k$.
Should there be a distribution of values of ϵ
our number will correspond to the rms value
of ϵ.

We have also measured T_1 at 0.3°K and find
it to be equal to the value[16] at 4.2°K to within
experimental error. Unfortunately our reso-
lution was very poor ($\sim 25\%$) because of heat-
ing of the sample chamber by rf pulses.

The error of $\pm 2.1 \times 10^{-3}$ °K in ϵ/k is not in-
tended to indicate the absolute accuracy of the
measurement but only the accuracy of the fit
of the corrected free-induction decay to $G(t)$.
The procedure used for extracting the desired
contribution to the damping of the free-induc-
tion decay is an approximation used in the ab-
sence of a detailed theory for solid H_2. We
note, however, that if the correction for re-
sidual quadrupolar interactions is neglected
entirely, the resulting change in ϵ/k is much
smaller than the uncertainty. It is quite pos-
sible that strains play a role in splitting the
$J = 1$ level; if so the value we have deduced
is an upper limit on the true value of ϵ.

The large value of ϵ obtained from specific-
heat measurements[3,4] may be due to the fact
that the quadrupole coupling constant used in
correcting for residual quadrupole interactions
was in error[15]; a definitive answer cannot be
given until the effect of the crystal polariza-
bility on the quadrupole-quadrupole interaction
at small separations is known. Clustering of
the ortho-H_2 molecules,[5] which results in a
larger number of ortho-ortho pairs than would
be predicted for a random distribution, could
also affect the value of ϵ deduced: The specif-
ic-heat data were corrected for residual qua-
drupolar interactions under the assumption

of a random distribution.[17] If, however, the clustering is due solely to the electrostatic quadrupole-quadrupole interaction, then it can be shown that the deviation from a random distribution is less than 2%.[18] Another possibility is that the presence of an ortho molecule produces a local distortion of the para crystal. This will disturb the c/a ratio locally and can induce a crystal-field splitting in a nearby ortho-H_2 molecule. If we treat the para-H_2 as an isotropic elastic solid, then it is easy to show that the lowest order term in this additional ortho-ortho interaction (from the isotropic part of the disturbance) has a $1/r^3$ dependence on the ortho-ortho separation. Thus although this interaction is expected to be much smaller than the electric quadrupole coupling at short distances, it has a longer range and may be important in samples with low concentrations of ortho-H_2.

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[11]For ortho concentrations down to 0.2%, molecular reorientation in solid H_2 is dominated by the adiabatic process of mutual reorientation of the molecular electric quadrupoles. The correlation times are of the order of 10^{-8} sec for a sample having 0.2% ortho. See W. N. Hardy and J. R. Gaines, Phys. Rev. Letters 17, 1278 (1966).

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[15]It has been brought to the authors' attention by Dr. J. Van Kranendonk that the recently calculated and presumably very reliable value of the quadrupole moment of H_2 [G. Karl and J. D. Poll, J. Chem. Phys. 46, 2944 (1967)] differs somewhat from the value used by Nakamura (Ref. 1) and later authors (Refs. 4, 5, and 9), and we have used the new value. In addition, Dr. Donald McQuarrie has pointed out that the dielectric properties of the para-H_2 host must be taken into account when applying the free-space electric quadrupole-quadrupole interaction to the case of two ortho-H_2 molecules in solid para-H_2. When the ortho-H_2 are separated by many lattice distances, the interaction will simply be reduced by a factor equal to the dielectric constant of the medium. It is doubtful that this approximation holds for molecules at the nearest-neighbor distance but this will have little effect on the result of the present calculation. Taking the dielectric constant to be 1.29 for H_2 at 4.2°K, and $a_0 = 3.78$ Å, the value 7.43°K is obtained for the over-all separation of the energy levels.

[16]A unique value of T_1 does not exist but $\langle 1/T_1 \rangle^{-1}$ is of the order of 10^{-3} sec. W. N. Hardy and J. R. Gaines, Phys. Rev. Letters 17, 1278 (1966), and to be published.

[17]Dr. J. Van Kranendonk brings our attention to the result of H. P. Gush and J. Van Kranendonk, Can. J. Phys. 40, 1461 (1962), who found the effect of the lattice polarizability to be negligible for a nearest-neighbor pair.

[18]The authors are indebted to Dr. Donald McQuarrie and Dr. John McTague for discussions on this point.