

## THE ROTATIONAL MOTION OF MOLECULES IN CRYSTALS

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## ABSTRACT

It is shown by the discussion of the wave equation for a diatomic molecule in a crystal that the motion of the molecule in its dependence on the polar angles  $\theta$  and  $\phi$  may approach either one of two limiting cases, oscillation and rotation. If the intermolecular forces are large and the moment of inertia of the molecule is large (as in  $I_2$ , for example), the eigenfunctions and energy levels approach those corresponding to oscillation about certain equilibrium orientations; if they are small (as in  $H_2$ ), the eigenfunctions and energy levels may approximate those for the free molecule, even in the lowest quantum state.

It is found in this way that crystalline hydrogen at temperatures somewhat below the melting point is a nearly perfect solid solution of symmetric and antisymmetric molecules, the latter retaining the quantum weight 3 for the state with  $j=1$  as well as the spin quantum weight 3. This leads to the expression

$$S = -n_A R \log n_A - (1 - n_A) R \log (1 - n_A) + n_A R \log 9 + S_{tr},$$

in which  $S_{tr}$  is the translational entropy, for the entropy of the solid at these temperatures. At lower temperatures (around 5°K) the solid solution becomes unstable relative to phases of definite composition, and the entropy falls to

$$S = n_A R \log 3 + S_{tr},$$

the entropy of mixing and of the quantum weight 3 for  $j=1$  being lost at the same time. Only at temperatures of about 0.001°K will the spin quantum weight entropy be lost.

Gradual transitions covering a range of temperatures and often unaccompanied by a change in crystal structure, reported for  $CH_4$ ,  $HCl$ , the ammonium halides, and other substances, are interpreted as changes from the state in which most of the molecules are oscillating to that in which most of them are rotating. The significance of molecular rotation in the interpretation of other phenomena is also discussed.

## I. INTRODUCTION

THE calculation of the difference in entropy of gaseous molecular hydrogen and crystalline hydrogen has recently been made by Giauque and Johnston.<sup>1</sup> At temperatures between the melting point (14°K) and about 10°K the heat capacity of the solid is well represented by a Debye function with  $\beta\nu = 91^\circ$ . Assuming the validity of extrapolation to 0°K by means of this function, it is found that the difference in entropy of the solid at 0°K and the gas at standard conditions is  $29.7 \pm 0.1$  E. U. The molal entropy of the gas at standard conditions is given by the Sackur-Tetrode equation as 34.00 E. U., using the band spectrum value of the moment of inertia, and taking into account the symmetry number term ( $-R \log 2$ ), the entropy of mixing of sym-

<sup>1</sup> W. F. Giauque and H. L. Johnston, J. A. C. S. **50**, 3221 (1928).

metric and antisymmetric molecules, present in the ratio of  $1:3(-1/4 R \log 1/4 - 3/4 R \log 3/4)$ , and the nuclear spin quantum weight of the antisymmetric molecules ( $3/4 R \log 3$ ). Thus the molal entropy of ordinary crystalline hydrogen (the metastable mixture of symmetric and antisymmetric molecules in the ratio of 1:3) at temperatures somewhat below the melting point is found to be  $4.3 \pm 0.1$  E. U. in addition to the translational entropy. In the attempt to account for this deviation from the value zero to be expected from the third law of thermodynamics, it was found necessary to carry through the quantum mechanical discussion of the motion of molecules in crystals.

Before proceeding with this task, it may be illuminating to mention the concept of the motion of a molecule in a crystal which we would form on the basis of classical mechanics. All but six of the degrees of freedom for the molecule can be assigned to represent relative motions of the atoms within the molecule, corresponding to internal oscillations. The six remaining degrees of freedom can be represented by the three coordinates  $x, y, z$  of the center of mass of the molecule referred to an arbitrarily chosen set of axes, and the Eulerian angles  $\varphi, \theta, \chi$  determining the orientation of the molecule with respect to the same axes. In case the forces between atoms in a molecule are much stronger than those between atoms in different molecules, a crystal of the substance may be considered as a first approximation to be a collection of rigid molecules held in a regular arrangement by the rather weak intermolecular forces. Each molecule will remain in the neighborhood of its equilibrium position, the coordinates  $x, y, z$  varying through only a small region of values about  $x_0, y_0, z_0$ . Similarly, there will be one or more sets of values of  $\varphi, \theta, \chi$  for which the potential energy is a minimum, corresponding to equilibrium orientations of the molecule. There are two types of motion then possible for the molecule. If the potential energy for values of  $\varphi, \theta, \chi$  in the neighborhood of  $\varphi_0, \theta_0, \chi_0$  is very small compared with that for other values, the difference being much larger than  $kT$ , the average molecule at the temperature  $T$  will carry out only small vibrations about its equilibrium orientation. This may be spoken of as oscillation about the equilibrium orientation. But if the potential energy undergoes a total variation smaller than  $kT$ , the kinetic energy of the average molecule will suffice to carry it into any orientation, so that the molecule will undergo non-uniform rotation, speeding up as it passes through the equilibrium orientations and slowing down as it goes over the potential maxima. A molecule with a given amount of energy and acted upon by a given potential would according to the classical theory assume a succession of orientations corresponding either to one or to the other of these possibilities, oscillation or rotation.

The introduction of the quantum mechanics does not require this picture to be changed essentially. The allowed states of the system can approximate either of two extremes, oscillation and rotation, or can lie between these extremes, approximating neither more closely than the other. For with the quantum mechanics, in contradistinction to the classical theory, the transition from one extreme to the other is unbroken.

## II. THE DIATOMIC MOLECULE IN A CRYSTAL

In Fig. 1 there is shown the structure of the orthorhombic crystal iodine as determined with the use of x-rays.<sup>2</sup> The atoms are joined in pairs to form molecules by strong shared-electron-pair bonds, and the molecules are

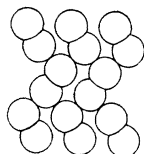


Fig. 1. The arrangement of atoms in one layer in a crystal of iodine. It is seen that the atoms are in groups of two (the molecules  $I_2$ ) which are oriented by the intermolecular forces. grouped together in such a way that the figure axis for each assumes a definite orientation. This is the equilibrium orientation, with the polar angle  $\theta = 0$ , say. The symmetry of the molecule requires that there also be another equilibrium orientation at  $\theta = \pi$ .

Let us consider a diatomic molecule in such a crystal. As a first approximation we may neglect the translational oscillations of the molecule under consideration and both the translational and rotational motion of the other molecules in the crystal. The wave equation then may be written

$$\nabla^2 \psi + \frac{8\pi^2 I}{h^2} (W - V) \psi = 0, \quad (1)$$

in which  $I$  is the moment of inertia of the molecule and  $V = V(\theta, \varphi)$  is a potential function representing the averaged interaction of the molecule with surrounding molecules. The simplest form that can be given this function and have it represent a diatomic molecule with two equilibrium orientations is

$$V = V_0(1 - \cos 2\theta), \quad (2)$$

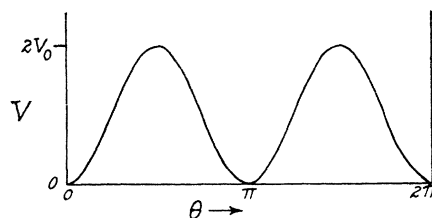


Fig. 2. The potential function  $V = V_0(1 - \cos 2\theta)$ .

in which  $V_0$  is a constant. This potential function is shown in Fig. 2. The wave equation then becomes

$$\frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi}{\partial \theta} + \frac{8\pi^2 I}{h^2} (W - V_0 + V_0 \cos 2\theta) \psi = 0. \quad (3)$$

<sup>2</sup> P. M. Harris, E. Mack and F. C. Blake I. A. C. S. **30**, 1583 (1928).

The characteristic value equation in  $\theta$  obtained from this has not been solved except for limiting cases. The corresponding problem in a plane has, however, been fully treated. If the molecule were restricted to motion in a plane the wave equation would be

$$\frac{d^2\psi}{d\theta^2} + \frac{8\pi^2 I}{h^2} (W - V_0 + V_0 \cos 2\theta)\psi = 0 \quad (4)$$

or, writing

$$\alpha = \frac{2\pi^2 I}{h^2} (W - V_0)$$

$$q = \frac{\pi^2 I V_0}{2h^2},$$

$$\frac{d^2\psi}{d\theta^2} + (4\alpha + 16q \cos 2\theta)\psi = 0. \quad (5)$$

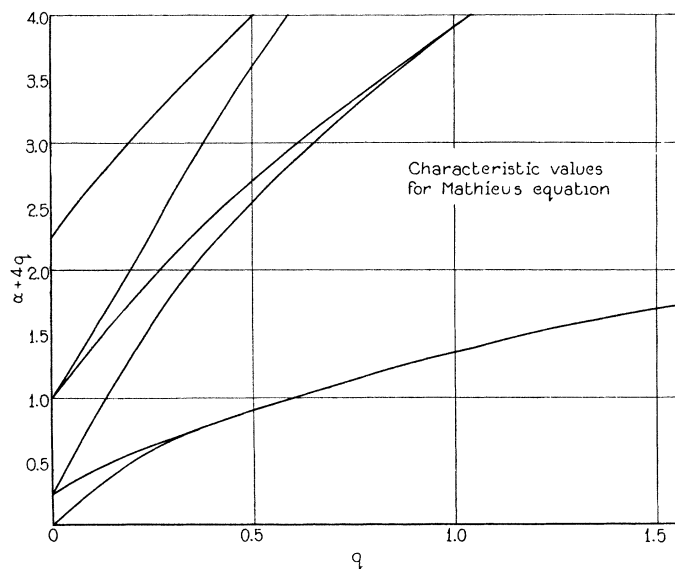


Fig. 3. The characteristic values for the six lowest Mathieu functions.

This equation is Mathieu's equation in the usual form.

The requirement that  $\psi$  be periodic in  $\theta$  with the period  $2\pi$  leads to the functions known as Mathieu functions.<sup>3</sup> These are usually designated by the symbols  $ce_0$ ,  $se_1$ ,  $ce_1$ ,  $se_2$ ,  $ce_2$ , etc. The functions and the corresponding characteristic values of  $\alpha$  as functions of  $q$  have been evaluated by Goldstein.<sup>4</sup> The energy values for the five lowest states are shown in Fig. 3. It is seen

<sup>3</sup> E. Mathieu, *Liouville's Jour.* **13**, 137 (1868); Whittaker and Watson, "Modern Analysis," pp. 404-428. E. U. Condon, *Phys. Rev.* **31**, 891 (1928), pointed out that the Mathieu functions of even order are the eigenfunctions for the plane pendulum.

<sup>4</sup> S. Goldstein, *Trans. Cambridge Phil. Soc.* **23**, 303 (1927).

that for  $q=0$  Eq. (5) reduces to the equation for the plane rotator, with energy levels  $W_m = (m^2 h^2 / 8\pi^2 I)$ . For  $q$  large the eigenfunction  $\psi$  is appreciably different from zero only for values of  $\theta$  close to 0 and  $\pi$ , and approximates a combination of Hermite orthogonal functions, the eigenfunctions for the harmonic oscillator. The energy levels for this case are  $(n+1/2) h\nu_0$ , in which  $\nu_0 = h(2q)^{1/2} / \pi I$ . Each energy level shows two-fold degeneracy, the corresponding eigenfunctions being approximately

$$\frac{1}{2^{1/2}} \{ \psi_n(\theta/\theta_0) + \psi_n(\theta - \pi)/\theta_0 \} \quad \text{and} \quad \frac{1}{2^{1/2}} \{ \psi_n(\theta/\theta_0) - \psi_n(\theta - \pi)/\theta_0 \},$$

in which  $\psi_n(\theta/\theta_0)$  and  $\psi_n((\theta - \pi)/\theta_0)$  represent Hermite orthogonal functions of the indicated arguments, and  $\theta_0$  is given by the equation  $h\nu_0/2 = V_0\theta_0^2$ .

This can be used as the basis of a perturbation treatment of the problem, using the method of variation of constants,<sup>5</sup> as in the treatment of aperiodic phenomena.<sup>6</sup> It is found that in case it were possible to carry out an experiment to determine whether the molecule were undergoing vibrations about  $\theta=0$  or about  $\theta=\pi$ , with the use of a method of investigation involving an interaction unsymmetrical in the two atoms composing the molecule, the probability of observing the molecule in one orientation rather than the other would vary in a way corresponding to the molecule's changing end for end with a frequency given by the separation of adjacent energy levels ( $ce_0$  and  $se_1$ ,  $ce_1$  and  $se_2$ , etc) divided by  $h$ . Reference to Fig. 3 shows that this frequency is very small for  $q$  large, justifying the interpretation of the corresponding states as oscillational states, the molecule oscillating about an equilibrium orientation and changing end for end only rarely. But for  $q$  small this frequency becomes large, approaching the principal frequency of motion of the molecule; then we say that the molecule is rotating, its rotation being made somewhat non-uniform through interactions with other molecules. The energy levels in this case approximate those for the free plane rotator, and their behavior for small values of  $q$  can be conveniently followed by perturbation methods using the rotator eigenfunctions as zero<sup>th</sup> order eigenfunctions.

These considerations, involving a hypothetical investigation of the orientation of the molecule, are, while illuminating, not essential to the discussion of the type of motion of the molecule. We can define the motion of the molecule in a given state as oscillational in case the eigenfunction for that state can be closely approximated by a combination of Hermite functions and the energy of the state is given approximately by  $(n+1/2) h\nu_0$ . For rotational motion the eigenfunction and energy level should approximate those for a free rotator. This definition is equivalent to that given above: the study of Goldstein's Fourier series representation of the Mathieu functions shows that the transition of the eigenfunctions from approximation to Hermite

<sup>5</sup> P. A. M. Dirac, Proc. Roy. Soc. **A112**, 661 (1926); J. C. Slater, Proc. Nat. Acad. **13**, 7104 (1927); M. Born, Zeits. f. Physik **40**, 172 (1926).

<sup>6</sup> See the clear exposition given the process of radioactive decomposition by M. Born, Zeits. f. Physik **58**, 306 (1929).

functions to approximation to sines and cosines takes place rather sharply at the value of  $q$  where the separation of adjacent energy levels becomes appreciable. A similar treatment can be applied to the spatial rotator with two potential minima. The discussion of the qualitative course of the energy levels and the nature of the eigenfunctions is similar to that given above, and a detailed treatment is not needed for our purposes.

### III. ROUGH CRITERIA FOR OSCILLATION AND ROTATIONAL MOTION

Let us tentatively assume that the motion is oscillation. Then we can approximate the lower part of  $V(\theta) = V_0(1 - \cos 2\theta)$  by a parabola by expanding in powers of  $\theta$  and  $\theta - \pi$  obtaining  $-2V_0\theta^2$  and  $-2V_0(\theta - \pi)^2$  as the expansions in the neighborhood of  $\theta = 0$  and  $\theta = \pi$ . These correspond to energy levels

$$W_n = (n + 1)h\nu_0, \quad n = 0, 1, 2, 3, \dots \quad (6)$$

for the two-dimensional harmonic oscillator, with

$$\nu_0 = \frac{1}{\pi} \left( \frac{V_0}{I} \right)^{1/2}. \quad (7)$$

In case that  $W_n = (n + 1)h\nu_0$  is less than  $2V_0$ , the top of the potential hill separating the two-valleys, the molecule will change orientation only rarely. (The exceptional case with  $V_0$  and  $n$  small for which there is a large probability of the molecule turning end for end even when its energy is not sufficient to carry it over the hill, is discussed later). But for  $W_n$  larger than  $2V_0$  the motion will be rotational. Thus we obtain the following criteria:

$$\begin{aligned} n + 1 &< \frac{2\pi(IV_0)^{1/2}}{h}, & \text{oscillational motion,} \\ n + 1 &> \frac{2\pi(IV_0)^{1/2}}{h}, & \text{rotational motion.} \end{aligned} \quad (8)$$

The uncertain quantity of these expressions is  $V_0$ . A rough value for it can be obtained from the observed heat capacity of the solid. If the molecules oscillate about equilibrium orientations the molal heat capacity would be given as a first approximation by the sum of a Debye function of parameter  $\beta\nu$ , corresponding to the translational oscillations, and twice an Einstein function of parameter  $\beta\nu_0 = h\nu_0/k$ , with  $\nu_0$  the characteristic frequency of Eq. (7). It is found that such a curve does not give a very close fit with observed heat capacities since the model is too greatly simplified; but the heat capacity curve does show that  $\beta\nu$  and  $\beta\nu_0$  are nearly the same for many substances and a rough value for them can be obtained by taking three times the temperature at which the heat capacity reaches 5 cal/mole degree; that is, half the high-temperature value for five degrees of freedom.<sup>7</sup> Values of

<sup>7</sup> This procedure is based on the fact that an Einstein function reaches half its maximum value at the temperature  $0.33\beta\nu_0$ .

TABLE I.

Molecule	$\beta\nu_0$	$\Theta$	$n_0+1$	$V_0$	Heat of fusion and transition
				cal/mole	cal/mole
I <sub>2</sub>	75°	0.053°	350	25000	4000
N <sub>2</sub>	65°	2.33°	7.0	450	222
O <sub>2</sub>	70°	2.06°	8.5	600	306
CO	75°	2.65°	7.1	500	354
CH <sub>4</sub>	55°	8.5°	1.6	90	242
HCl	160°	14.9°	10.7	1700	760
HBr	125°	11.9°	10.5	1300	803
HI	105°	9.2°	11.4	1200	897
H <sub>2</sub>	<135°	82° <sub>0</sub>	<0.4	<56	28

$\beta\nu_0$  for several substances<sup>8</sup> are given in Table I, together with the characteristic temperature for rotational degeneracy,  $\Theta$ , which is related to the moment of inertia  $I$  (obtained from band spectral data) by the equation

$$\Theta = \frac{h^2}{8\pi^2 I k} \quad (9)$$

The heat capacity of solid hydrogen provides no information regarding  $\beta\nu_0$  for H<sub>2</sub>. An upper limit for  $\beta\nu_0$  can, however, be found in the following way. It is seen that for many substances the total heat change accompanying transitions and fusion is about equal to  $V_0/2$  (compare columns 6 and 7 of Table I). Assuming this to hold for H<sub>2</sub>, we find  $V_0 = 56$  cal/mole, which, from the trend of the ratio  $V_0/\Delta H$  with molecular weight, can be accepted as a maximum value. This corresponds to  $\beta\nu_0 < 135^\circ$ . The approximate constancy of  $\beta\nu_0$  in the series I<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> suggests a value of this order of magnitude for H<sub>2</sub> also; it and derived quantities are included in Table I.

In terms of  $\beta\nu_0$  and  $\Theta$  the criteria 8 become

$$n + 1 < \beta\nu_0/4\Theta, \quad \text{oscillational motion,} \quad (10)$$

$$n + 1 > \beta\nu_0/4\Theta, \quad \text{rotational motion.}$$

The transition from oscillational to rotational motion should occur for  $n = n_0$ , with

$$n_0 + 1 = \frac{\beta\nu_0}{4\Theta} \quad (11)$$

Values of  $n_0+1$  are given in Table I. There are also included data for unsymmetric molecules such as HCl. For these a reasonable potential function

<sup>8</sup> Since these calculations were made some direct verification of them has been provided by the work of L. Vegard (Nature **125**, 14 (1930)) who has obtained spectra from solid nitrogen at very low temperatures involving an electronic transition, a change in oscillation within the molecule, and an additional energy change corresponding to frequencies of 40 cm<sup>-1</sup> and 69 cm<sup>-1</sup> which he interprets as oscillational jumps for the molecule in the lattice. One of these frequencies probably is the frequency of rotational vibration of the molecule. 40 cm<sup>-1</sup> and 69 cm<sup>-1</sup> correspond to  $\beta\nu_0 = 57^\circ$  and  $99^\circ$  respectively, the first of which is in good agreement with the rough value  $65^\circ$  of Table I.

is  $V = V_0(1 - \cos \theta)$ , corresponding to an electric dipole in a uniform field. This leads to a transitional value  $n_0$  given by

$$n_0 + 1 = \frac{\beta\nu_0}{\Theta} \quad (12)$$

For CO it is doubtful as to whether 11 or 12 is more nearly applicable; the former has been used.

The value  $n_0 + 1 < 0.4$  found for  $H_2$  shows that *even in the lowest state* the molecules are rotating freely, the intermolecular forces producing only small perturbations from uniform rotation. Indeed, the estimated  $\beta\nu_0 < 135^\circ$  corresponds to  $V_0 < 28k$ , which is small compared with the energy difference  $164k$  of the rotational states  $j=0$  and  $j=1$ , giving the frequency with which the molecule in either state reverses its orientation. The perturbation treatment shows that with this value of  $V_0$  the eigenfunctions and energy levels in all states closely approximate those for the free spatial rotator.<sup>9</sup>

The other extreme is provided by  $I_2$ , for which the transition from oscillation to rotation takes place at about  $n = 300$ . At the melting point the molecules are in states with  $n = 10$  or  $15$ , so that there are no rotating molecules in this crystal. This agrees with the fact that equilibrium positions for the atoms have been found by x-ray methods.

The remaining substances form intermediate cases, the molecules in lower states oscillating and in higher states rotating. Whether the transition to rotational states takes place in the main before the crystal melts will be considered in Section V.

#### IV. CRYSTALLINE HYDROGEN AND ITS ENTROPY

In ordinary crystalline hydrogen there are three molecules with  $j=1$  for every one with  $j=0$ . The eigenfunctions for these molecules approximate those for free molecules, namely

$$\begin{aligned} j = 0, \psi_0 &= 1/(4\pi)^{1/2}, \\ j = 1, \psi_1 &= (3/4\pi)^{1/2} \cos \theta, (3/4\pi)^{1/2} \sin \theta \cos \phi, (3/4\pi)^{1/2} \sin \theta \sin \phi, \end{aligned} \quad (13)$$

in terms of angles  $\theta$  and  $\phi$  relative to an arbitrary coordinate system. These rotating molecules interact with each other as though they were nearly spherically symmetrical.<sup>10</sup> Hence we expect the crystal to have a close-packed structure—cubic close-packed, say, with molecules at  $000$ ,  $0\frac{1}{2}\frac{1}{2}$ ,  $\frac{1}{2}0\frac{1}{2}$ ,  $\frac{1}{2}\frac{1}{2}0$ . This agrees with the known cubic symmetry of crystalline hydrogen.<sup>11</sup> The

<sup>9</sup> It is worthy of especial mention that in the state with  $j=0$  the molecules are to be considered as rotating when  $V_0$  is sufficiently small (less than the separation of the levels  $j=0$  and  $j=1$ ) even though the energy of the state ( $\sim V_0$ ) is not sufficient to carry the molecule over the potential maximum ( $2V_0$ ). This is shown by the close approximation of the corresponding eigenfunction to the lowest tesseral harmonic and by the high frequency of end-for-end interchange given by the perturbation treatment, starting with oscillational eigenfunctions.

<sup>10</sup> The forces holding the rotating molecules result from interpenetration of the molecules, as for the noble gases.

<sup>11</sup> The observed density  $0.0808$  at  $11^\circ K$  corresponds to a unit with  $a = 5.46\text{\AA}$ , the distance between adjacent molecules being  $3.86\text{\AA}$ .



x-ray investigation of the crystals should not lead to the determination of atomic positions, but only of molecular positions.

In cubic close-packing each molecule is surrounded by twelve others, whose interaction with the central molecule can be represented by a potential function of cubic point-group symmetry in case that the twelve molecules are spherically symmetrical or oriented at random. The energy change produced by this potential function,  $f$  say, is

$$W^1 = \int \int \psi f \bar{\psi} \sin \theta d\theta d\phi,$$

which is easily shown by the consideration of the symmetry of  $f$  to be the same for all four eigenfunctions. Thus a molecule of symmetrical hydrogen, with  $j=0$ , has in a crystal the same energy as a molecule of antisymmetrical hydrogen, with  $j=1$ . As a result the two forms of hydrogen should form a complete series of nearly perfect solid solutions, and, moreover, the energy content of the crystal, aside from rotational energy, should be independent of the composition. This has been verified by the measurements of Clusius and Hiller,<sup>12</sup> who found symmetrical hydrogen to have the same heat capacity and heat of fusion as the 1:3 mixture.

Additional experimental verification that molecules of hydrogen in condensed phases are in states approximating those for free molecules is provided by the Raman effect measurements of McLennan and McLeod.<sup>13</sup> A comparison of the Raman frequencies found by them and the frequencies corresponding to the rotational transitions  $j=0 \rightarrow j=2$  and  $j=1 \rightarrow j=3$  (Table II) shows that the intermolecular interaction in liquid hydrogen produces only a very small change in these rotational energy levels.

TABLE II.

Transition	Raman effect	Band spectra
$j=0 \rightarrow j=2$	354 $\text{cm}^{-1}$	347 $\text{cm}^{-1}$
$j=1 \rightarrow j=3$	588	578
0 $\rightarrow$ 1 in intramolecular oscillation	4149	4159

These considerations permit a calculation of the entropy of crystalline hydrogen at temperatures somewhat below the melting point. Ordinary crystalline hydrogen, consisting of the symmetrical and antisymmetrical forms in the ratio of 1:3, has an entropy of mixing of  $-(1/4)R \log (1/4) - (3/4)R \log (3/4)$ , for the solid solution can be considered ideal. The symmetrical molecules have a quantum weight 1 in the normal state, with  $j=0$ , and the antisymmetrical molecules a quantum weight 9, corresponding to the three rotational eigenfunctions for  $j=1$ , each of which is associated with any one of the three spin eigenfunctions. This gives a predicted total entropy of the solid at temperatures just below the melting point of

$$S_{H_2} = -\left(\frac{1}{4}\right)R \log \left(\frac{1}{4}\right) - \left(\frac{3}{4}\right)R \log \left(\frac{3}{4}\right) + \left(\frac{3}{4}\right)R \log 9 + S_{tr} = 4.39 \text{ E. U.} + S_{tr}, \quad (14a)$$

<sup>12</sup> K. Clusius and K. Hiller, *Zeit. f. phys. Chem.* **B4**, 158 (1929).

<sup>13</sup> J. C. McLennan and J. H. McLeod, *Nature* **123**, 160 (1929).

in which  $S_{tr}$  is the translational entropy. This value is in excellent agreement with the experimental value  $4.3 \pm 0.1 + S_{tr}$  of Giauque and Johnston.<sup>14</sup> In general a mixture containing  $n_A$  mole-fraction of antisymmetric molecules would have

$$S = -n_A R \log n_A - (1 - n_A) R \log (1 - n_A) + n_A R \log 9 + S_{tr}. \quad (14b)$$

At very low temperatures a separation of the three rotational levels with  $j=1$  will take place. This is a second-order effect, depending on the mutual orientation of two or more molecules. As an illustration, let us assume that we could obtain a crystal of pure antisymmetric hydrogen. At temperatures not too near 0°K the molecules would be in cubic close-packing, and an arbitrary molecule could be represented by any one of the three eigenfunctions with  $j=1$ . But there are possible states of the crystal somewhat more stable than those in which the three rotational eigenfunctions with  $j=1$  are represented by random molecules. Thus if each molecule were in the state with  $j=1$ ,  $m=0$ , corresponding to the eigenfunction  $(3/4\pi)^{1/2} \cos \theta$ , with  $\theta$  referred to trigonal axes which for the various molecules are oriented as are the figure axes of CO<sub>2</sub> in crystals of this substance, then the energy of the crystal would be less than that of a crystal in which the three eigenfunctions with  $j=1$  were represented at random. In crystalline CO<sub>2</sub> each molecule is surrounded by twelve others, of which the six in the equatorial plane point towards the central molecule, bringing six oxygen atoms to within 3.25Å, while the other six molecules place oxygen atoms 4.12Å away. As a result the stable orientation for the central molecule is along the trigonal axis. The distribution function  $\psi^2 = 3/4\pi \cos^2\theta$  for a hydrogen molecule with  $j=1$  and  $m=0$  shows a tendency for the molecule to line up parallel to the axis  $\theta=0$ , leading to the decreased energy of the CO<sub>2</sub>-similar structure described above. Since this is a second-order effect the energy decrease will be considerably smaller than  $V_0$ , of the order of magnitude of  $V_0/5$ . With  $V_0$  equal to about 28  $k$  at the most, the temperature at which this structure would become stable relative to the random one would be of the order of magnitude of 5°K.

With other simple ratios of symmetric to antisymmetric molecules other structures might become stable at very low temperatures. Since the energy change depends on the interaction of two antisymmetric molecules, which would drop off very rapidly as the molecules were separated, crystals containing only a small fraction of antisymmetric molecules would be unstable, breaking down into two phases, pure crystalline symmetric hydrogen and crystals with  $n_A$  (the mole-fraction of antisymmetric molecules) equal to 1, 1/2, or some other simple fraction. This process, involving diffusion of the molecules, might take some time, so that care would be necessary to insure equilibrium in the study of mixtures with  $n_A$  small.

The entropy change accompanying this transition is predicted to be

<sup>14</sup> The possibility of the expression of the entropy of hydrogen as the sum of these terms was first noted by Giauque, who observed that it indicated the formation of nearly ideal solid solutions between symmetrical and antisymmetrical hydrogen and the retention of the quantum weight 9 for the latter.

$$S = -n_A R \log n_A - (1 - n_A) R \log (1 - n_A) + n_A R \log 3 \quad (15)$$

corresponding to the restriction of each antisymmetric molecule to one of the three rotational states with  $j=1$ , and to the removal of the entropy of mixing of the solid solution existing above the transition temperature.<sup>15</sup> The entropy of the crystals then becomes

$$S = n_A R \log 3 + S_{tr}. \quad (16)$$

The discovery of a transition which we identify with this has been reported by Simon, Mendelssohn, and Ruhemann,<sup>16</sup> who measured the heat capacity of hydrogen with  $n_A = 1/2$  down to 3°K. They found that the heat capacity, after following the Debye curve down to about 11°K, rose at lower temperatures, having the value 0.4 cal/deg., 25 times that of the Debye function, at 3°K. The observed entropy of transition down to 3°K, at which the transition is not completed, was found to be about 0.5 E.U. That predicted by Eq. (15) for the transition is 2.47 E.U.

In crystals for which  $n_0$  is large, such as iodine, the lowest symmetric and the lowest antisymmetric state have practically the same energy and properties, and each corresponds to one eigenfunction only. As a result a mixture of symmetric and antisymmetric molecules at low temperatures will behave as a perfect solid solution, each molecule having just its spin quantum weight, and the entropy of the solid will be the translational entropy plus the same entropy of mixing and spin entropy as that of the gas. This has been verified for I<sub>2</sub> by Giauque.<sup>17</sup> Only at extremely low temperatures will these entropy quantities be lost.

#### V. THE TRANSITION FROM OSCILLATIONAL TO ROTATIONAL MOTION

A consideration of the values of  $n_0$  for CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, and the hydrogen halides indicates that these molecules oscillate at low temperatures but go over mainly to rotational states before the melting point is reached. This process should be accompanied by thermal phenomena, as is shown by the following argument. With  $n < n_0$  the eigenfunctions in  $\theta$  and  $\phi$  change only slightly as  $n$  is increased; the probability function  $\psi\bar{\psi}$ , with maxima in the neighborhood of the equilibrium values of  $\theta$  and  $\phi$ , falls off rapidly from these maxima, and increase in  $n$  causes only some spread, corresponding to larger amplitudes of oscillation. But a radical change takes place as  $n$  goes through the transition value. The eigenfunctions change completely in nature, becoming much more nearly constant, as may be verified by a study of the Fourier series coefficients given by Goldstein for the Mathieu functions. This change increases the repulsive forces between molecules, and tends to spread the crystal lattice

<sup>15</sup> The entropy  $n_A R \log 3$  arising from the three spin eigenfunctions for antisymmetrical molecules will be lost only at temperatures of the order of magnitude of 0.001°K, at which the very small nuclear interaction energy would become appreciable. It may be pointed out that the magnitude of the interaction energy with other molecules for the three states with  $j=1$  as compared with the spin-rotation interaction energy is such as not to permit coupling of  $i$  and the spin moment to form a resultant.

<sup>16</sup> F. Simon, K. Mendelssohn, and M. Ruhemann, *Naturwiss.* **18**, 34 (1930).

<sup>17</sup> Personal communication.

as soon as an appreciable number of molecules have begun to rotate. But spreading the lattice decreases the forces between molecules and decreases  $\beta\nu_0$  and  $V_0$ , so that more molecules can rotate. The effect builds up to give a transition, which often is not accompanied by an essential change in the structure of the crystal. The transition is usually not sharp, but covers a range of temperature of several degrees, and is foreshadowed on the low temperature side by an abnormal increase in heat capacity.

Such a transition is shown by methane.<sup>18</sup> The heat capacity rises rapidly from 18°K to a very sharp maximum (over 48 cal/mole deg.) at 20.4°, and then drops sharply to 4.6 cal/mole deg. at 22.8°. The temperature of transition agrees with the low value (about 1) predicted for  $n_c$ . A methane crystal between 20° and 90.6°K (the melting point) would be described as consisting of rotating molecules in cubic close-packing;<sup>19</sup> below 20° the tetrahedral molecules oscillate about equilibrium orientations. It would be very interesting to have Raman effect or infrared spectral data for solid methane; above 20° the lines should very closely approximate the rotation lines for the gaseous molecules, and below that temperature should show pronounced changes, the frequencies of the lines increasing and tending to become constant as the motion approaches harmonic oscillation.

The course of the heat capacity curves also indicates that the transitions shown by N<sub>2</sub> and O<sub>2</sub> at 35.4° and 43.76° respectively are accompanied by the setting in of rotation of the molecules. This is supported by the known crystallographic symmetry of the high temperature forms; nitrogen cubic (indicating cubic close-packing of N<sub>2</sub> molecules) and oxygen hexagonal (indicating hexagonal close-packing).

The gradual transitions shown<sup>20</sup> by HCl (at 98°K), HBr (at 89°, 113°, and 117°K), and HI (at 70° and 126°K) are to be given a similar interpretation.<sup>21</sup> Each of the successive transitions in HBr and HI may be connected with incipient rotation about one crystal axis and the expansion of the crystal along that axis alone. In every case freely rotating molecules would assume a close-packed arrangement (cubic close-packing of molecules has been found with x-rays by Simon and Simson<sup>22</sup> for the high temperature form of HCl); on cooling below the temperature at which oscillation sets in the molecules may merely orient themselves, giving a structure similar to that of CO<sub>2</sub>, for example, or the orientation may be accompanied by a change of position of molecular centers. That this takes place for HCl is indicated by the low symmetry of the low-temperature form shown by Simon and Simson's powder photographs.

<sup>18</sup> K. Clusius, *Zeits. f. phys. Chem.* **B3**, 41 (1929).

<sup>19</sup> J. C. McLennan and W. G. Plummer, *Phil. Mag.* **7**, 761 (1929), have found that powder photographic data indicate cubic close-packing of the molecules.

<sup>20</sup> W. F. Giaque and R. Wiebe, *J. Am. Chem. Soc.* **50**, 101 (1928); **50**, 2193 (1928), **51**, 1441 (1929).

<sup>21</sup> Giaque and Wiebe suggested essentially this explanation, writing "The results suggest the following possibility: the transition starts as a changing thermal equilibrium between energy states of the hydrogen iodide molecule, both in the same crystal lattice, but when a sufficient concentration of the higher energy state has been reached, the system becomes unstable and changes to a new crystalline form."

<sup>22</sup> F. Simon and C. v. Simson, *Zeits. f. Physik* **21**, 168 (1924).

It is predicted that the dielectric constants of solid HCl, HBr, and HI at temperatures just below the melting points will be very high and dependent on the temperature, the values being given by Debye's theory of the orientation of electric dipole molecules; while the low-temperature forms will have low dielectric constants nearly independent of the temperature.

In general it is to be expected that rotational motion of molecules and complex ions of sufficiently low moment of inertia will set in below the melting point of the crystals. This condition of low moment of inertia is satisfied by complexes containing hydrogen atoms and one heavy atom. Thus the forces orienting the tetrahedral ammonium ion in an ammonium salt are much stronger than those acting on a methane molecule, so that the ion will oscillate until a much higher temperature than 20°K is reached; but this temperature of transition to rotational motion is still considerably below the melting point.

The transitions have been observed. Simon<sup>23</sup> and co-workers found from heat capacity measurements that ammonium chloride, bromide, and iodide show a gradual transition covering about a 10° range in the neighborhood 240°K, the nature of the phenomenon not depending essentially on the anion.<sup>24</sup> X-ray studies showed the crystal structure to be the same before and after the transition, which is accompanied by a small volume change, less than 1%. These investigators attribute the transition to the ammonium ion, but make no other suggestions as to its nature. The observed phenomena are just those expected to accompany the transition from oscillation to rotation of the ammonium ion, however. The increase in the transition temperature in the series NH<sub>4</sub>I (-42.5°C), NH<sub>4</sub>Br (-38.0°C), NH<sub>4</sub>Cl (-30.4°C) further shows the expected effect of increasing interionic forces accompanying decreasing anion radius.<sup>25</sup>

The rotation of the ammonium ion in salts at ordinary temperatures provides justification for the customary treatment of the ion as spherically symmetrical in the theoretical discussion of the structure of ionic crystals. Further, the rotation of molecules such as NH<sub>3</sub> and H<sub>2</sub>O about symmetry axes accounts for the fact that these molecules occupy positions in crystals with symmetry elements not compatible with those of the non-rotating molecule. Thus in Ni(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> the NH<sub>3</sub> molecules lie on four-fold axes, and in alum the H<sub>2</sub>O molecules on three-fold axes. The rotation of the molecules,

<sup>23</sup> F. Simon, *Ann. d. Physik* **68**, 263 (1922); F. Simon and C. v. Simson, *Naturwiss.* **38**, 880 (1926); F. Simon, C. v. Simson, and M. Ruhemann, *Zeit. f. phys. Chem.* **129**, 339 (1927).

<sup>24</sup> A very small hump in the heat capacity curve at -30° was also found for ammonium fluoride; the interpretation of this is uncertain (the structure of this crystal is not the same as that of the other ammonium halides).

<sup>25</sup> Small maxima in the heat capacity curves of organic compounds are probably often due to the transition from oscillational to rotational motion of a part of the molecule. Thus the maxima shown by *o*-xylene, *m*-xylene, and hexamethylbenzene (reported by H. M. Huffman, G. S. Parks and A. C. Daniels, *J.A.C.S.*, **52**, 1547 (1930) would be attributed to the rotation of the methyl groups, which have a low moment of inertia and can rotate about the single bond holding the group to the rest of the molecule. *p*-xylene shows no maximum, indicating that the orienting forces on the methyl group are larger, raising the transition temperature above the melting point.

however, gives them an effective infinite symmetry axis, which is compatible with these positions.

The possibility of rotation introduces considerable uncertainty in the conclusions reached by Hendricks<sup>26</sup> in regard to the nature of the aliphatic carbon chain. From the x-ray study of crystals of the mono-alkyl substituted ammonium halides he found that in a number of these crystals the alkyl ammonium ion lies on a four-fold axis of symmetry, a result which apparently excludes the usual staggered chain of carbon atoms, and which caused him to suggest that the chain really is straight. But the moment of inertia of a staggered chain about an axis along the chain would be very small, and we would expect rotation about this axis at ordinary temperatures, giving the chain an effective infinite symmetry axis, which is compatible with the x-ray data. Accordingly, Hendricks' investigation does not require that the staggered aliphatic chain be given up.<sup>27</sup>

It has been found by Lyons and Rideal that solid unimolecular films on water of long chain hydrocarbons with polar ends exist in two possible forms, one with an area of  $20.6\text{A}^2$  per molecule, and the other, stable at higher temperatures, with an area of  $26.2\text{A}^2$  per molecule.<sup>28</sup> These authors suggest<sup>29</sup> that in the more compact form the staggered chains are interlocked, and fit together more closely than at higher temperatures when interlocking is not effective. This explanation is made somewhat more precise by the application of the considerations discussed in this paper. At low temperatures interlocking does take place, the molecules oscillating about certain equilibrium orientations. With increasing temperature rotation sets in, and the film expands; in this state the molecules would be well represented as circular cylinders with a radius equal to the maximum radius of the staggered chain. The phenomenon is exactly analogous to that giving rise to gradual transitions in crystals.

In molecules  $\text{C}_2\text{X}_6$ , such as ethane,  $\text{C}_2\text{H}_6$ , there exists the possibility of the two ends of the molecule rotating or oscillating relative to each other. In case that X is a large atom, as in  $\text{C}_2\text{I}_6$ , the interaction of the two ends of the molecule will be large, and they will carry out small oscillations about the relative orientation in which the atom groups fit closely together, the six atoms X defining the corners of an octahedron. But in  $\text{C}_2\text{H}_6$  the interaction of the two ends of the molecule will be small, and they will rotate freely about the single bond connecting the carbon atoms, with a frequency which is simply related to the rotational frequency of the entire molecule about its figure axis. The determination of the energy levels characteristic of this motion for molecules of this type, by means of Raman effect or infrared measurements, would permit the evaluation of the potential energy of the molecule as a function of the relative orientation of its ends.

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<sup>26</sup> S. B. Hendricks, *Zeits. f. Krist.* **67**, 465 (1928); **68**, 189 (1928); additional paper *ress.*

<sup>27</sup> Dr. Hendricks has informed me that he agrees with this conclusion.

<sup>28</sup> I am indebted to Professor J. W. Mc Bain for directing my attention to this w ..

<sup>29</sup> C. G. Lyons and E. K. Rideal, *Nature* **125**, 455 (1930).