accounts for the small differences in the values of G reported by Claiborne and Einspruch,[7] by Perz and Dobbs,[8] and in this experiment.

In Eq. (9), $\alpha_N(T_c)$ has been used instead of the correct quantity $\alpha_N(T)$. If the temperature is well into the region where the sample shows impurity-limited conductivity, this procedure is valid. Otherwise, it can lead to small errors. A measurement of this temperature dependence for our samples was made in a 400-G field and showed a maximum change between 3.72 and 2.0°K of 0.3 dB/cm, with no change below 2.0°K. This change will produce an error in the value of G obtained from our analysis of less than 0.2%, which is considerably less than the experimental reproducibility in the values of G.

CONCLUSIONS

Ultrasonic attenuation measurements of the superconducting energy gaps in Sn have been made as a function of hydrostatic pressure. The "zero pressure" measurements of the gap parameter G for propagation down to [100], [110], and [001] crystal axes are in fair agreement with previous measurements. While the multigap character of Sn prevents the direct measurement of a single energy gap, three separate averages over the energy gaps could be measured. The pressure dependence of each of these averages was the same, within experimental error, as the pressure dependence of T_c. Thus we conclude that the linear relation between the energy gap and the critical temperature predicted by the BCS theory holds for the weak-coupled superconductor Sn.

ACKNOWLEDGMENT

The authors wish to thank James Thomas for the design and construction of the current regulator for the resistance thermometer and also for other technical assistance.

PHYSICAL REVIEW VOLUME 175, NUMBER 2 10 NOVEMBER 1968

Observation of Pair Interaction between Ortho Molecules in Solid H_2†

A. Brooks Harris*
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania
AND
Larry I. Amstutz, Horst Meyer, and Samuel M. Myers
Department of Physics, Duke University, Durham, North Carolina

(Received 13 May 1968)

A study of the electric quadrupole-quadrupole (EQQ) interaction between ortho-H_2 molecules in solid H_2 is presented. This work consists in recording and interpreting the pair spectrum of proton nuclear magnetic resonance for low ortho-H_2 concentrations. In the theoretical part of this paper, a calculation of the absorption spectrum for an isolated pair of ortho molecules is presented, and the temperature dependence of this spectrum is derived as a function of the rotational states of the isolated ortho pair. Furthermore, the results of similar calculations on the absorption spectrum of isolated triangles of ortho-H_2 molecules in solid H_2 are briefly discussed. This spectrum is expected to be less pronounced than the pair spectrum and to be mostly responsible for a broad absorption background. The experimental work, carried out at temperatures between 0.45 and 14°K on several low ortho-H_2 concentrations shows the maxima expected from theory. From the analysis of the results, and assuming the interactions between molecules to be purely EQQ, the coupling constant $\Gamma/k_B=6e^2Q^2/25R^5k_B$ is found to be 0.82°K. This value is smaller than that expected for the solid rigid lattice, where $\Gamma/k_B=1.00$°K. One also obtains from the analysis a dipolar coupling constant $d=54.5$ kHz which is smaller than that measured for the free H_2 molecule, where $d=57.7$ kHz. It is suggested that the departures both in Γ and in d from expectations are caused by the interactions between lattice vibrations and rotations, since solid H_2 will behave more like a quantum crystal with large zero-point motion than like a classical rigid crystal.

I. INTRODUCTION

The orientational state of solid alloys of ortho-para hydrogen has been studied by many authors. For most applications one assumes that J is a good quantum number: $J=0$ for para molecules and $J=1$ for ortho molecules. Accordingly, to describe the orientational state of ortho-para alloys one need consider only the removal of degeneracy of the ortho molecules. In this connection, Nakamura[1] was the first to show that the electric quadrupole-quadrupole (EQQ) interaction is the most important orientationally dependent term in the intermolecular potential. This interaction is

---

* Alfred P. Sloan Foundation Fellow.

† The part of this research conducted by one of us (A.B.H.) was supported by the Advanced Research Projects Agency and also by a National Science Foundation Grant. The part of the research carried out at Duke University was supported by grants of the Army Research Office (Durham) and the National Science Foundation.

[1] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

described[2] in terms of the coupling constant $\Gamma = 6e^2Q^2/25R^5$ where eQ is the molecular quadrupole moment and R the nearest-neighbor separation. In addition there exist smaller static fields tending to align the molecules. Although several parameters are needed to fully specify this crystalline field Hamiltonian $\mathcal{H}_c$ we may conveniently discuss its magnitude in terms of the root mean square splitting Δ defined as

$$\Delta^2 = \tfrac{1}{3}\,\mathrm{Tr}\mathcal{H}_c^2. \tag{1}$$

Generally speaking, Δ will be a function of position of the ortho molecule, as it depends on the local environment. Depending on the experiment one observes certain weighted averages of Δ over position.

Since the molecular quadrupole moment eQ is known rather precisely from quantum-mechanical calculations for the hydrogen molecule,[3,4] one can calculate Γ quite accurately within the rigid-lattice approximation where R^{-5} is computed from the observed lattice constant. There are at least two mechanisms that will cause a discrepancy between this value of Γ and that deduced from experiments on solid hydrogen. First, as one of us has pointed out,[5] it is important to replace R^{-5} by its average over the vibrational motion in the solid. If the crystal were described by harmonic phonons, this effect would be small since it would then depend on the anisotropy of the phonon spectrum. However, the theory of "quantum crystals"[6] should be applied to solid hydrogen. In this theory the motion of the molecules is correlated in such a way as to lead to a reduction in Γ, calculated[5] to be about 8%. Second, Nakamura's argument about the dominance of the EQQ interactions may not be conclusive. His treatment was based on the quantum mechanical calculations of de Boer.[7] However, as is discussed in Ref. 8, de Boer's calculations can not be regarded as being definitive. Thus it would be interesting to carry out Nakamura's analysis using more accurate quantum-mechanical calculations of the interaction energy of two H_2 molecules as a function of their orientation. Hence we conclude that the theoretical value of Γ is not known with great certainty.

Accordingly, a direct and accurate experimental determination of Γ in the solid phase is of great interest. Several experiments have already been done from which one might attempt to deduce[5] a value of Γ. In most cases the difficulties in interpretation or in the experiment are such that the value of Γ so obtained is not reliable to better than about 10%.

The situation with regard to the crystal-field parameter Δ is also uncertain. The mechanism responsible for the crystalline field is not understood. Consequently it is of obvious value to determine the crystalline field as a function of ortho concentration. Hardy and Gaines[9] have done this at low concentration, where the crystalline field they observe is that of an isolated ortho molecule in pure para H_2. The estimates of Van Kranendonk and Sears[10,11] are more indirect and hence we use the estimate of Ref. 9. The determinations of Δ at higher ortho concentration from second moments of the NMR spectrum[12] are doubtful because of the slow convergence of the high-temperature expansion used to interpret the results. Perhaps the most reliable estimate of the crystalline field at moderately low ortho-H_2 concentration, e.g., $0.01 < c < 0.1$, is that of Sung.[13] Using the statistical model to calculate T_1 he finds agreement with experiment for a crystal-field splitting of between 0.007 and 0.035 cm^{-1}.

Note added in proof. This estimate of the crystalline field may not be completely reliable because Sung's model does not yield quantitative agreement with the experimental values of T_1. The apparent agreement obtained in Ref. 13 is the result of some computational errors as will be discussed by one of us (A.B.H.) in a forthcoming publication.

Accordingly, we will describe here and in subsequent papers the results of a systematic program to determine the experimental values of Γ and Δ for various concentrations of the $J=1$ species of hydrogen in the solid phase. As a first step in such a program we have studied the NMR spectrum of solid H_2 at low ortho concentration, where one expects to observe the resonance of isolated single and pairs of ortho molecules. This research was also partially prompted by the failure of previous authors[14,15] to observe a pair spectrum at low ortho concentration. From the pair spectrum we are able to obtain a rather precise estimate of a certain linear combination of Γ and Δ. Combining this result with the limit placed on from Sung's work, we are able to conclude that $\Gamma/k_B = 0.82 \pm 0.06$°K for solid H_2. An additional result we have obtained concerns the ground-state value of the order parameter $\langle 3\cos^2\theta_{a,R} - 1\rangle$, where $\theta_{a,R}$ specifies the orientation of the molecule "a" relative to the local symmetry axis. By NMR one measures the quantity $d\langle 3\cos^2\theta_{a,R} - 1\rangle$, where d is the intramolecular dipolar field constant. As first observed by Reif and Purcell,[16] and subse-

---

[2] J. Van Kranendonk, Physica **25**, 1080 (1959).

[3] G. Karl and J. D. Poll, J. Chem. Phys. **46**, 2944 (1967).

[4] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

[5] A. B. Harris, Int. J. Quantum Chem. (to be published).

[6] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967), and references cited therein.

[7] J. de Boer, Physica **9**, 363 (1942).

[8] J. D. Hirschfelder, C. F. Curtiss, and R. B. Bird, in *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1083 and ff.

[9] W. N. Hardy and J. R. Gaines, Phys. Rev. Letters **19**, 1417 (1967).

[10] V. F. Sears and J. Van Kranendonk, Can. J. Phys. **42**, 980 (1964).

[11] J. Van Kranendonk and V. F. Sears, Can. J. Phys. **44**, 313 (1966).

[12] A. B. Harris and E. Hunt, Phys. Rev. Letters **16**, 845 (1966).

[13] C. C. Sung, Phys. Rev. **167**, 271 (1968).

[14] T. Sugawara, Y. Masuda, T. Kanda, and E. Kanda, Sci. Rept. Res. Inst., Tohoku Univ. **A7**, 67 (1955).

[15] J. R. Gaines, E. M. de Castro, and J. G. Daunt, Phys. Rev. **140**, A319 (1965).

[16] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

quently confirmed in this laboratory,[17] the experimental value of this quantity is about 5% lower than expected theoretically. We find a similar reduction here, which has led one of us[5] to attribute this discrepancy to interactions between the rotational and vibrational motions.

Briefly, this paper is organized as follows. In Sec. II we calculate the NMR spectrum of an isolated pair of ortho molecules. We also discuss the spectrum of three interacting ortho molecules. In Sec. III the apparatus is briefly described. The experimental results are analyzed and discussed in Sec. IV. Finally, the conclusions of this study are summarized in Sec. V.

II. CALCULATION OF THE NMR PAIR SPECTRUM

In this section we calculate the energy levels of the nuclear spin system and the NMR absorption spectrum due to the classical dipolar interactions between the protons of an isolated pair of ortho molecules. The spectrum of three isolated ortho molecules will also be discussed. Electric quadrupole-quadrupole interactions produce a progressive quenching of the rotational motion of the molecules as the temperature is reduced. As a result, the observed splittings of the NMR satellites show a strong temperature dependence.

First, consider the case of an isolated pair of ortho molecules. For this purpose let us consider the magnetic energy of two spins I_i and I_j in a strong magnetic field which is given as

$$\mathcal{H}=\mathcal{H}_{\text{Zeeman}}+\mathcal{H}_{\text{dip}}, \tag{2}$$

where

$$\mathcal{H}_{\text{Zeeman}}=-g\beta H_0(m_i+m_j), \tag{3a}$$

$$\mathcal{H}_{\text{dip}}=-\tfrac{1}{2}g^2\beta^2R_{ij}^{-3}[1-3\cos^2\theta_{R_{ij},H_0}][\mathbf{I}_i\cdot\mathbf{I}_j-3m_im_j]. \tag{3b}$$

Here g is the proton gyromagnetic ratio, R_{ij} is the distance between the spins, β the nuclear magneton, m_i and m_j the projections of the spin vectors along the direction of the external field H_0, and θ_{R_{ij},H_0} the angle between the vector R_{ij} and the direction of H_0. Consider two ortho molecules a and b subjected to these interactions. We define

$$\mathbf{I}_1+\mathbf{I}_2=\mathbf{I}_a,$$
$$\mathbf{I}_3+\mathbf{I}_4=\mathbf{I}_b, \tag{4}$$

where $I_a^2=I_b^2=2$, since the molecules are ortho molecules. Also we define

θ_{a,H_0} = angle between axis of molecule a and H_0,

θ_{b,H_0} = angle between axis of molecule b and H_0,

R_{ab} = distance vector between molecules a and b,

θ_{aR} = angle between axis of molecule a and R_{ab},

θ_{bR} = angle between axis of molecule b and R_{ab},

θ_{R,H_0} = angle between R_{ab} and H_0.

The total dipolar energy is given by

$$\mathcal{H}_{\text{dip}}=\mathcal{H}_{\text{dip}}^{(1,2)}+\mathcal{H}_{\text{dip}}^{(3,4)}+\mathcal{H}_{\text{dip}}^{(a,b)}, \tag{5}$$

where $\mathcal{H}_{\text{dip}}^{(i,j)}$ is the interaction energy between spins i and j and, where

$$\mathcal{H}_{\text{dip}}^{(a,b)}=\mathcal{H}_{\text{dip}}^{(1,3)}+\mathcal{H}_{\text{dip}}^{(1,4)}+\mathcal{H}_{\text{dip}}^{(2,3)}+\mathcal{H}_{\text{dip}}^{(2,4)}. \tag{6}$$

For the spins 1 and 2 on molecule a we have[16]

$$h^{-1}\mathcal{H}_{\text{dip}}^{(1,2)}=-\tfrac{5}{2}d(1-3\cos^2\theta_{a,H_0})(\mathbf{I}_1\cdot\mathbf{I}_2-3m_1m_2), \tag{7a}$$

$$=-\tfrac{5}{2}d(1-3\cos^2\theta_{a,H_0})(1-\tfrac{3}{2}m_a^2), \tag{7b}$$

where $d=\frac{4}{5}g^2\beta^2\langle r^{-3}\rangle h^{-1}=57.68$ kHz for free molecules.[18] We must average the factor $(1-3\cos^2\theta_{a,H_0})$ over the rotational motion. Since R_{ab}, along which we take the z axis, is a symmetry axis, one may write Eq. (7b) as

$$h^{-1}\mathcal{H}_{\text{dip}}^{1,2}=-\tfrac{5}{4}d(3\cos^2\theta_{R,H}-1)(1-\tfrac{3}{2}m_a^2)\times\langle 1-3\cos^2\theta_{a,R}\rangle, \tag{8a}$$

$$=-\tfrac{3}{4}d\langle 2-3J_z^2\rangle(3\cos^2\theta_{R,H_0}-1)(m_a^2-\tfrac{2}{3}), \tag{8b}$$

where the brackets $\langle\ \rangle$ indicate averages over the rotational states of the pair of molecules. The quantity $\langle 2-3J_z^2\rangle$ will be a function of temperature and an explicit form will be given in Eq. (17) below. For the time being we write

$$\langle 2-3J_z^2\rangle=\tfrac{1}{2}f(T). \tag{9}$$

Similarly, we also have

$$h^{-1}\mathcal{H}_{\text{dip}}^{3,4}=-\tfrac{3}{8}df(T)(3\cos^2\theta_{R,H_0}-1)(m_b^2-\tfrac{2}{3}). \tag{10}$$

Now consider the dipolar interactions between the spins located on different molecules separated by a distance R_{ab}. Here we make the approximation that the magnetic moments are at the center of gravity of the molecules. This can be justified, since the ratio $\rho=(r/R_{ab})^3$ is much smaller than unity. We then obtain

$$h^{-1}\mathcal{H}_{\text{dip}}^{(a,b)}=\tfrac{5}{2}d\rho(3\cos^2\theta_{R,H_0}-1)(\mathbf{I}_a\cdot\mathbf{I}_b-3m_am_b). \tag{11}$$

Thus the total nuclear spin Hamiltonian is given by

$$h^{-1}\mathcal{H}=-g\beta H_0(m_a+m_b)+d(3\cos^2\theta_{R,H_0}-1)\times[\tfrac{5}{2}\rho(\mathbf{I}_a\cdot\mathbf{I}_b-3m_am_b)-\tfrac{3}{8}f(T)(m_a^2+m_b^2-\tfrac{4}{3})]. \tag{12}$$

The energy states may be classified according to the value of $m=m_a+m_b$ and are given, together with their energy, in Table I. Due to the perturbation of the rf field one observes transitions between energy levels with intensities proportional to the square of the matrix elements of $I_{ax}+I_{ay}$. As a result one observes the transitions as indicated in Table II. We see that the spectrum consists of two triplets symmetrically positioned on each side of the central resonance at $\nu_0\equiv g\beta H_0h^{-1}$. Note that the frequency splittings $\delta\nu_i=$

---

[17] L. I. Amstutz *et al.* (to be published).

[18] N. F. Ramsey, Phys. Rev. **85**, 60 (1952).

TABLE I. Nuclear spin eigenstates of an ortho pair.

m	State	$(E+mh\nu_0)/dh$ $\times(3\cos^2\theta_{R,H_0}-1)$
2	$\Phi_2=\|1,1\rangle$	$-5\rho-\frac{1}{4}f(T)$
1	$\Phi_1{}^s=(1/\sqrt{2})\{\|1,0\rangle+\|0,1\rangle\}$	$\frac{5}{2}\rho+\frac{1}{8}f(T)$
	$\Phi_1{}^a=(1/\sqrt{2})\{\|1,0\rangle-\|0,1\rangle\}$	$-\frac{5}{2}\rho+\frac{1}{8}f(T)$
0	$\Phi_0{}^s=(1/\sqrt{2})\{\|1,-1\rangle+\|-1,1\rangle\}$	$5\rho-\frac{1}{4}f(T)$
	$\Phi_0=\|0,0\rangle$	$\frac{1}{2}f(T)$
	$\Phi_0{}^a=(1/\sqrt{2})\{\|1,-1\rangle-\|-1,1\rangle\}$	$5\rho-\frac{1}{4}f(T)$
-1	$\Phi_{-1}{}^s=(1/\sqrt{2})\{\|-1,0\rangle+\|0,-1\rangle\}$	$\frac{5}{2}\rho+\frac{1}{8}f(T)$
	$\Phi_{-1}{}^a=(1/\sqrt{2})\{\|-1,0\rangle-\|0,-1\rangle\}$	$-\frac{5}{2}\rho+\frac{1}{8}f(T)$
-2	$\Phi_{-2}=\|-1,-1\rangle$	$-5\rho-\frac{1}{4}f(T)$

$\nu_i-\nu_0$ are proportional to $(3\cos^2\theta_{R,H_0}-1)$. Thus, performing a powder average, each of the three symmetrically positioned components will give rise to a spectrum of the type shown by Reif and Purcell[16] in their Fig. 4(a). The positions of the six peaks and their relative intensities $\mathcal{I}_i$, are:

$$\delta\nu_1=-\delta\nu_4=d(\tfrac{15}{2}\rho+\tfrac{3}{8}f(T))\,;\qquad \mathcal{I}_1=\mathcal{I}_4=2 \tag{13a}$$

$$\delta\nu_2=\delta\nu_5=d(-\tfrac{5}{2}\rho+\tfrac{3}{8}f(T))\,;\qquad \mathcal{I}_2=\mathcal{I}_5=3 \tag{13b}$$

$$\delta\nu_3=\delta\nu_6=d(-\tfrac{15}{2}\rho+\tfrac{3}{8}f(T))\,;\qquad \mathcal{I}_3=\mathcal{I}_6=1. \tag{13c}$$

The intensity-weighted average splitting of the two triplets is then

$$\langle\delta\nu_+\rangle_{\text{av}}=\sum_{i=1}^{3}\mathcal{I}_i\delta\nu_i\Big/\sum_{i=1}^{3}\mathcal{I}_i=\tfrac{3}{8}f(T), \tag{14a}$$

$$\langle\delta\nu_-\rangle_{\text{av}}=\sum_{i=4}^{6}\mathcal{I}_i\delta\nu_i\Big/\sum_{i=4}^{6}\mathcal{I}_i=-\tfrac{3}{8}f(T). \tag{14b}$$

Hence the center of gravity of the triplet is unaffected by intermolecular dipolar interaction. Outer wings of the absorption spectrum [see Fig. 4(a) of Ref. 16] occur at frequencies double those given in Eq. (13).

Let us now calculate the temperature dependence $f(T)$ of the splittings. For convenience we show in Table III the wave functions and energies[19] (expressed as E/Γ) of the rotational states of an isolated pair of ortho molecules assuming only EQQ interactions. The thermal average $\langle 2-3J_z{}^2\rangle_T$ is

$$\langle 2-3J_z{}^2\rangle_T=\sum_n\langle n\,|\,2-3J_z{}^2\,|\,n\rangle\exp(-E_n/k_BT)\Big/\sum\exp(-E_n/k_BT). \tag{15}$$

In the ground state at $T=0$, we have

$$\langle 2-3J_z{}^2\rangle=\tfrac{1}{2}. \tag{16}$$

Using the results of Table III the normalized ratio of $\langle 2-3J_z{}^2\rangle$ is then found to be

$$\frac{\langle 2-3J_z{}^2\rangle_T}{\langle 2-3J_z{}^2\rangle_{T=0}}=f(T)=\frac{2[1-\exp(-5\Gamma/k_BT)]^2}{[2+4\exp(-4\Gamma/k_BT)+2\exp(-5\Gamma/k_BT)+\exp(-10\Gamma/k_BT)]}. \tag{17}$$

The most striking result is that at $T=0$, the separation of the center of gravity of the satellites, $\langle\delta\nu_+\rangle_{\text{av}}-\langle\delta\nu_-\rangle_{\text{av}}=3d/4$, is one-fourth of the value for the satellites in the cubic phase. This is seen from the ground-state wave functions, which give respectively $\langle J_z{}^2\rangle=0$ in the ordered cubic phase,[20] and $\langle J_z{}^2\rangle=\frac{1}{2}$ for ortho pairs in hcp H_2.

Even at low ortho concentrations, there are ortho molecules forming triangles of nearest neighbors. One distinguishes six such configurations, which are

type 1: $R_{12}=R_{23}=R_0,\quad R_{13}=R_0,$
type 2: $R_{12}=R_{23}=R_0,\quad R_{13}=(3)^{1/2}R_0,$
type 3: $R_{12}=R_{23}=R_0,\quad R_{13}=(2)^{1/2}R_0,$
type 4: $R_{12}=R_{23}=R_0,\quad R_{13}=2R_0,$
type 5: $R_{12}=R_{23}=R_0,\quad R_{13}=(11/3)^{1/2}R_0,$
type 6: $R_{12}=R_{23}=R_0,\quad R_{13}=(8/3)^{1/2}R_0,$

where R_{kl} is the distance between two ortho neighbors k and l, and R_0 is the nearest-neighbor distance. For the purposes of the following discussion we consider a cluster of molecules as being "isolated" if there are no other ortho molecules which are nearest neighbors to any molecules in the cluster. This type of definition will be useful if kT is large compared with the interactions energy between clusters. The relative concentration of clusters of isolated molecules P_A, of isolated pairs P_B, and of isolated triangles of type i, P_i, of ortho molecules vary with ortho concentration. For ortho concentration, $c=0.04$, for instance, we find $P_A=0.6127$, $P_B=0.1151$, $P_1=0.0052$, $P_2=0.0108$, $P_3=0.0075$, $P_4=P_6=0.0018$, and $P_5=0.0036$. The fraction of ortho molecules P_{other} in larger isolated clusters is

$$P_{\text{other}}=1-P_A-2P_B-3\sum_{i=1}^{6}P_i=0.0648. \tag{18}$$

The calculation of the spectrum for the different

---

[19] R. J. Elliott and W. M. Hartmann, Proc. Phys. Soc. (London) 90, 671 (1967).
[20] H. M. James and J. C. Raich, Phys. Rev. 162, 649 (1967), and references cited therein.

Table II. Allowed nuclear spin transitions for ortho pair.

Transition	$(\nu-\nu_0)/d(3\cos^2\theta_{R,H_0}-1)$	Intensity $\mathcal{g}$ (arbitrary units)
$\Phi_2\rightarrow\Phi_1{}^s$	$-(15/2)\rho-\frac{3}{8}f(T)$	4
$\Phi_1{}^s\rightarrow\Phi_0$	$\frac{5}{2}\rho-\frac{3}{8}f(T)$	4
$\Phi_1{}^s\rightarrow\Phi_0{}^s$	$-\frac{5}{2}\rho+\frac{3}{8}f(T)$	2
$\Phi_1{}^a\rightarrow\Phi_0{}^a$	$-(15/2)\rho+\frac{3}{8}f(T)$	2
$\Phi_0{}^a\rightarrow\Phi_{-1}{}^a$	$+(15/2)\rho-\frac{3}{8}f(T)$	2
$\Phi_0\rightarrow\Phi_{-1}{}^s$	$-\frac{5}{2}\rho+\frac{3}{8}f(T)$	4
$\Phi_0{}^s\rightarrow\Phi_{-1}{}^s$	$\frac{5}{2}\rho-\frac{3}{8}f(T)$	2
$\Phi_{-1}{}^s\rightarrow\Phi_{-2}$	$(15/2)\rho+\frac{3}{8}f(T)$	4

triangle configurations neglecting intermolecular dipolar interactions has been carried out. The calculated positions of the peaks, some of them very broad, are presented in Figs. 1 and 2. In order to identify unambiguously a line in the spectrum with one shown in Figs. 1 or 2 it is necessary to compare the observed and calculated temperature dependence. Lines which are too near the central peak will be rather difficult to resolve. Accordingly, one concludes from Figs. 1 and 2 that except for configuration four (three ortho molecules in a row) one can not hope to observe the spectrum of triangular configurations of ortho molecules. The spectrum from these configurations will thus form a broad background for the sharper spectrum of the ortho pairs and will not be discussed further here.

In Sec. IV, the theoretical spectrum given by Eqs. (13) and J17) will be fitted to the experimental results, using as free parameters the energy Γ and the effective dipolar parameter d_{eff} instead of the value d for the free H_2 molecule in the rigid lattice.[21]

Table III. Rotational states for ortho pair.[a]

State	E/Γ
$\psi_1=(1/\sqrt{6})(\vert 1,-1\rangle+2\vert 0,0\rangle+\vert -1,1\rangle)$	6
$\psi_2=\vert 1,1\rangle$	1
$\psi_3=\vert -1,1\rangle$	1
$\psi_4=(1/\sqrt{2})(\vert 1,0\rangle-\vert 0,1\rangle)$	0
$\psi_5=(1/\sqrt{2})(\vert -1,0\rangle-\vert 0,1\rangle)$	0
$\Psi_6=(1/\sqrt{2})(\vert 1,-1\rangle-\vert -1,1\rangle)$	0
$\psi_7=(1/\sqrt{3})(\vert 1,-1\rangle-\vert 0,0\rangle+\vert -1,1\rangle)$	0
$\psi_8=(1/\sqrt{2})(\vert 1,0\rangle+\vert 0,1\rangle)$	−4
$\psi_9=(1/\sqrt{2})(\vert -1,0\rangle+\vert 0,-1\rangle)$	−4

[a] See Ref. 19.

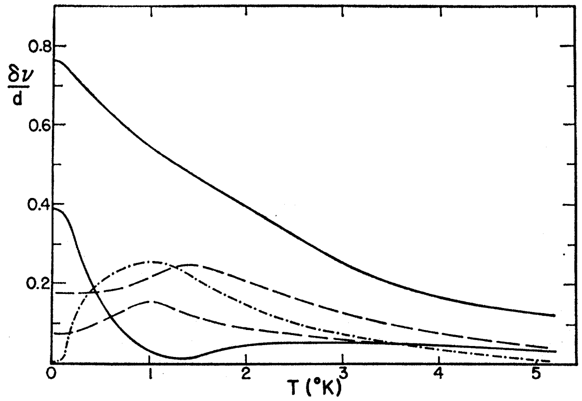

Fig. 1. The NMR spectrum of nearest ortho neighbors forming triangles, plotted in terms of reduced frequency $\delta\nu/d$ as a function of T. For those configurations having two maxima, the peak with the lowest frequency is the most intense. Dot-dash line, type-1 triangles; dashed line, type-2 triangles; solid line, type-4 triangles.

III. EXPERIMENTAL

The experiment consists of measuring the proton absorption line on samples with ortho concentrations between $c=0.034$ and $c=0.09$ at frequencies of about 12 MHz. The detection system is a low-level Robinson[22] oscillator, the frequency of which is determined by an electronic counter. The frequency is swept slowly through the absorption line, while the magnetic field is modulated about a constant value. The derivative of the line is recorded as a function of frequency simultaneously on a chart recorder and on IBM punch cards. A computer program is used to produce the absorption line shape and the second and fourth moments. The H_2 with a suitable ortho concentration is condensed into a small Teflon container surrounded by an rf coil and screwed onto a copper gland. Copper wires of 45 SWG protrude into the solid H_2 for better thermal contact with a heat sink and its thermometer. Temperatures between 0.45 and 15°K can be maintained and monitored.

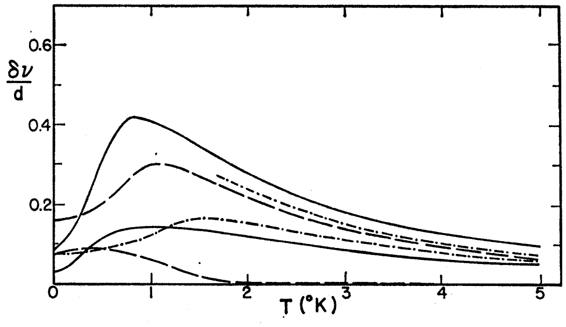

Fig. 2. The NMR spectrum of nearest ortho neighbors forming triangles plotted in terms of reduced frequency $\delta\nu/d$ as a function of temperature T. Dot-dash line, type-3 triangles. Below about 2°K, this type of triangle shows only one distinct maximum. Solid line, type-5 triangles; dashed line, type-6 triangles.

---

[21] The results, Eqs. (13) and (17), can be used to describe the resonance of isolated pairs of ortho molecules at larger separation by the appropriate scaling of Γ and ρ.

[22] F. N. H. Robinson, J. Sci. Instr. **36**, 481 (1959).

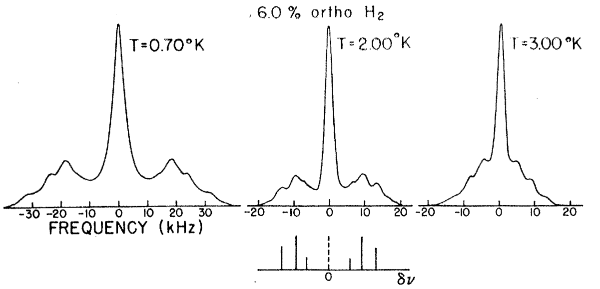

FIG. 3. The proton absorption line shape for $c=0.06$ at three temperatures. The spectrum under the central curve represents the three pairs of satellites expected according to Eqs. (13a), (13b), and (13c) with their respective intensities.

During an experiment it is possible to melt and recrystallize a H_2 sample at a desired rate. A fast crystallization rate, achieved by making thermal contact with the main liquid-helium bath, takes place within about 5 sec. Crystallization times up to about 40 min have been used. The cooling rate is monitored by a carbon resistance thermometer and by the broadening of the proton resonance spectrum.

The ortho concentration is analyzed before and after each experiment using the standard method of thermal conductivity of the gas.[23]

IV. RESULTS AND DISCUSSION

Measurements on ortho concentrations of $c=0.034$, 0.042, 0.060, and 0.090 show the peaks expected for pair interaction. At the next higher concentration investigated, $c=0.16$, the absorption line shape does not clearly show the pair spectrum. For the concentrations studied the NMR absorption line does not exhibit structure above about 4°K. Below this temperature, satellite peaks begin to appear. Figure 3 shows the line shape for $c=0.06$ at three temperatures. The central peak is attributed to ortho molecules whose nearest neighbors are all para molecules. This peak becomes broader as the temperature is decreased.

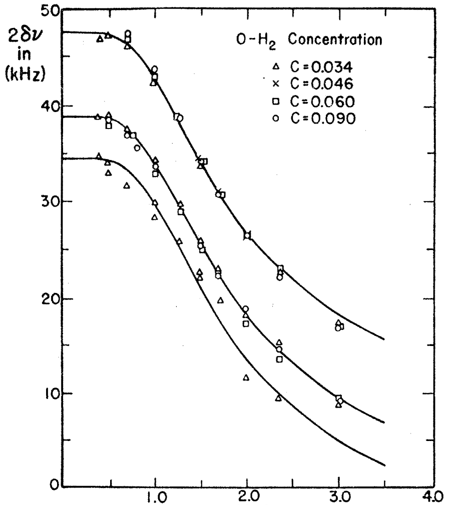

FIG. 4. The splittings $2\delta_1$, $2\delta_2$, and $2\delta_3$ between the three pairs of satellites as a function of temperature for several ortho concentrations. Since the satellites $2\delta_1$ show off best at low ortho concentrations, they have been evaluated only for $c=0.034$. Triangles, $c=0.034$; crosses, $c=0.046$; squares, $c=0.060$; circles, $c=0.090$, solid lines, calculated from Eqs. (13) and (17) taking $\Gamma/k_B=0.82$°K and $d_{\mathrm{eff}}=54.6$ kHz.

The splittings $2\delta\nu_i$ (in kHz) for the satellites shown in Fig. 3 are plotted in Fig. 4 as a function of temperature. One sees that the results for different ortho concentrations are consistent. although the over-all shape of the absorption line is strongly dependent on ortho concentration (Fig. 5). These satellites are attributed to isolated pairs. It is noticed, however, that there are some small systematic differences in their frequencies, even among samples having the same ortho concentration. This is confirmed by observing the spectrum for $c=0.06$ at 1.2°K after fast crystallization, then melting the sample and recrystallizing it slowly over a period of about 20 min and remeasuring the spectrum at 1.2°K. We therefore attribute these differences in the spectrum to the way the sample crystallizes. It may not form a perfect powder, but sometimes only a few crystals, if the crystallization is sufficiently slow. Averaging the term $(3\cos^2\theta_{R,H_0}-1)$ for a powder would then be only approximately valid. Furthermore, we would then expect to find a dependence of the spectrum on the orientation of the applied magnetic field. We have observed such an orientational dependence whose analysis will be presented elsewhere.[17] Although the size of the crystallites gives rise to systematic variations in the frequencies it should not influence the temperature dependence of $f(T)$.

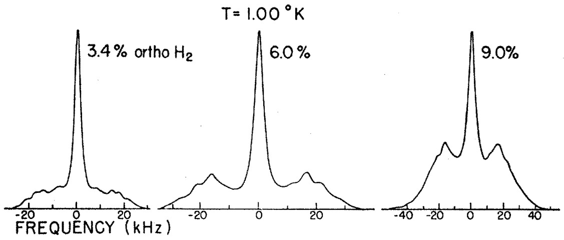

FIG. 5. Line shapes of three ortho concentrations at 1.0°K.

Note added in proof. Recently two of the present authors (L.I.A. and H.M.) and J. R. Thompson have extended the NMR measurements down to temperatures of about 0.15°K using a H_2 sample with $c=0.005$. There, the pair spectrum shows up still better than at the lowest concentration reported in this paper. The experimental splitting results, however, are the same. The temperature dependence of the splittings is

---

[23] See, for instance, E. M. Grilly, J. Sci. Instr. **24**, 72 (1953).

negligible below 0.45°K, in agreement with the theoretical curve in Fig. 4. These new results, the first ones of a study of solid H_2 below 0.45°K, will be published elsewhere.

The observed splittings are satisfactorily represented by Eq. (13) and (17) with $d_{\text{eff}}=54.5$ kHz and $\Gamma/k_B=0.82\pm0.03$°K. The measured d_{eff} compares with $d=57.7$ kHz for the free molecule. It is interesting that from about ten lineshapes observed in different samples in the cubic phase below 1°K, the separation between the satellites is found to fluctuate between 150 and 160 kHz, again probably as a consequence of different crystallization rates. The average splitting of 155 kHz then gives $d_{\text{eff}}(\text{cubic})=54.6\pm2$ kHz when the slight effect of frequency pulling due to intermolecular dipolar broadening is taken into account as described by Reif and Purcell.[16] Since the effect of intermolecular dipolar interactions on the more diffuse spectrum of ortho pairs is less pronounced, we have not attempted to make any such corrections to our data. This reduction in d in the cubic phase was already noted by Reif and Purcell.

It is unlikely that the difference between d_{eff} and d is caused by a difference in the bond length r of H_2 in the solids and the gas phases. An estimate based on the infrared absorption data of H_2 in both phases,[24] and the use of the potential curve[25] between the protons gives $r_{\text{solid}}-r_{\text{gas}}/r_{\text{gas}}\approx 6\times10^{-4}$. Since d is proportional to r^{-3} we have $(d_{\text{gas}}-d_{\text{solid}})/d_{\text{gas}}\approx 2\times10^{-3}$. The possible reason for the smaller value of d_{eff} may be due to zero-point motion of the lattice.[5]

The experimental value $\Gamma/k_B=0.82$°K is to be compared with the expected value $\Gamma/k_B=1.00$°K calculated from the quadrupole moment for a free molecule,[3] $Q=0.137\times10^{-16}$ cm^2, and[26] $R=3.755\times10^{-8}$ cm. The fit of theory to the experiment was made under the assumption that there was no crystalline field causing further splittings. As mentioned previously, Sung[13] has shown that the crystal-field splittings are small. In that work the crystal field was assumed to coincide with the c axis of the crystal. However, Hardy and Gaines[1] have found that for isolated ortho molecules in para H_2 the crystalline field splittings are less than 6×10^{-3} cm^{-1}. This result would seem to indicate that the component of the crystalline field along the c axis is very small. It is possible that for ortho pairs strain-induced effects create a larger crystalline field splitting. Accordingly, we have also analyzed the data admitting the possibility of a crystalline field symmetric about the line joining the two ortho molecules. The associated Hamiltonian is given by

$$\mathcal{H}_c=V_c\{J_{z1}^2+J_{z2}^2-\tfrac{4}{3}\}. \tag{19}$$

With the new $f(T)$ calculated using $\mathcal{H}_c$, one does not obtain as good a fit to the data as that in Fig. 4, although satisfactory agreement is obtained providing V_c and Γ are related by

$$\Gamma/k_B=0.82-0.32V_c/k_B$$

with

$$-0.5°\text{K}<V_c/k_B<0°\text{K},$$

the agreement becoming worse as V_c increases.

Assuming Sung's conclusions also hold with respect to the size of this crystalline field Hamiltonian for pairs of ortho molecules, we have that

$$|V_c/k_B|\ll 0.05°\text{K}$$

so that

$$\Gamma/k_B=0.82\pm0.06°\text{K}.$$

V. SUMMARY

The value of $\Gamma/k_B=0.82$°K that we find is consistent with the results of a recent re-analysis[5] of other data for solid H_2, which indicates a smaller value of Γ than expected for a rigid lattice. Also, the fact that d_{eff} is smaller than d can be understood as evidence of interactions between molecular rotations and phonons.

ACKNOWLEDGMENTS

The authors are indebted to D. Ramm and to C. Smith for help in several experiments.

---

[24] E. J. Allin, T. Feldman, and H. L. Welsh, J. Chem. Phys. **24**, 1116 (1956).

[25] B. P. Stoicheff, Can. J. Phys. **35**, 738 (1957).

[26] R. L. Mills and A. Schuch, Phys. Rev. Letters **15**, 722 (1965).